AsCA '01

IVth Meeting of
Asian Crystallographic Association
at
Indian Institute of Science
Bangalore, India

18 - 21 November 2001

As C A

ABSTRACTS

INDIAN INSTITUTE OF SCIENCE

V. Streltsov

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ABSTRACTS

Keynote Address

Remote Address

DIRECT METHODS FOR SOLVING CRYSTAL STRUCTURES FROM DIFFRACTION DATA.

Henk Schenk, Laboratory for Crystallography, IMC, FNWI, University of Amsterdam, Nieuwe Achtergracht 166, 1018WV Amsterdam, The Netherlands.

Direct Methods to solve crystal structures from diffraction data have a long history, as long as the history of the Journals of the IUCr themselves. Already in the first issue of Acta Crystallographica back in 1948, the article of Harker and Kasper about the inequalities appeared and since then almost no issue of Acta was without contributions to the field. For instance, most of the publications of the Nobel laureates Herbert Hauptman and Jerome Karle came out in Acta. In 1952 there was the famous article of David Sayre about the squaring equation. Also the breakthrough of Direct Methods in real structure determination with Isabella Karle and Michael Woolfson in essential roles can be followed there. And much, much more, too much for an abstract. Our community is very fortunate that for present subscribers of Acta in due course all back issues will be available Online, so that all of this will be available at a mouse click.

I was a primary school kid at the time of the start of Direct Methods and as a student in Chemistry I became interested in crystallography in 1962. From 1965, when I took up a PhD study with Carolina MacGillavry, I am a crystallographer. At the time in Amsterdam, we were living in the ALGOL programming world and most programs available were in the other language, FORTRAN. Therefore we had to write many computer programs ourselves and so I became active in Direct Methods in 1967.

My lecture will be dealing with the past, present and future of Direct Methods for solving Crystal Structures. As a matter of course, I will give special attention to some of the contributions of the Amsterdam group in this field, such as:

1. The symmetry properties of triplet solutions in different space groups.
2. Positive and negative quartet relations.
3. Enantiomorph specific phase extension and refinement.
4. Structure determination from powder data.

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Plenary Lecture

PL-1

EVIDENCE OF SUBTLE ELECTRONIC TRANSITIONS IN X-RAY DIFFRACTION STUDIES OF MATERIALS UNDER PRESSURE

S.K. Sikka, Atomic and Condensed Matter Physics Group, Bhabha Atomic Research Centre, Mumbai 400 085, India

Use of x-ray diffraction for detection and characterization of phase transitions and determination of equations of state of materials is now very well established in high pressure science. Though these, many theoretical concepts in the electronic band structure theory of solids like s-d electron transfer, f electron delocalization, valence transitions, insulator to metal transitions etc. have been verified. With the availability of synchrotron sources, precision x-ray powder diffraction is increasingly being used to detect subtle effects due to Fermi surface tropology changes like Lifshitz transitions etc. These manifest here as second order like phase transitions or deviations from linearity in universal forms of equations of state. In this talk, we illustrate this aspect by examples mostly taken from our own work.

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PL-2

CRYSTAL STRUCTURE OF THE ADRENALINE SYNTHESISIZING ENZYME PNMT

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Adrenaline, also known as epinephrine, is a catecholamine produced in the adrenal glands and in the CNS to induce specific biologic effects. In the periphery, the effects of adrenaline are well-known. Its release from the adrenal medulla is triggered by excitement or physical stress and induces the "flight-fight" response, so-called because it prepares the body for immediate and energetic activity. The response results in an increase in heart rate, blood pressure, blood sugar, metabolic rate and bronchodilation. In the CNS, the effects of adrenaline are not so well understood. Ideally, to investigate the central effects of adrenaline a chemical is required that crosses the blood brain barrier, potently inhibits the adrenaline synthesizing enzyme PNMT and does not affect other catecholamine processes. Currently available PNMT inhibitors do not meet these criteria. We have determined the structure of PNMT to enable the design of such compounds.

The crystal structure of human PNMT is solved at a resolution of 2.4 Å and includes a bound cofactor product and inhibitor. The structure reveals a highly decorated methyltransferase fold, with an active site protected from solvent by an extensive cover formed from several discrete structural motifs. The inhibitor interacts with the enzyme in a different mode from the modeled substrate noradrenaline. Specifically, the position and orientation of the amines are not equivalent. An unexpected finding is that the structure of PNMT provides independent evidence of both backwards evolution and fold recruitment in the evolution of a complex enzyme from a simple fold.

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PL-3

STRUCTURE ANALYSES BY THE MAXIMUM ENTROPY METHOD

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The Maximum Entropy Method (MEM) is a statistical deduction that can yield a high-resolution electron density distribution from a limited number of X-ray diffraction data without using any structural model. Because of this ability, MEM enables us to obtain an accurate electron density distribution from X-ray powder diffraction data, particularly from synchrotron powder data. For the above purpose, a sophisticated method has been developed, that is, the MEM/Rietveld analysis.

The MEM/Rietveld analysis is an iterative way in combination with the MEM and Rietveld analyses. In this method, the final MEM electron density distribution is derived self-consistently with the structural model used in the Rietveld refinement. In the process of the iteration, the structural model for Rietveld refinement is normally constructed from the previous MEM electron density distribution. At the start of the iteration, it is necessary to have a primitive structural model. The method has been successfully applied to the structure studies of fullerene compounds, intermetallic compounds, manganites, etc.

In the talk, not only the methodology but also quite a few recent results, mostly obtained from third generation SR data, will be presented. The experimental technique for high or low temperature structure analyses by MEM will be also given.

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PROTEIN CRYSTALLOGRAPHY IN THE 21ST CENTURY: STRUCTURES AND MECHANISMS

G. Guy Dodson, Department of Chemistry, University of York, York YO1 5DD, England.

Synchrotron radiation has made possible high throughput techniques in X-ray crystallography. The capacity to solve crystal structures is now starting to match the enormous challenge of genome sequences. It is however not just in simple structure determination that the new techniques are important, it is now increasingly possible to dissect the structural and chemical basis of protein reactions such as catalysis. The serine hydrolases have been a key enzyme in the history of biochemistry and protein crystallography. Recent research has revealed the complexity of their evolutionary pattern and the intricate geometrical adjustments that occur in substrate binding and catalysis. It is possible to illustrate these phenomena from a range of such enzymes as subtilisin, trypsin, penicillin acylase and other serine hydrolases.

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A1 : Foundation, theory and history of crystallography

AN EMPIRICAL STUDY ON USING FREE R-VALUES IN CRYSTAL STRUCTURE ANALYSIS OF SMALL MOLECULES: RESOLUTION OF SPACE GROUP AMBIGUITY

A. Abdul Ajees, S. Parthasarathy, Department of Crystallography and Biophysics, University of Madras, Guindy campus, Chennai – 600 025, India.

The utility of free R-value in macromolecular crystal structure analysis is now well known. In this paper a possible application of this concept to small molecule crystallography is discussed. It is not infrequent that in crystals whose space group could be either Cc or C2/c, crystallographers generally determine and refine the structure in both space groups and choose the one which leads to better values for bond lengths and angles. It would be useful to device a somewhat simpler method for doing this. In this paper a method of using the free R-value concept for this purpose is discussed. The advantage of the present method is that it enables us to choose the correct structure by comparing the values of a single index (i.e., free R-value) for the structures in the two possible space groups and choosing the one leading to a lower free R-value.

Various types of R-values have been proposed in the literature for use in crystal structure analysis and they have been found to behave differently in the various stages of structure analysis[1]. It is therefore useful to make a comparative study of the different types of free R-values in order to find their relative efficacy in relation to the present problem of resolution of space group ambiguity. The results obtained from such a study will also be reported.

1.Srinivasan, R. & Parthasarathy, S. (1976). *Some statistical Applications in X-ray Crystallography*, Pergamon press ltd., UK.

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A STACKING FAULTED STRUCTURE REQUIRING A STATISTICAL DISTRIBUTION THAT VARIES BETWEEN MOSAIC BLOCKS

A. David Rae, Anthony C. Willis, Connie K. Y. Lee and Christopher J. Easton, Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia.

Layers of 4-methoxycarbonyl-5-methyl-3-phenyl-D2-isoxazole, [apparent cell *a* 20.9645(6), *b* 9.4287(3), *c* 10.8461(3) Å, β 90.0°, $P2_1/c$, Z = 8] have $P2_1/c$ symmetry but stack perpendicular to a* so that adjacent layers are related by either a translation of $1/2+x,y,z$ or a 2_1 screw axis $1/2+x,1/2-y,-z$. Only adjacent layers related by the 2_1 screw axis can contribute to the *h* odd reflections which show orthorhombic diffraction symmetry with systematic absences consistent with $P2_1ca$. The structure factor can be written as the sum of the contributions of two layers, each unequally disordered between sites related by $x,1/2-y,-z$. Possible ordered structures are two $x,1/2-y,-z$ related $P2_1/c$ structures and two $1/2+x,y,z$ related *Pbca* structures. Refining layer populations and including a twinning parameter does not give a satisfactory refinement. However, successful refinement was possible if the observed reflections were considered to have intensities that were the sum of contributions from individual mosaic blocks with widely varying parameters for the layer disordering. Details will be presented.

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A1-3

PREDICTION OF BIJVOET RATIO MEASUREMENT FOR MACROMOLECULES NEAR THE L-ABSORPTION EDGES OF Hg AND Pt WITH SYNCHROTRON RADIATION

D.Velmurugan[a], K.Sekar[b], S.Shanmuga Sundara Raj[c] and Takashi Yamane[c], [a]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai, 600025, [b]Bio-Informatics Centre, Raman Building, Indian Institute of Science, Bangalore, 560012, [c]Department of Biotechnology, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

Multi wavelength anomalous scattering experiment has become a powerful tool in the structure elucidation of macromolecules using synchrotron radiation. The use of data measurement at a single wavelength near the absorption edge is also pointed out recently. In these methods the Bijvoet difference measurement is mainly involved. The presentation will describe the statistical method of predicting the percentage of reflections, which will have a Bijvoet ratio greater than a given threshold limit for a truncated data. The analysis involves macromolecules of various complexities with Hg or Pt derivative and results are presented for a wide range of wavelengths used in data collection using synchrotron radiation. The results clearly confirm the advantage one can obtain in Bijvoet ratio measurement at wavelengths where pronounced anomalous scattering effect occurs. Furthermore, the availability of a sufficiently large percentage of reflections with large values of Bijvoet ratio due to the enhanced anomalous scattering effect with synchrotron radiation may make the phase determination procedure in macromolecules more effective.

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A1-4

REAL-SPACE REPRESENTATION OF ATOMIC FLUCTUATIONS IN TERMS OF QUANTITATIVE ANALYSIS OF X-RAY DIFFUSE SCATTERING - APPLICATION TO DISORDERED PEROVSKITE RELAXOR PMN

Naohisa Takesue[a], Yasuhiko Fujii[a], and Hoydoo You[b], [a]Neutron Scattering Laboratory, Institute for Solid State Physics, The University of Tokyo, 106-1 Shirakata, Tokai, Ibaraki 319-1106, Japan, and [b]Argonne National Laboratory, Materials Science Division, 9700 South Cass Avenue, Argonne, Illinois 60439, USA.

Disordering of atoms, ionic charges, and electron spins in crystals occasionally causes remarkable variation of the physical properties. Keys to elucidate the mechanisms are sometimes given by studying local crystal structures through quantitative analysis of diffuse scattering. This kind of investigations has been applied to chemical short-range order in alloys since 1950s, and the applicability is to extend toward different matters such as dielectric systems and strongly-correlated electronic systems, in the present time. In this study, we selected from the former systems a special kind of ferroelectrics, relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), exhibiting a diffuse cubic-to-rhombohedral phase transition and dielectric dispersion near 270K, and investigated the atomic fluctuations using an x-ray diffuse scattering technique to explain a mechanism of the abnormal behavior. From the measurement, ionic-pair displacement correlation functions have been determined quantitatively around 270K. The results show the strong rhombohedral-polar correlations regarding Pb-O, Mg/Nb-O, and O-O' pairs. Their spatial distribution at 300K forms an ellipse or a sphere with the diameters of 30-80Å, and the sizes are reduced to 30-40Å on cooling through local condensation of thermal lattice fluctuations. This direct observation of the local structure proves the presence of the polar microregions in the paraelectric state which leads to the dielectric dispersion.

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A1-5

X-RAY RESONANCE PHASE: MULTI-BEAM DIFFRACTION EXPERIMENTS AND THE RESONANCE PERTURBATION BETHE APPROXIMATION

Y.P. Stetsko[a,b], G.Y. Lin[a], Y.S. Huang[a], C.H. Chao[a], Y.R. Lee[a], and S.L. Chang[a,b], [a]Department of Physics, National Tsing Hua University, [b]Synchrotron Radiation Research Center, Hsinchu, Taiwan, R.O.C.

X-ray diffraction/scattering for atoms in excited states or under resonance conditions has currently been used to probe atomic and electronic structures of matter. In the case of multiple diffraction at atomic absorption edges, the effects of anomalous dispersion on multi-wave x-ray interference in crystals are interesting and important topics to investigate. In this paper, highly phase-sensitive profiles of the diffraction intensity ratios of two inversion-symmetry-related multiple diffractions at absorption edges exhibiting strong asymmetric characteristics, compared with those far from the edges, are experimentally and theoretically observed. The changing of asymmetry of these ratios results from the anomalous dispersion corrections in the structure factors due to the significant change of the resonance phase at the absorption edge. The excellent agreement between the experimental and theoretical results is obtained. The proposed resonance perturbation Bethe (RPB) approach allows for the determination of the changes of x-ray reflection phases under resonance conditions. This provides a highly sensitive way for experimental investigation of the spectral distribution of reflection phase shift due to the resonance.

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PHASE DETERMINATION FOR MACROMOLECULAR CRYSTALS USING STEREOSCOPIC MULTI-BEAM IMAGING: DATA ANALYSIS AND THEORETICAL CONSIDERATION

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A detailed analysis of multiple diffraction data collected by the stereoscopic multi-beam imaging technique from a hexagonal lysozyme crystal is reported. Calculations based on the dynamical theory are employed for macromolecular crystals subject to the crystal rotation for stereoscopic imaging and the conventional Renninger azimuthal scan. The multi-beam intensity profile formation and the relationship and mutual influence between the two scans are investigated. A simple practical method of quantitative estimation of the reflection phases of structure-factor multiplets from the experimental data obtained with two inversion-symmetry-related diffractions is proposed. The procedures for data handling and for distinguishing "partial" diffraction images from "full" diffraction images are also developed considering the multi-beam geometry and experimental conditions. These procedures provide a practical way of reconstructing diffraction profiles for experimental phase determination.

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DIRECT DETERMINATION OF RESONANCE PHASE OF X-RAY REFLECTON BY MULTIPLE DIFFRACTION

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X-ray diffraction/scattering for atoms in excited states or under resonance conditions has currently been used to probe atomic and electronic structures of matter. In the case of multiple diffraction at atomic absorption edges, the effects of anomalous dispersion on multi-wave x-ray interference in crystals are interesting and important topics to investigate. In this paper, highly phase-sensitive profiles of the diffraction intensity ratios of two inversion-symmetry-related multiple diffractions at absorption edges exhibiting strong asymmetric characteristics, compared with those far from the edges, are experimentally and theoretically observed. The changing of asymmetry of these ratios results from the anomalous dispersion corrections in the structure factors due to the significant change of the resonance phase at the absorption edge. Excellent agreement between the experimental and theoretical results is obtained. The proposed resonance perturbation Bethe (RPB) approach allows for the determination of the changes of x-ray reflection phases under resonance conditions. This provides a highly sensitive way for experimental investigation of the spectral distribution of reflection phase shift due to the resonance.

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X-RAY FLUORESCENCE MEASUREMENT UNDER MULTIPLE DIFFRACTION CONDITION

Y. R. Lee[a], G.G. Lin[a], Y.P. Stetsko[a, b], S.Y. Cheng[a], C.C. Kuo[a], Y.R. Jou[a], P.S. Fang[a], and S.-L. Chang[a,b], [a]Department of Physics, National Tsing Hua University, [b]Synchrotron Radiation Research Center, Hsinchu, Taiwan, R.O.C.,

Angular distribution of X-ray fluorescence under three-beam diffraction condition is investigated using synchrotron radiation for GaAs single-crystals. The fluorescence yield and multiply diffracted intensities as a function of the Bragg angle and the azimuth angle of rotation of a symmetric Bragg primary reflection are measured. It is found that fluorescence yield may first increase and then decrease as the azimuth angle moves across the exact three-beam diffraction position, or vice versa, depending on the polarization of the incident beam and the triplet phases involved in the diffraction process. However, the corresponding multiple diffraction intensities show almost opposite characteristic to fluorescence. The relationship between fluorescence yield and diffraction intensity is thoroughly examined. A theoretical interpretation of the observed behavior is also given.

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A2 : Instrumentation and techniques

A2 : Instrumentation and
techniques

A2-1

DEVELOPMENT OF A MICROSTRIP GAS COUNTER

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Since their introduction in 1986 by Oed, microstrip gas detectors have attracted a lot of interest in the field of gas detectors. This is due to their many promising features such as high gain, high count rate capabilities, and better spatial and energy resolution characteristics. We report here design and development of a one dimensional position sensitive microstrip detector. The microstrip pattern is generated on an insulating borosilicate glass substrate and consists of alternate anodes and cathodes generated by deposition of chromium and photolithography technique. The anode width is 25μm, cathode width 150μm, and separation between them is 250μm with a pitch of 675μm. The anodes are connected at one end by a meandering chromium resistive strip 0.1 mm in width for position sensing using charge division technique. The effective active area of the microstrip detector plate is 30mm x 30mm. The microstrip was tested with x-rays and neutrons using appropriate fill gases. Energy resolution of 17%(FWHM) for 5.9 keV x-rays and 12.5% for 760keV neutrons was obtained. At present a position resolution of 900μm (FWHM) has been achieved with x-rays.

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A2-2

TWO-DIMENSIONAL POSITION SENSITIVE DETECTORS FOR NEUTRON AND X-RAY SCATTERING APPLICATIONS

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Two-dimensional Position Sensitive Detectors have been developed at Trombay for small angle neutron and x-ray scattering work. The neutron detector is a ^3He and $Ar+CO_2$ filled MWPC with charge division readout and has sensitive area of 345mm x 345mm. The detector is designed for 70% efficiency for 4Å neutrons. A prototype of this detector was tested at different gas pressures with a well-collimated neutron beam inclined at 90°. Excellent linearity, detection homogeneity and spatial resolution of about 5mm x 5mm were found. To test the performance of the detector for SANS, experiments were carried out using standard alumina sample. Broadening of the peak and significant increase in scattered intensity in the tail region of the profile arising from small angle neutron scattering by alumina particles was detected. The x-ray 2-D PSD has an active area of 100mm x 100 mm and has been tested with Ar, Kr and Xe gases at various pressures. A spatial resolution of 1.2mm x 1.4mm and gas gain of $5x10^4$ is obtained with Ar + CH_4(10%) gas at 300 kPa gas pressure.

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A2-3

GRAZING INCIDENCE SYNCROTRON X-RAY DIFFRACTION STUDY OF MELTING IN ULTRA-THIN ORGANIC FILMS

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Structural change as a function of temperature in Langmuir-Blodgett (LB) films of cadmium salts of a long-chain fatty acid (arachidic acid) has been studied by grazing incidence diffraction (GID) of x-rays from a synchrotron source (HASYLAB, Germany). Films with 3, 5, 9 and 13 monolayers (each about 25 Å thick) of cadmium arachidate (CdAr) were heated from room temperature to 100°C in an evacuated scattering chamber and GID data collected in situ. The lattice in the plane perpendicular to the hydrocarbon chains is found to be hexagonal with a distortion in the nearest neighbor (NN) direction, to around 90°C. At 90°C an abrupt structural change takes place. For the 3 monolayer film this is a transition to a regular hexagon with reduced domain size. For films with more monolayers this change causes a large reduction in the NN distortion, followed by a slower transition to the regular hexagonal structure, at a temperature that increases with the number of monolayers. On cooling back to 50°C the original distorted hexagonal structure is recovered but the domain size remains small. Bragg Rod scans for all samples show a correlation length of about 3 monolayers along the hydrocarbon chains. Structures are found to be unaffected by synchrotron radiation. The motivation of this study is to understand the transition from two-dimensional to three-dimensional melting as the number of monolayers increases. X-ray reflectivity data has also been collected using a rotating-anode source and the BESSY synchrotron source, to understand the structural change in the growth direction as a function of temperature.

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SUB-SECOND X-RAY DIFFRACTION MEASUREMENT AND STRUCTURE ANALYSIS.

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Rapid X-ray diffraction measurement technique is an essential to realize the time-resolved observations of crystalline-state reactions, unstable species in excited state and reaction intermediates. To achieve time resolution of seconds or sub seconds order, the use of photon counting type two-dimensional detector is required.

Recently, MSGC (Micro Strip Gas Chamber) was developed for the rapid X-ray data collection. MSGC is a gaseous detector having both photon counting and two-dimensional imaging properties. The features of the detector are a large detective area of 10 x 10cm, a fine positional resolution of 100 micrometer and an excellent capability for high counting rate up to 10^7 cps suitable for the synchrotron radiation experiments.

With the measurement system consists of a MSGC detector, one axis goniometer and a laboratory X-ray generator, complete data set from typical organic crystals were recorded within several minutes to seconds range and the results of structure analyses were satisfactory. In the experiment using the synchrotron radiation at SPring-8, structure analysis of sub-second diffraction data was successfully achieved. For an application of monitoring the diffraction pattern, the timing resolution of sub-second can be achieved to observe the change of cell dimensions caused by the excited molecules in the crystal.

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A2-5

ELECTRICAL CONDUCTANCE MEASUREMENT THROUGH $ErSi_2$ NANOWIRE USING DOUBLE-PROBE SCANNING TUNNELING MICROSCOPY

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We have constructed a multi-probe scanning tunneling microscope (MP-STM) which would be a novel technique to develop future nanoscale devices. In this work we apply the MP-STM for the direct measurement of the conductance of one-dimensional (1D) nanostructures. We prepare $ErSi_2$ nanowires that are self-assembled on the Si (001) clean surface. $ErSi_2$ nanowires run along a <110> axis of the Si(001) substrate, having sizes of 1-5nm, 1-2nm and <1000nm, in width, height, and length, respectively. To investigate crystallographic and electric properties of such crystalline $ErSi_2$ nanowires, we use a double-probe scanning tunneling microscopy (DP-STM) as a 'nano-tester'. DP-STM measurements show that $ErSi_2$ nanowires are 1D metal conductors judging from the following experimental results. The current-voltage curves, which are measured on a single $ErSi_2$ nanowire, always show linear dependence. And the resistance of $ErSi_2$ nanowires is proportional to their length. Interestingly, the resistance per unit length is 1.2 MΩ/nm along the $ErSi_2$ nanowire, being 4-5 orders of magnitude larger than the resistance expected from the known resistivity of bulk $ErSi_2$. One of the reasons for such a high resistance may be due to an elastically-elongated lattice spacing along the $ErSi_2$ nanowire as a result of lattice mismatch between the $ErSi_2$ and Si(001) substrate*.

*Yong Chen, Douglas A. A. Ohlberg, Gilberto Medeiros-Ribeiro, Y. Austin Chang and R. Stanley Williams, Appl. Phys. Lett., 76 (2000) 4004.

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A2-6

RECENT DEVELOPMENT OF INELASTIC X-RAY SCATTERING SPECTROMETER AND *in-situ* MBE DIFFRACTOMETER AT BL-11XU IN SPring-8

J. Mizuki, Synchrotron Radiation Research Center, Japan Atomic Energy Research Institute (JAERI) and Core Research for Evolutional Science and Technology (CREST)

We will present here two new spectrometers installed at JAERI beamline in SPring-8, which are an Inelastic X-ray Scattering (IXS) spectrometer and another *in-situ* MBE diffractometer. Particularly IXS experiments have been stimulated by the high brilliance synchrotron radiation sources, so called Third Generation Sources. In comparison with neutrons, X-rays can interact directly with electrons. This makes IXS possible to investigate the nature of excited electron states in energy-momentum space, which are the essential information in condensed matter physics. The IXS spectrometer designed has 0.1 eV energy resolution and 0~30 eV energy transfer with 6~10 keV incident X-ray energies.

We have also installed an *in-situ* MBE diffractometer for studying layer-by-layer crystal growth especially focused on III-V semiconductors and related materials at our beamline. This diffractometer allows us to investigate dynamic growth process as well as elaborate crystallography.

The orbital excitation spectrum on manganites taken by IXS and the preliminary data on GaAs growth will be shown in the talk.

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A LARGE SIZE SOLID-STATE DETECTOR FOR PROTEIN CRYSTALLOGRAPHY

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A fully solid-state detector inaugurating the post-CCD era will be described.

The fully solid-state detector is based on the direct conversion of the absorbed X-rays into electric charges. The charges follow electric field lines in the photoconductor. This direct conversion makes the use of phosphors and optical elements (e.g. fibre optic tapers) obsolete. Consequently, the spatial resolution is extremely high. The point-spread function is well within 1 pixel. Measurements have shown that the reflection spot sizes and separation depend solely on the source size, beam size, crystal size and the beam divergence.

The size of the present detector is 35 cm x 43 cm, or 2560 x 3072 pixels of 140 $(\mu m)^2$. Thus, in addition to the excellent spatial resolution, the system has the advantage of an untiled large size. The readout time of the whole area will be one second. The combination of high spatial resolution, large size and fast readout makes this system a first choice for the most demanding applications at the 3rd generation synchrotron sources. Due to the high resolution, reflections occupy a low number of pixels. The favorable influence on the signal to noise ratio will be discussed.

Crystallographic data collected at 3rd generation synchrotron sources will be shown and discussed.

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A2–8

ROTATIONAL MOTIONS IN SOLIDS: QUASIELASTIC NEUTRON SCATTERING STUDY

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Quasielastic neutron scattering (QENS) technique has been successfully used to elucidate the molecular motions and physical properties related to it, in variety of systems. Thermal neutron is a powerful probe to study the dynamics in condensed matter for its matching energy with the excitations of the solid. Further systems containing protons are more suitable for its large scattering cross-section. Periodic motions give rise to characteristic frequency in the spectrum whereas the random motion leads to Doppler broadening of the scattered neutrons, which result in the broadening of the elastic line known as quasielastic broadening. QENS is a unique technique provides information on the time scale of the motion as well as the geometry of the motions. In this paper, we shall discuss some of the systems studied using the facility available at Dhruva, Trombay and other mega-facilities, with particular emphasis on reorientational motion of pyridinium ion in pyridinium iodide, reorientaional motions of different units of a liquid crystal at different phases, alkyl chain motions in monolayer protected metal clusters, molecular motions in polymeric systems and in confined media like different zeolites etc.

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NEW GENERATION QUANTITATIVE X-RAY MICROSCOPY FOR MATERIALS SCIENCE AND OTHER APPLICATIONS.

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We briefly outline a new approach to X-ray ultramicroscopy using projection imaging in a scanning electron microscope (SEM)[1]. Compared to earlier approaches (see e.g. Refs 2-4), the new approach offers spatial resolution of ≤0.1 micron and includes novel features such as: i) phase contrast to give additional sample information over a wide energy range, ii) rapid phase/amplitude extraction algorithms to enable new real-time modes of microscopic imaging[5-8] widespread applications are envisaged to fields such as materials science, biomedical research, and microelectronics device inspection. Some illustrative examples are presented. The quantitative methods described here are also very relevant to X-ray projection microscopy using synchrotron sources. Studies of bio materials, microelectronic devices, natural fibres and a number of other materials will be presented.

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IMAGING PLATE WEISSENBERG CAMERA AT THE BL04B2 BEAMLINE OF SPRING-8 AND ITS APPLICATION TO THE STRUCTURE DETERMINATION OF POLYOXOTUNGSTATE CRYSTALS

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An imaging plate Weissenberg camera has been installed into the BL04B2 beamline of SPring-8 in order to provide a facility for single crystal structure analyses of small molecules. This camera is equipped with a cylindrical imaging plate and an integrated imaging plate reader, allowing fully automatic data collection. Obtained diffraction images are automatically processed using the program DENZO. As the beamline is designed for providing a high-flux, highly focused and high-energy (> 37.78 keV) X-ray beam, this camera is ideal for performing absorption-free diffraction experiments for heavily X-ray absorbing crystals. Note that most elements show the absorption coefficients for the 37.78 keV X-ray less than the seventh of those for the MoKα radiation. The performance of this instrument has been exemplified by an analysis of the crystal structure of $[(n\text{-}C_4H_9)_4N]_2[W_6O_{19}]$. Its absorption coefficients for 37.78 keV X-ray is 1.91 mm^{-1} while it is 14.3 mm^{-1} for MoKα radiation. The structure analysis led to precise positional parameters and well-behaved displacement parameters not only for heavy atoms but also for light atoms. Also, final residual electron densities were −1.85 to 2.20 $e\text{Å}^{-3}$, although an asymmetric unit contains six independent W atoms. Other examples will also be discussed.

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A2-11

SINGLE-CRYSTAL NEUTRON DIFFRACTION AT ANSTO.

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The current and future single-crystal neutron diffraction capabilities at ANSTO will be presented. At HIFAR there is currently a 4-circle diffractometer. The Replacement Research Reactor (RRR) will come online in 2005. At a workshop December 11-12, 2001, at ANSTO, the main goal will be to determine what type of single-crystal diffractometer will be developed for RRR, and what should be the specifications. The choice will be between a 4-circle diffractometer and a quasi-Laue type diffractometer.

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A2-12

RECENT PROGRESS OF A CRYSTAL AND MAGNETIC STRUCTURE ANALYSIS BY USING A SINGLE CRYSTAL NEUTRON DIFFRACTOMETER FONDER

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Very recently, we have developed a 4-circle diffractometer FONDER (Four-Circle Off-center Type Neutron Diffractometer) for a single crystal experiment as well as a horizontally and vertically bend monochromator with silicon (422) plates, at the guide-hall of the reactor JRR3M-JAERI (Japanese Research Reactor) at Tokai. Wavelength of the neutron is 1.57A and the maximum scattering angle of a sample is 156 degree. As a test sample, we studied crystal and magnetic structures of manganese fluoride MnF_2. The crystal size is 2.5 x 2.5 x 2.5 mm^3. Good R-factor was obtained: R=1.77% (at 80K > T_N) and R=1.90% (at 7K <T_N) for crystal structures. Concerning the magnetic structure, additional magnetic parameters *S*, *g* and B(*3d*-electron) were obtained with R=3.39%. The electron density, which is carrying spins, was obtained. We also investigated several hydrogen bond materials like squaric acid ($C_4O_4H_2$), MeHPLN ($C_{14}O_2H_{14}$, 5-methyl-9hydroxyphenalenone), and the characteristic feature of hydrogen atom is observed. Other examples such like $(NH_4)PtCl_6$ will be also shown.

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A3 : Crystallography in physics and earth sciences

A3 : Crystallography in physics
and earth sciences

A3-1

HIGH PRESSURE AND HIGH TEMPERATURE STUDIES OF $LiYF_4$ AND $LiYbF_4$

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Remarkably low lasing thresholds in the rare earth (e.g. Nd^{3+}, Er^{3+}or, U^{3+}) doped tetragonal fluoroscheelites, $LiYF_4$ and $LiYbF_4$, mainly because of their superior thermal and optical properties, cater to several optical domains of application, primal to which is the wide range (UV-IR) thermally tunable solid state lasers with astoundingly high efficiency. As an extension of the bountiful works done over the years on these complex crystals, we report here the lattice dynamical calculations of the pressure as well as temperature dependence on their structures and properties (optical and thermodynamic). Our computations, based on a rigid ion model, suggest that the observed phase transition in $LiYF_4$, at a pressure of 7 GPa may be initiated due to a dynamical instability of a transverse acoustic phonon mode at a small wave vector along the [1 3 0] direction. For $LiYbF_4$, our predicted value is 6 GPa. We calculated the volume compressibility for $LiYF_4$ as 14.4×10^{-3} GPa^{-1}, which is in congruence with the experimental value of 12.5×10^{-3} GPa^{-1}. The linear compressibilities for lattice lattice parameters a and c of $LiYF_4$ are predicted by our model as 6.0×10^{-3} GPa^{-1} and 2.3×10^{-3} GPa^{-1} against 5.4×10^{-3} $GPa^{-1}$and 2.6×10^{-3} GPa^{-1} of $LiYbF_4$.Our model further suggests the average Gruneisen parameter for zone center phonon modes of $LiYF_4$ and $LiYbF_4$ as 1.12 and 1.09 respectively. The same potential model would be used in molecular dynamics simulations for a microscopic understanding of the possible phase transitions at the atomic level.

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A3-2

POWDER DIFFRACTION AT MEGABAR PRESSURES: ANALYSIS OF THE LATTICE STRAINS

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The diamond anvil cells (DACs) have been used to record x-ray diffraction patterns from the samples compressed to a few hundred gigapascals. Over the years such experiments have provided valuable information on equation of state and pressure-induced phase transitions in solids. A well-characterised stress state (ideally hydrostatic pressure) of the sample is essential for a rigorous interpretation of the diffraction data. However, the stress state of the sample compressed in a DAC tends to become nonhydrostatic, especially when the pressure exceeds ~50 GPa. The modelling of the actual stress state of the sample and its effect on the measured lattice strains has led to a considerable understanding of this subject. The presence of nonhydrostatic stress component is no longer considered undesirable. On the other hand, it has now become possible to analyse the peak-position data to derive the volume compression data corresponding to equivalent hydrostatic pressures and the shear strength, as a function of pressure, of the sample material. Of particular interest is the possibility of determining the single-crystal elastic moduli as a function of pressure. More recent work has shown that additional information becomes available from the analysis of the diffraction line widths.

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A3-3

STUDY OF ANTI-COMPTON SCATTERING FROM BORIC ACID POWDER

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When the momentum of x-ray quantum becomes comparable to or larger than m0c (mo is the rest mass of electron and c is the velocity of light), the momentum of the photon gets modified. This is known as the quantum mechanical effect. It is quite logical to think that anti-Compton effect occurs from collision of Compton ejected electron and other photons of the incident x-ray beam. We reported an observation of anti-Compton scattering from polyethylene terepthalate and low-density polyethylene in a separate paper with its relevant quantum mechanical derivation. Boric acid powder (H_3BO_3) of 99.5% purity was compressed in a die to form a flat-faced sample of 60x23x5 mm^3 size. The experimental set up used by us for spectroscopic analysis of the diffuse anti-Compton scattering was a Philips analytical x-ray instrument having bent graphite crystal monochromator employing Bragg-Brentano parafocusing optics in reflection-reflection mode. CuKα (1.54056Å) radiation of incident line beam from a high power ceramic tube was used for this study. Wavelengths of Compton and anti-Compton modified scattered radiation at 1100 were calculated to be 1.56938Å and 1.51749Å respectively and the corresponding wavelengths at 1200 were also estimated to be 1.57841Å and 1.50760Å respectively. Ratio of the intensities (anti-Compton/ unmodified) at 1100 and 1200 were found out to be 1.0242 and 1.1218 respectively. The above ratio goes on increasing with scattering angle as in Compton scattering. For these scattering angles the total scattering cross-section for anti-Compton photon were computed as 6.55361 (10-25 cm^2/electron and 6.59349 (10-25 cm^2/electron respectively. The above data leads us to believe that anti-Compton scattering does exist. Quantum mechanical expression and details of this discovery will be presented.

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EXPERIMENTAL STUDIES OF PHASE TRANSITIONS IN ABO_3 PEROVSKITES

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The structural variants of ABO_3 perovskites and the phase transitions between them have long been fascinating in chemistry, physics and the earth sciences. This interest has been further fuelled by the remarkable properties displayed by perovskites and related oxides near structural instabilities, including colossal magneto-resistance, superconductivity and ferroelectricity. The cubic perovskite is a simple but demanding structure, having only one variable, the lattice parameter. Numerous perovskites have lower symmetry structures that involve tilting of the BO_6 octahedra. Considering only tilting of the BO_6 octahedra, group theory provides a method by which sequences of phase transitions can be predicted. In the present paper we will describe some of our recent variable temperature experimental powder neutron and synchrotron X-ray diffraction studies of a number of "simple" perovskite systems including $SrMO_3$ M = Ru, Hf and Zr and some substituted analogues including $Sr_{1-x}Ba_xZrO_3$ and $La_{1-x}Sr_xCr_{1-x}Ti_xO_3$. The systems studied display an array of room temperature structures ranging from orthorhombic through rhombohedral, tetragonal to cubic. Transitions between these variants are observed. The paper will demonstrate the predictive ability of the group theory analysis and highlight the advantages of both high resolution and fine temperature intervals in unravelling the detail of phase transitions.

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A3-5

CRYSTAL STRUCTURE AND EXCHANGE INTERACTIONS IN A DOUBLE CHAINS SYSTEM NH_4CuCl_3

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NH_4CuCl_3 crystallizes in a monoclinic structure and belongs to $KCuCl_3$ family. The space group of this compound is $P2_1/c$ and the crystal structure comprises double chains of edge sharing $CuCl_6$ octahedral along the *a*-axis. The Jahn-Teller effect distorts all of the octahedral. The elongated axes of the octahedral are aligned in the same direction. For the *bc*-plane, the double chains are located at the corners and center of the unit cell and separated by NH_4^+ ions. The lattice parameters of NH_4CuCl_3 are: a= 4.066 Å, b=14.189 Å and c=9.003 Å with $\beta = 97^o$ 30'. Due to the crystal structure, it is considered that the exchange interaction in the double chains are described by the spin ladder with diagonal interaction or the alternating chain with the next nearest neighbor interaction. Configuration of the hole orbital $d(x^2-y^2)$ of the Cu^{2+} ions on their sites give a suggestion that the exchange interactions J_2 and J_3 are both antiferromagnetic. The nature of J_1 interaction is not clear from the crystal structure. The values of the exchange interaction constants in NH_4CuCl_3 are presently not known. From the chemical viewpoint, NH_4CuCl_3 seems to be described as a spin ½ alternating Heisenberg chain consisting J_2 and J_3 interactions with the next nearest neighbor interaction J_1. Thus the remarkable quantum effect characteristic of the spin ladder or alternating chain is expected in the present system.

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HIGH TEMPERATURE PHASE TRANSITIONS IN TUNGSTEN TRIOXIDE

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Seventy years have elapsed since the first crystal structure determination in tungsten trioxide, WO_3, and studies of its high temperature phase transitions were in vogue almost fifty years ago. The material is of technological interest, for example, as the preferred active component in electrochromic windows. Despite a protracted effort, including several significant studies published as recently as 1999, there has been until now a measure of uncertainty about the structures of the high temperature phases and the nature of the transitions occurring.

We have undertaken neutron powder diffraction measurements on WO_3, in fine temperature steps from room temperature to 1000 °C, using the High Resolution Powder Diffractometer (HRPD) at the ISIS facility, UK. HRPD is currently the highest resolution neutron powder diffractometer in the world. By inspection and analyses of the very high quality neutron data, and making reference to the results from a group theoretical analysis, we discovered and identified a new high temperature monoclinic phase existing over a narrow temperature range, and confirmed one of two models proposed previously for the orthorhombic structure. We present for the first time a complete and correct account of the high temperature phases in perovskite-like WO_3 and of the transitions occurring between them.

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A3-7

SINGLE CRYSTAL EPR STUDIES ON Mn(II) IN SARCOSINE CADMIUM CHLORIDE/BROMIDE : STUDY OF ZERO FIELD SPLITTING TENSOR IN ISOSTRUCTURAL COMPLEXES.

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Single crystal EPR spectra of Mn(II) doped sarcosine cadmium chloride (SCC) and sarcosine cadmium bromide (SCB) are studied at room temperature. Single crystals of SCC and SCB are grown by slow evaporation technique using sarcosine and cadmium cloride / cadmium bromide in stoichiometric composition. SCC crystallizes in the monoclinic system with four formula units in the unit cell. Preliminary X-ray measurements indicate that SCC and SCB are iso-structures. EPR spectra are recorded in Q-band and in X-band for SCC and SCB respectively. Two magnetically inequivalent sites are observed in both the lattices. The spin Hamiltonian parameters are extracted from standard procedure and found to have rhombic symmetry. The angular variations have been simulated using the values of a,D ane E by second order perturbation theory. The values are $a=10\times10^{-4}cm^{-1}$, $D=480\times10^{-4}cm^{-1}$, $E=-115\times10^{-4}cm^{-1}$ for Mn(II)/SCC and are $a=10\times10^{-4}cm^{-1}$, $D=460\times10^{-4}cm^{-1}$, $E=-98\times10^{-4}cm^{-1}$ for Mn(II)/SCB. The observed large value of zero field tensor is due to the steric effects of the crystal packing caused by the ligand. Relative signs of A and D are evaluated from second order effects. Matamura's plot predicts an average covalency of 8.8 % and 7.7 % for the manganese-ligand bond and it is in reasonable agreement with the values reported for the manganese-oxygen bond.

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AN ALTERNATIVE APPROACH TO THE MATRIX CORRECTION PROCEDURE IN QUANTITATIVE X-RAY POWDER DIFFRACTION STUDIES OF SAMPLES IN MICA - KAOLINITE – QUARTZ SYSTEM.

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Matrix effect correction in the quantitative X-ray powder diffraction of multicomponent earth samples is a problem difficult to tackle both by internal standard method and standardless methods. Behavioural pattern of the matrix effect in the tertiary system of Mica – kaolinite – quartz has been investigated using a mixing scheme in which presence of one of the phases has been gradually increased within a matrix of the other two relative proportions of which also got changed in the process. Three such sampling models were used to collect data. XRD tested pure sample of each of the phases were used to prepare the samples followed by a weighing scheme using a Perkin-Elmer microbalance. X-ray diffraction data were collected using APD-1700 system in conjunction with PC-APD software from M/s. Philips, Holland. Quantitative data in counts per step/time were collected against d(002), d(001) & d(112) spacings for mica, kaolinite and quartz respectively. It is observed that the variation of mica and kaolinite within a varying matrix of kaolinite - quartz & mica – quartz respectively show a definite patterns whereas variation of quartz within a varying matrix of mica – kaolinite is irregular and unpredicatable within the percentage ranges examined. Estimation of the wt. percentages of the three phases present in unknown samples of this type of clay like tertiary system is possible using the two former variation patterns with reasonably fair consistency with an added advantage of mutual cross checking.

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A3-9

RESONANT FORBIDDEN REFLECTIONS FROM GERMANIUM

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Forbidden reflections, excited owing to anisotropic environment of atoms, are referred to as ATS (anisotropic tensor of susceptibility) reflections. Most of the ATS scattering observed up to now can be explained by dipole transitions. However, unexpected phenomena from dipole approximation were reported in some cases, which may be explained by higher order approximation.[1, 2] In the dipole approximation, ATS scattering cannot be excited from a Ge crystal because of its high symmetry. Therefore, the ATS reflection from Ge was presumed to originate in dipole-quadrupole transition.[3] However, if the thermal motion of the atoms is taken into account, the ATS scattering can be observed even in the dipole approximation.[4] In the present work, we investigated the Ge 006 forbidden reflection near the Ge K-absorption edge using synchrotron radiation in Tsukuba. We observed one peak in the energy spectrum just near the edge. At the peak position the azimuthal angle dependence agrees with a calculation based on the dipole-quadrupole transition. However, we cannot determine the origin, whether it is due to the dipole–quadrupole transition or the thermal motion, because the azimuthal dependence shows the same profile in both cases. Therefore we measured the temperature dependence of the reflection. From room temperature to 30 K the intensity decreases to be about a quarter. This result indicates that the forbidden reflection is mainly due to the TMI (thermal-motion-induced) ATS scattering.[5]

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A3-10

NEW MODIFICATION OF PYRRHOTITE FOUND IN INTERPLANETARY DUST PARTICLES (IDPs)

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Iron-nickel sulfides are the key minerals to understand the early solar system history, because they are the only phases present in all types of extraterrestrial materials.

All the diffraction experiments were carried out at the BL-4B1 of the Photon Factory, KEK, by using diffraction equipment developed for a micrometer-sized specimen and a micro-area of a larger sample.

The chemical formula of the sample (IDPs: L2005 AG17) was determined to be $Fe_{0.83}S$ by EPMA. Oscillation patterns were taken by monochromatic synchrotron radiation, and all of the diffraction spots can be well indexed based on the 3C type pyrrhotite. Four week, but distinct, powder lines are also observed in all oscillation patterns; these lines correspond to those of magnetite (Fe_3O_4).

According to the chemical composition of present sample and the existence of magnetite in the same sample, the crystal structure of the present 3C type must be different from that reported previously having a chemical formula of $Fe_{0.875}S$. The structure was analyzed based on 'extraordinary conditions of missing reflections'. From the obtained structure, the chemical formula of the present 3C type is represented as $Fe_{0.5}S$. This type of modification is entirely new and hash not been known before either natural or synthetic.

The structure exhibits the phenomena of 'homometry' and 'diffraction enhancement of symmetry'.

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A3-11 = A9-5

REFINEMENT OF CRYSTAL STRUCTURAL PARAMETERS AND CHARGE DENSITY USING CONVERGENT-BEAM ELECTRON DIFFRACTION

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We developed a new method to refine crystal structural parameters using convergent-beam electron diffraction (CBED), which is applicable to *nanometer-size* crystal structure analysis (K. Tsuda and M. Tanaka: Acta Cryst. A55, (1999) 939). The method is based on the fitting between theoretical calculations and experimental intensities of energy-filtered *two-dimensional* CBED patterns containing zeroth-order Laue-zone (ZOLZ) and higher-order Laue-zone (HOLZ) reflections. The use of HOLZ reflections is essential for the present method because small displacements of atoms can be sensitively detected using HOLZ reflections with large reciprocal vectors. For this purpose, we developed an energy-filter transmission electron microscope (JEM-2010FEF) and an analysis program (MBFIT) to refine structural parameters based on the dynamical diffraction theory.

Using this method, we have refined the atom positions and anisotropic Debye-Waller factors of the high-temperature phase of $LaCrO_3$. Clear anisotropy of the thermal vibration of the oxygen atoms has been successfully detected by electron diffraction for the first time. The low-order structure factors, which are sensitive to valence electrons, were refined together with these structural parameters, and were converted to deformation charge density. The result clearly shows charge transfer from La and Cr atoms to O atoms.

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HIGH-PRESSURE LATTICE DYNAMICAL STUDIES OF THE Al_2SiO_5 POLYMORPHS

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The Al_2SiO_5 polymorphs, sillimanite, andalusite and kyanite, are important high temperature ceramic materials as well as geophysically important minerals. Sillimanite and andalusite are orthorhombic, while kyanite is triclinic. These polymorphs are structurally complex and have two distinct types of Al atoms, with one type being in octahedral coordination in all of them. The other aluminium atom is in four, five and six –coordination respectively in sillimanite, andalusite and kyanite. The silicon atom is in tetrahedral coordination. Earlier we had undertaken lattice dynamics shell model calculations and inelastic neutron scattering experiments to determine the phonon density of states (Rao et al. (1999) Phys. Rev. B60, 12061). We now report calculations of the high pressure structure and thermal properties of these minerals. The computed high-pressure crystal structure, equation of state, phonon properties, mean squared atomic displacements and specific heat of the Al_2SiO_5 polymorphs are found to be in good agreement with available experimental data. The model can be fruitfully used to explore the possible existence of new phases.

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A3-13

HIGH PRESSURE LATTICE DYNAMICS OF THE Si_3N_4 POLYMORPHS

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Silicon nitride Si_3N_4 is an important ceramic material finding numerous applications. Recently, a new cubic spinel polymorph of Si_3N_4 synthesized under high pressure-temperature conditions has been identified; this phase is harder than the known α and β phases, making it a likely candidate for several important applications. While all the silicon atoms are in tetrahedral coordination in the α and β phases, two-thirds of the silicon atoms are in octahedral coordination in the spinel phase. To understand how the changes in silicon coordination manifest in the vibrational and thermodynamic properties, we have undertaken detailed lattice dynamics calculations of α, β and cubic Si_3N_4. The calculated crystal structures, bulk moduli, neutron-weighted density of states, specific heat, thermal parameters and equation of state are found to be in good agreement with available data. The compressibility and phonon density of states in the cubic phase are significantly different from that in the α and β – phases. These differences arise from the changes in silicon coordination accompanying the transitions.

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A3-14

EQUATION OF STATE AND THERMODYNAMIC PROPERTIES OF BaFCL

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The matlockite structured compounds (e.g. BaFCl) are of technological importance by virtue of their image storage properties on dilute-doping with rare earth ions. The structure of BaFCl (body centered tetragonal, space group P4nmm, Z=2) consists of alternate sheets of BaF_2 and $BaCl_2$. We have developed a rigid ion model for the study of the structure, dynamics and thermodynamic properties of this material. The model has been validated by phonon density of states measurements from polycrystalline sample of BaFCl by the technique of inelastic neutron scattering at the Dhruva reactor. The calculated crystal structure, equation of state, thermal expansion and temperature factors are in good agreement with available experimental data. The calculated bulk modulus of 43.3 GPa is in good agreement with the experimental value of 44 ± 5 GPa. These studies have enabled a microscopic understanding of the thermodynamic properties of BaFCl.

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A3-15

DISCOVERY OF AN ANTIFERROELECTRIC PHASE TRANSITION IN $Sr_{0.70}Ca_{0.30}TiO_3$: X- RAY, DIELECTRIC AND RAMAN STUDIES

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We show that Sr_{1-x} Ca_xTiO_3 (SCT) undergoes an antiferroelectric (AFE) phase transition in the composition range $0.18 \leq x \leq 0.40$ [Ranjan *et al* Phys. Rev. Lett. 84, 3726, (2000)]. Curie - Weiss fit to the ε_r' (T) data reveals negative value of Curie- Weiss temperature as expected for an antiferroelectric transition. The XRD measurements below phase transition temperature show new superlattice reflections. Rietveld analysis of XRD data reveals that structure of the antiferroelectric phase is doubled along c- axis of the paraelectric phase. The space group of the antiferroelectric phase is shown to be Pbcm. The paraelectric to antiferroelectric phase transition is marked by the appearance of new Raman lines around $79cm^{-1}$ and $128cm^{-1}$ with a concomitant enhancement in the intensity of the modes near 170 cm^{-1} and $541cm^{-1}$ on approaching the antiferroelectric phase transition temperature. Correlating the XRD and Raman measurements, it is concluded that the new Raman lines are due to $q \neq 0$ phonons which become Raman active due to folding of the corresponding special points into the zone centre (q=0) below the cell- doubling antiferroelectric phase transition temperature [S.K. Mishra *et al* Phys. Rev. B 64, (9), 092302, (2001)].

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MODELING OF POTENTIAL IN TRIGLYCINE SULPHATE (TGS) USING SINGLE CRYSTAL NEUTRON STRUCTURE OF (TGS)

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It is well known that out of three glycine molecules of Triglycine Sulphate (TGS) labeled GI, GII and GIII, it is GI located near the plane perpendicular to b axis at 0.25b (mirror plane in paraelectric state) plays the most important role in polarization reversal and ferroelectric phase transition. It is attempted to model the double well potential seen by GI using hydrogen bond potential given by Ramanadham *et.al.* (1978) and the potential for non-bonded interactions. The Neutron structure of TGS reported by Kay *et.al.*(1972) is taken as a starting point in this attempt to model the potential seen by Glycine I as it flips between two of its equivalent sites in the unit cell.

The results indicate a deep double 'well' kind of potential with the value of barrier height much more than the value of thermal energy KT at room temperature. This result is supported by the Ising kind of behavior exhibited by TGS.

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PHASE TRANSITION IN K2Fe(SO_4)$_2$ .4H_2O

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In substances related to Mohr's salt, three compounds $K_2Fe(SO_4)_2 \cdot nH_2O$ (n=2, 4 or 6) are known. The title compound showed anomalies of both specific heat and dielectric constant at 285k. Structure analyses were performed, therefore, at 303K [monoclinic, space group C2/m; a=11.853(1), b=9.544(1), c=9.951(1)Å; β=94.81(1)°; V=1121.7(5)Å^3; Z=4] and 123K ($P2_1/a$, Z=4). The cell dimensions showed no drastic changes above and below the transition temperature. The crystal consists of potassium cations and octahedral *trans*-[$Fe(SO_4)_2(H_2O)_4$] complex anions. Two complex anions with similar geometry exist in the cell, which are chemically equivalent but crystallographically independent taking different orientations. Each anion is highly symmetric in the high-temperature phase: the Fe atom occupies a center of symmetry, the Fe-O-S-O bonding lie in the mirror plane, and there exists a two-fold rotation axis along the Fe-O(water) bond in one anion and that along the bisector of the O(water)-Fe-O(water) angle in the other. The anions lose the mirror and two-fold symmetries in the low-temperature phase, and slightly deform. This transition feature differs from that of $K_2Fe(SO_4)_2 \cdot 2H_2O$ in which large rotational changes of the H_2O molecules were observed along with the halved cell volume in the high-temperature phase as was already reported by the authors' group.

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A3-18

THE EFFECT OF PRESSURE ON ARSENIC TELLURIDE (As_{55} Te_{45}) PHASE TRANSITION

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The semiconducting As_{55} Te_{45} glasses are prepared by melt quenching method. The amorphous nature of the quenched material is confirmed by X ray diffraction. High pressure differential thermal analysis system is used for this study. As_{55} Te_{45} is heated in the DTA cell at ambient pressure. Two exothermic peaks have been recorded at two different temperatures 312.42 and 390.30 K respectively. These two peaks show the double stage thermal crystallization. Later pressure is applied and the sample is heated. The first exothermic peak is shifted to higher temperature 320.11 K and becomes sharp. One endothermic peak which does not appear at ambient pressure, now exists at 0.13 GPa and at 323.96 K. The second peak also shifts to higher temperature 405.69 K. The sample As_{55} Te_{45} glasses , when heated starts restructuring towards longer range order and tries to go to stable condition, by releasing some amount of heat. The first exothermic peak is accounted for the same. This can be explained by Percolation theory. After translational movement of the atoms, the electronic distribution starts. This is known as localization or delocalization of electrons and is explained by Anderson transition. The appearance of endothermic peak might be due to the fact that, there is one more orientation or the restructuring of the phase at that temperature. The details are discussed in this paper.

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A3-19

X-RAY ANOMALOUS SCATTERING STUDY OF THE LOW-TEMPERATURE PHASE OF NaV_2O_5 BY USING ITS MONOCLINIC SINGLE DOMAIN

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The quarter-filled spin-ladder compound NaV_2O_5 undergoes a novel phase transition at *Tc*=35K associated with its spin, charge and lattice system. Its orthorhombic phase (Pmmn) above *Tc* has a charge-disordered state as nominally represented as $V^{4.5+}$, while below *Tc* charge-ordering as V^{4+} and V^{5+} [PRL 85 (2000) 4349], formation of spin singlet ground state [JPCS 60 (1999) 1099] and atomic displacement modulated with q=(1/2,1/2,1/4) [JPSJ 66 (1997) 326] take place cooperatively. For last several years, however, no conclusive structure for the low-temperature phase has been obtained. Very recently Ninomiya *et al.* [private commun.] succeeded in a very precise structure analysis, claiming a monoclinic phase (A112) and observed a concomitant monoclinic splitting of fundamental reflections by synchrotron x-rays.

In the present study, we have carried out an anomalous scattering experiment across the K-edge of V ions (V^{4+} and V^{5+}) to fully determine a charge-ordering pattern by using a single domain at Photon Factory. A significant difference in superlattice intensity spectrum as a function of x-ray energy is observed between two kinds of monoclinic domains to offer a key information on the charge ordering and a full structure analysis is under way to complement Ninomiya's structure analysis.

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A3-20

LOW-TEMPERATURE TEM STUDIES ON CHARGE-ORDERING AND FERROMAGNETIC DOMAINS IN MANGANITES

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Low-temperature analytical and Lorentz TEMs are applied to the phenomena of charge-orbital ordering and ferromagnetic domains in manganites. Most of experiments were made by two 300kV Cold-FEG TEMs (Hitachi: HF-3000): (a) analytical TEM with EDX and EELS-based imaging system (GIF), and (b) Lorentz-type TEM in which specimen is isolated from the magnetic field of the objective lens. Both liq.He and liq.N_2 cooling holders (Oxford Inst.) were used to cool the specimen below T_{co} (charge-order temperature) or T_c (Curie temperature). Charge-orbital ordered structures of layered manganites, $Nd_{1-x}Sr_{1+x}MnO_4$ (x=2/3 & 3/4), were studied by analytical TEM, and sinusoidal structural distortion giving rise to the superstructure was successfully observed in HRTEM images taken below 150K. The observation suggests that the "Wigner-crystal" model best explains the charge-orbital ordered structures in manganites. Direct observation of ferromagnetic domains were made, by low-temperature Lorentz electron microscopy, for $Nd_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ (x=0-0.1), and it was confirmed for x=0.02 compound that small ferromagnetic domains coexist with charge-ordered matrix. Volume fractions of ferromagnetic domains dramatically increase with x, although charge-ordered domain survives even for x=0.1.

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A3-21

ORBITAL ORDERING OF TRANSITION-METAL-OXIDES OBSERVED BY RESONANT X-RAY SCATTERING

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Orbital degree of freedom plays important roles in electric and magnetic properties in a strongly correlated electron system. The method of measurement for orbital ordering, however, has been limited so far. Recently it has been pointed out that synchrotron x-ray diffraction is a very powerful tool to observe the ordering. In particular the resonant x-ray scattering (RXS) technique has been developed to detect the orbital ordering for last few years[1]. This is a technique combining diffraction with spectroscopy. By using this technique the orbital states in various systems have been elucidated[2], though the microscopic mechanism of the resonant x-ray scattering is still controversial.. Here, we will report new results of perovskite transition-metal-oxides observed by RXS.

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A4 : Crystallography in chemistry

A4-1

CRYSTAL STRUCTURE ANALYSIS OF TWO CHROMANONES

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Two chromanones with different substitutions are taken for crystallographic study and the results are presented. The compound I crystallizes in monoclinic space group $P2_1/a$ with cell dimensions a= 16.412(4), b = 8.715(5), c = 16.524(2) Å, β = 118.61(1) °, V= 2072(8) $Å^3$ and Z= 4. The compound II crystallizes in monoclinic space group $P2_1/c$ with a = 10.366(1), b = 14.145(1) c = 15.334(1) Å, β= 99.14(2)°, V =2222.7(4)$Å^3$ and Z= 4. Both the structures were solved by direct methods and refined to final R-value of 0.0638. C-H...O type of intermolecular interactions help to stabilize the molecules in the unit cell in addition to van der Waals forces. It is interesting to note the presence of C-H...π interactions in both the compounds.

Chromanones are less toxic when compared to flavanoids. There exists a marked difference between the toxicity of the chromanones and the simple flavanoids and this was attributed to the absence of the side phenyl ring in the chromanones. The chromanones were claimed to be active against trichomonas, Gram- positive and Gram- negative bacteria and fungi. Many 4-chromanone derivatives are used as starting materials for the synthesis of natural products such as hematoxylin, brazillin --etc.

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STRUCTURAL ANALYSIS OF TWO DIFFERENT PIPERIDONES

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The transition of piperidones active form, from 'chemical' to 'pharmacological' be detected through the identification of structural relations between their different forms. To establish the structures, the following two piperidones are studied by cystallographic methods.

1.CADMPO(2,6-diphenyl-N-choloroacetyl-3,5-dimethyl-4-piperidone) crystallizes in monoclinic space group $P2_1$ with cell parameters a = 8.2082(1), b = 10.4899(1), c = 10.6175(1)Å, β = 91.833(1)°, V = 913.73(2)Å^3, Z = 2 and refined to a final R-value of 0.0399.
2. CAEPO(2,6-diphenyl-3-ethyl-4-piperidone) crystallizes in monoclinic space group $P2_1/n$ with cell parameters a = 10.3626(6), b = 8.5702(5), c = 21.6930(1)Å, β = 92.250(1) °, V = 1925.06(2)Å^3, Z = 4 and refined to a final R-value of 0.0623.

The displacement of alkyl groups in going from CADMPO to CAEPO sets forth only a very few uncommon features in their geometry. The two piperidones exhibit akin structural features like involvement of C-H...O type interactions in their packing and adoption of twist-boat conformation by their heterocyclic rings, imputing structural stability.

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A4-3

X-RAY CRYSTAL STRUCTURES OF THREE ISOQUINOLINE DERIVATIVES

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Isoquinoline is a ligand, which is used as a complexing agent for different metals. Tetrahydroisoquinolines represent a class of biologically active phenylethylamines. The 4-substituted tetrahydroisoquinolines have potent pharmacological activity. The title compounds [$C_{16}H_{12}ClNO_2$ (I), $C_{16}H_{12}BrNO_2$ (II) and $C_{15}H_9Cl_2NO_2$ (III)] crystallize in monoclinic space groups $P2_1/n$ for I and II and $P2_1/c$ for III. The asymmetric unit contains three molecules for one molecule and I for II and III respectively. The structures were solved by Direct Methods using SHELXS97 and refined using SHELXL97 to the R-values 6.5%, 4.2% and 3.5% respectively. The molecular packing is stabilized by weak C-H...O hydrogen bonds. Conformational parameters are calculated and compared. The structural and conformational analysis of these three compounds will be discussed during presentation.

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STUDY OF WEAK INTERACTIONS IN (4-CHLOROPHENYL) (4-FLUOROPHENYL) PYRIDINE - 4 - YL - METHANOL AND BIS (4-FLUOROPHENYL) PYRIDINE - 4 - YL – METHANOL

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In continuation of our investigations on weak interactions involving fluorine, we present the crystal structure of two compounds. Both the compounds form chains with the molecules linked by O-H...N hydrogen bonds as observed in diphenyl (4-pyridyl) methanol.[1] In addition C-F...π interactions[2] are observed as a consequence of the fluorine atom being flanked by the phenyl rings of the neighboring molecules. In the first structure, we also observe a significantly short intermolecular Cl...Cl interaction[3] [type I, Cl...Cl = 3.4213(9) Å, $\angle$C-Cl...Cl' = 127.2°) but no other halogen...halogen interactions are present. However, the second structure does not have any F...F interaction. A comparative study of these structures in the context of weak interactions will be discussed.

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A4-5

X-RAY CRYSTAL STRUCTURE OF TWINNED BROMONITROSYL-BIS(TRIPHENYLPHOSPHINE)NICKEL

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The title complex was synthesized from the corresponding dibromo complex by reaction with nitrite anion as the source of the nitrosyl ligand. The diffractometer determined unit cell is triclinic containing four molecules of the complex. It was noted that the mosaicity parameter and cell parameters changed as the data reduction proceeded. Solution of the two molecule asymmetric unit was straightforward, but the two molecules appear to be nearly identical. Examination of the intensity data show the systematic condition $0kl$, k = odd absent, and examination of the cell packing suggests the presence of a glide operation and a screw operation in addition to the inversion center required by the *P-1* space group, leading to the conclusion that the true space group is $P2_1/c$. Synthetic precession photographs obtained from the frame data clearly show the twinning of the parent lattice giving rise to the apparent triclinic cell.

Crystal data: $C_{36}H_{30}NiNOP_2Br$; M_r = 693.17 Daltons; dark purple; 0.09 x 0.16 x 0.30 mm; hexagonal plate; triclinic; *P-1* (No. 2), a = 9.6411(1), b = 14.8944(2), c = 22.7806(4) Å, α= 79.5670(5) β = 85.9471(5) γ= 90.0044(9) °, V = 3208.85(8) Å^3 Z = 4, μ = 1.98 mm^{-1}; d_{calc} = 1.435 Mg/m^3., $\lambda_{MoK\alpha}$ = 0.71073 Å; T = 200 K. Data collection: Nonius KappaCCD; 0.5 mm *ifg* capillary collimator; Oxford Cryosystems LT device; 53796 data collected (triclinic); 18564 unique; 12720 observed.

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SYNTHESIS AND CRYSTAL STRUCTURES OF 6-(4-CHLOROPHENYL)-3-CYANO-4-[N'-BIS(4-FLUOROPHENYLMETHYL)PIPERAZINO]2H-PYRAN-2-ONE AND 4-(4-CHLOROPHENYL)-2-CYCLOPROPYL-6-[N'-(2-PYRIDYL)PIPERAZIN-1-YL]BENZONITRILE.

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6-(4-Chlorophenyl)-3-cyano-4-[N'-bis(4-fluorophenylmethyl) piperazino]2H- pyran-2-one **(1)** and 4-(4-chlorophenyl)-2-cyclopropyl-6-[N'-(2-pyridyl)piperazin-1-yl]benzonitrile **(2)**. Compounds **1** and **2** were synthesized by nucleophilic substitution by sec-amine on suitably functionalized 2H-pyran-2-one followed by ring transformation from cyclopropyl methyl ketone in presence of base. Diffraction quality crystals were obtained by slow evaporation of solvent at room temperature.

Structures of **1** and **2** were solved by direct methods and refined anisotropically by full-matrix-least-squares method on F_o^2. The molecular structure of **1** showed that the piperazine ring (B) adopts a chair conformation and the N7 and N10 substituents are in equatorial positions. There is an intramolecular H-bonding. The crystal packing revealed a network of various weak intermolecular H-bonding (C-H...O, C-H...N and C-H...F) and aromatic π–π interactions (APPI). Currently the importance of these interactions is being realized in crystal engineering and supramolecular design. Both the chlorobenzene (E) and lactone (A) rings are stacked in pair due to APPI. The molecules are stacked in such a way that ring A overlap with ring B and vice-versa. In addition, one of the fluobenzene rings, ring D, also shows APPI. Thus the combination of weak H-bonding and aromatic π–π interactions mainly stabilize the molecules in crystalline state. The crystal structure of **2** showed that the asymmetric unit contains two molecules of similar conformations. The piperazine ring (C) adopts a chair conformation. The crystal packing revealed the presence of weak intra- and intermolecular C-H...N and C-H...π interactions that play a fundamental role in three-dimensional organization of the molecules in solid state. The above pair of compounds **1** and **2** are highlighting the noncovalent weak intra-and intermolecular interactions. Knowledge of noncovalent interactions between molecules will help in understanding the molecular recognition process.

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C–HALOGEN···π SYNTHON IN POLAR CRYSTAL PACKING

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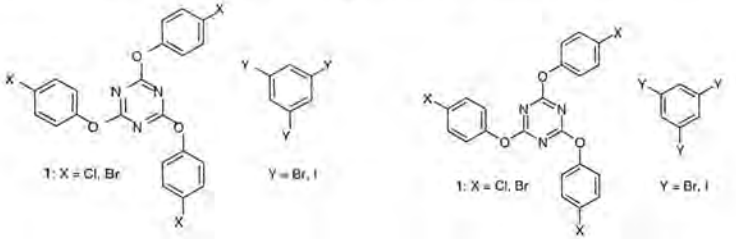
It has been shown by us that 4-halophenoxytriazines **1** self-assemble via the triangulo halogen synthon to produce hexagonal cavities and channels that include various guest species such as benzene, trinitrobenzene, hexachlorobenzene, hexamethylbenzene, hexamethylphosphoramide (1,2). These isomorphous host-guest clathrates crystallise in $P6_3/m$ space group with $a = b \equiv 15.5$ Å, $c \equiv 6.9$ Å. A notable feature of these crystal structures is that they are stabilised by the weak interactions, halogen···halogen, C–H···O, C–H···N, C–H···halogen.

Co-crystallisation of triazine **1** with tribromobenzene (tbb) and triiodobenzene (tib) guests afforded inclusion crystals in $P6_3$ space group with similar cell axes compared to the centrosymmetric family. Thus, internal reorganisation of tbb and tib guest species and host phenoxy rings in the hexagonal nanotubes does not perturb the lattice parameters compared to the $P6_3/m$ structures. A plausible reason for chiral crystallisation with trihalobenzene guests is the polar chain of alternating C–halogen(guest)···π(host) and C–H(guest)···π(host) interactions and the herringbone packing between screw axis related host phenoxy rings. The recurrence of $P6_3$ space group in four host-guest crystals suggests that the weak C–halogen···π synthon induce enantiomorphous crystallisation (3). The self-assembly of chiral crystals from achiral or racemic components is of importance in crystal engineering, materials applications and in the understanding of spontaneous resolution during crystallisation.



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X-RAY CRYSTAL STRUCTURE OF THE SUPRAMOLECULAR CALCIUM VANADIUM OXIDE, CaV_2O_6

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The title compound was prepared from calcium chloride and ammonium vanadate by hydrothermal synthesis. Examination of synthesized undistorted space precession photographs revealed weak non-Bragg intensities along the b^* axial direction which can be indexed to the parent cell with a fourth index q such that $q = k + nq$. Only the $q = \pm1$ intensities can be seen in In the hkm zones, while the $q = \pm1$ and ±2 intensities can be seen in the nkl zones.

The parent structure easily refines to $R_1 = 0.0401$ for the 347 unique independent parent data collected. Orientations of individual anisotropic atomic displacement parameters suggest positional movements to account for the observed structure modulation.

Crystal data: CaV_2O_6; $M_r = 222.85$ Daltons; light green transparent 0.075 x 0.20 x 0.60 mm needle crystal; monoclinic parent cell; $C2/m$ (No. 12), $a = 10.086(1)$, $b = 3.672(1)$, $c = 6.995(1)$ Å, $\beta = 105.19(1)$ °, $V = 250.02$ Å^3 $Z = 2$, $\lambda_{MoK\alpha} = 0.71073$ Å; T = 200 K (Nonius KappaCCD / Oxford Cryosystems).

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X-RAY STRUCTURE CHARACTERIZATION OF DISORDERED FRIEDELIN-3-ONE AND EPIFRIEDELIN-3-OL

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Preliminary results of a structure correlation study of the friedelanes that have been previously characterized (taken from the Cambridge Crystal Structure Database) by single crystal x-ray studies revealed an anomaly in the sum of the C-C-C and two O-C-C angles about the oxygen substituted C_3 position in ring A. The distance, 1.33 Å, and the sum of angles, 343.1 °, in epifriedelin-3-ol are intermediate between the ideal values (1.21 Å and 360.0 °) for sp^2 hybridization and (1.43 Å and 328.5 °) for sp^3 hybridization.

An explanation for the anomalous case can be suggested from an independent structure determination based on a crystal obtained from the rhizome of *Davallia solida* Sw, and having the same cell constants and space group as the anomalous compound; colorless clear plate crystal, 0.12 x 0.40 x 0.42 mm, of mixed friedelin-3-one, $C_{30}H_{50}O$, / epifriedeliln-3-ol, $C_{30}H_{52}O$. Monoclinic *C2* (No. 5), a = 13.437(3), b = 6.430(1), c = 29.599(6) Å, β = 91.97(3)°, 295 K, Z = 4, d_{calc} = 1.109 Mg/m^3. Data collected on a Bruker/Siemens SMART equipped with MoKα x-radiation. The single crystal structure exhibits two well-separated peaks for the oxygen atom position. The two peaks were modeled as partial oxygen atoms with occupancies onstrained to a sum of one. One peak corresponds to a ketone at position C_3 and the other to a hydroxyl group at position C_3. The average of the C-O distances and the average of the sum of the angles about C_3 for the disordered structures corresponds to the anomalous values

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A4-10

RARE EARTH COMPLEXES OF P-T-BUTYLTETRATHIACALIX[4]ARENE

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The calixarene, p-t-butyltetrathiacalix[4]arene (LH4) has exhibited a propensity for the stabilisation of transition metal clusters and the term cluster keeper has been coined to describe this calixarene. The clusters are stabilised because in the cone conformation of L the S and O donor atoms act as a surface which can accommodate more than one cation. The key to the coordinating properties of L is due to the bonding of the S atoms with the metal ions, which is not the case for methylenes in conventional calixarenes. To continue on with our investigations into the coordination chemistry of L, we switched our focus to the rare earths where it was found that these cations also form clusters on mixing with L. Two types of clusters were isolated, a neutral 3Eu + 2L (1) and a charged 4Nd or 4Pr + 2L (2, 3) cluster. In both types the rare earth ions are sandwiched between the two calixarenes. Each cation is bonded to sulfur and also to two small ligands, either dmf, the reactant solvent, or dmso, which is present in starting materials.

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A4-11

X-RAY CRYSTAL STRUCTURE OF AN ANTIDEPRESSANT CLASS OF DRUGS: DESIPRAMINE-HYDROCHLORIDE

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The title compound is a tricyclic antidepressant of dibenzazepine class of drugs.

The dibenzazepine class of compounds encompass a broad spectrum of theoretical and applied disciplines. At the theoretical level,chemists are fascinated by these compounds from the molecular standpoint. At the applied end of the spectrum ,an enormous amount of research on depressive disorder has been conducted in pharmaceutical laboratories and the efficacy of dibenzazepine in elevating depression has been well established.

In view of the above medicinal importance , the X-ray crystal structure analysis of the title compound has been carried out. The compound crystallizes in triclinic spacegroup P1 with cell parameters a = 10.8504 (5)Å, b =16.2316(7)Å, c=20.6943Å, =72.057(2)^0, β = 89.980 (2)^0, γ =80.465(2)^0 z = 1. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares method using SHELXL-97 to a final R-factor of 0.10. The details of the crystal structure will be discussed.

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A4-12

CRYSTAL AND MOLECULAR STRUCTURE OF SYN-7-TRIMETHYLSILYL-2-NORBORNENE-ENDO-5, 6-DICARBOXYLIC ACID

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The structural elucidation of the title compound was undertaken as the regio and steriochemistry of the compound is essential to understand the steriochemical behaviour of trimethylsilyl-cyclopentadiene in Diels-Alder reaction. X-ray crystal structure analysis of the title compound has been determined. The compound crystallizes in monoclinic spacegroup $P2_1$ with cell parameters a =8.1506(2)Å, b = 7.6964(1)Å, c =22.5962(5)Å, β =90.33°, Z=2 and V= 1417.44 $Å^3$. The structure was solved by direct method using SHELXS-97 and refined by full-matrix least - squares method using SHELXL-97 program.The final R- value is 0.0478 for 2186 unique reflections. It is confirmed from the crystal structure that the trimethylsilylgroup is on the same side as the double bond and the two carboxylic groups are endo. This indicates that in the transition state the bulky trimethylsilyl group takes least hindered position. The details of the crystal structure will be discussed.

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A4-13

CRYSTAL AND MOLECULAR STRUCTURE OF CIS -1-(TRIMETHYLSILYL)-CYCLOPENTANE-1, 2,DIOL

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1,2,Dihydroxysilanes are versatile synthetic intermediates. The chemistry of cyclic cis-1,2-silyldiols is little explored. Their crystal structure study is of particular interest due to the possible Si....O interaction and the usual intra and inter molecular hydrogen bonding in diols.The title compound is one of the series of cyclic silyldiols which are being studied for understanding the conformational effects on hydrogen bonding.

The title compound crystallizes in the monoclinic space group C2/c with a=21.5441(15)Å b=9.0715(6)Å c=10.99956(7)Å β =100.83 (0)^0 and z =4.The title compond was solved by direct methods using SHELXS-97 and refined by full-matrix least- squares on F^2 using SHELXL-97 to an R-value of 0.0679 for 1042 reflections with I>2σ (I) collected using a Siemens Smart- CCD diffractometer with MoKα radiation.The structural and conformational analysis will be discussed in detail.

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CRYSTAL AND MOLECULAR STRUCTURE OF 2,6,-BIS -(THIOCARBONYL MORPHOLINE)P- CRESOL

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X-ray crystal structure analysis of the title compound has been determined. The compound crystallizes in monoclinic spacegroup $P2_{1/a}$ with cell parameters a =9.191(2) Å b =21.932(6)Å, c =9.609(2)Å, β =111.6(2)^0, z =4 and V=1800.1(8)Å^3 . The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least- squares method using SHELXL-97 program. The final R- value is 0.069 with I>2σ(I) collected using Enraf-Nonius CAD-4 diffractometer with CuKα radiation. The details of the crystal structure will be discussed.

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A4-15

CRYSTAL AND MOLECULAR STRUCTURE OF A BRIDGED CHLORO CYCLOMETALLATED COMPLEX OF CU(11) WITH ETHANOLAMINE AND p-CRESOL

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X-ray crystal structure analysis of the title compound has been determined. The compound crystallizes in monoclinic spacegroup $P2_1/c$ with cell parameters a =11.919(10)Å b =18.726(10)Å, c =15.586(10)Å, β =103.880(10)^0, z = 8and V=3377.14Å^3 . The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least- squares method using SHELXL-97 program. The final R- value is 0.1589 for unique 2720 reflections with I>2σ(I) collected using Enraf-Nonius CAD-4 diffractometer with CuKα radiation. Further refinement is under progress. The details of the crystal structure will be discussed.

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SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF TERTIARY COPPER(II) COMPLEXES OF REDUCED SCHIFF BASE *N*-(2-HYDROXYBENZYL) α-AMINO ACIDS AND 1,10-PHENANTHROLINE

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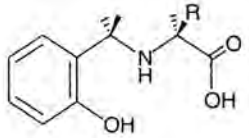
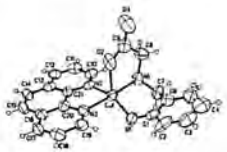
Copper(II) ternary complexes with reduced Schiff base ligands (*N*-(2-hydroxybenzyl)- α-amino acids) (H_2L) and 1,10-phenanthroline have been synthesized and characterized. By changing the metal-ligand ratio, counterions and pH of the solution, three types of compounds were synthesized and characterized in the solid state as well as in solution. They are neutral monomers, [Cu(L)(phen)] •xH_2O (L = sgly, sala, sval); monodeprotonated complexes, [Cu(HL)(phen)](ClO_4) •xH_2O and dimeric complexes, [Cu_2(L)(phen)$_3$](ClO_4)$_2$ •xH_2O. The molecular structures of the representative compounds are shown below.

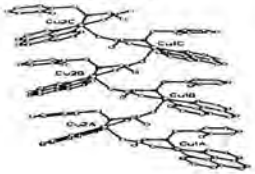


R=H, H_2sgly

CH_3, H_2sala

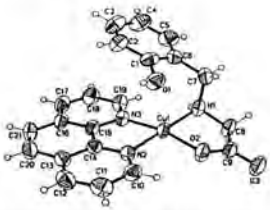
$CH(CH_3)_2$, H_2sval

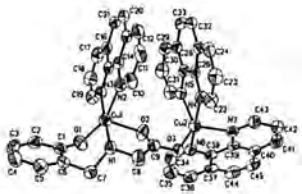




Neutral monomer
[Cu(sgly)(phen)]

Helical polymer
[Cu(Hsala)(phen)](ClO_4)





Deprotonated monomer
[Cu(Hsgly)(phen)](ClO_4)

Dimer
[Cu_2(sgly)(phen)$_3$](ClO_4)$_2$

The intra- and intermolecular weak interactions present in the solid state will be discussed in detail.

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HYDROGEN BONDING INTERACTIONS IN TERNARY Cu(II) COMPLEXES [Cu(X)(Y)] WHERE X=SQUARATE, Y=2,2'-BIPYRIDYL/1,10-PHENANTHROLINE: SYNTHESIS AND SINGLE CRYSTAL INVESTIGATIONS.

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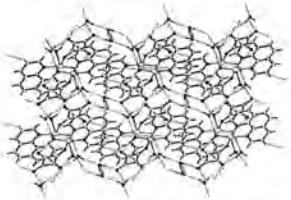
Two novel ternary Cu(II) networks [Cu(Sq)(2,2,bpy) $(H_2O)]_n$**1** [Cu(Sq) (1,10-phen) (H_2O)].$2H_2O$ **2** with squarate and N-donor lignds 2-2'bpyridyl and 1,10 phenanthroline has been synthesized and characterized by various phyico-chemical methods such as C, H, N, IR and single crystal X-ray diffraction technicque. The structural investigation revealed that [Cu(Sq)(2,2,bpy) $(H_2O)]_n$ **1** is a linear coordination polymer with the adjacent metal centers are bridged via squarate dianion. The O-H....O H-bonding interaction of the squarate and the water between the adjacent layers impart more dimensionality forming sheet like structural pattern .

Complex **2** can be described as a H-bonded two dimensional sheet. The discrete molecules are associated in pairs with the axial water molecules pointing in opposite direction and packed along b-axis with effective stacking interaction of the phenyl rings from adjacent pairs. Strong inter and intramolecular O-H...O interactions between the neighoubring layers along a-axis forms a two dimensional H-bonded network as shown in fig.2. The of the structural patterns in 1 and 2 may be may be governed by the stacking of the N-donor ligand and O-H...O H-bonding interactions. The various intermolecular interactions involved in the construction of supramolecular arcitecture will be dicussed in detail.



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CONTROLLING AUROPHILIC INTERACTIONS IN PHOSPHINEGOLD(I) THIOLATES

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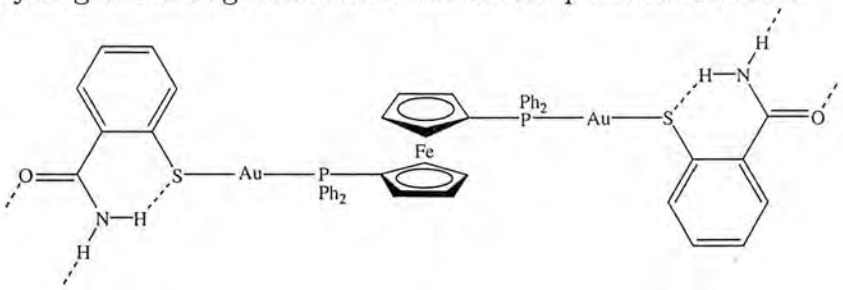
The energy of stabilization associated with hydrogen bonding and aurophilic (Au...Au) interactions in the solid state is about the same. This observation has sparked considerable interest into the examination of the complementarity, or indeed competition, between these modes of association. Our work on phosphinegold(I) thiolates, *i.e.* compounds with the general formula R_3PAuSR', has shown that it is possible to 'encourage' aurophilic interactions at the expense of hydrogen bonding interactions and *vice versa*. For example, ribbons of molecules are found in the crystal structure of {[2-$C(=O)NH_2]C_6H_4SAuPh_2PC_5H_4FeC_5H_4PPh_2AuSC_6H_4[C(=O)NH_2$-2]}, **I**, which features hydrogen-bonding interactions but no aurophilic interactions.



I

Substituting one hydrogen atom of the amide with a methyl group disrupts this structure in so far as *inter*molecular hydrogen bonding of the type seen in **I** no longer exists; the *intra*molecular hydrogen bonding between the N-H and S atoms persists. The removal of the dual hydrogen-bonding functionality now allows for the formation of aurophilic interactions.

The results of recent structural studies, including structures obtained with the aid of synchrotron radiation, as well as ramifications for the luminescence characteristics of these materials will be described.

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SYNTHESIS AND STRUCTURE OF THE INCLUSION COMPLEX OF CYCLOMALTOHEPTAOSE(β-CYCLODEXTRIN)WITH M-AMINOPHENOL

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Supramolecular compounds are systems with special functions, depending on the weak molecular interactions (such as Van der Waals, hydrogen bond, electrostatic and hydrophobic interactions). The supramolecular compound, β-CD-m-aminophenol [$(C_{42}H_{70}O_{35})$ $(C_6H_7O_1N_1)$ $(H_20)_{7.5}$ CH_3OH] was synthesized and determined by X-ray diffraction analysis. Monoclinic, $P2_1$ space group, with a = 1.5122(4), b = 1.0335(4), c = 2.0915(3) nm, β = 109.58(2) °, V = 3.0798(3) nm^3 and final R=0.0598. The perspective drawing of the title compound is shown in Fig 1. The system belongs to the "shallow inclusion" type which is rarely found, in which the guest is located over the narrow rim of the host. There are so many hydrogen bonds that they build a dense hydrogen bond net. The hydrogen-bond interaction is the main force to form the whole system and keep it stable.

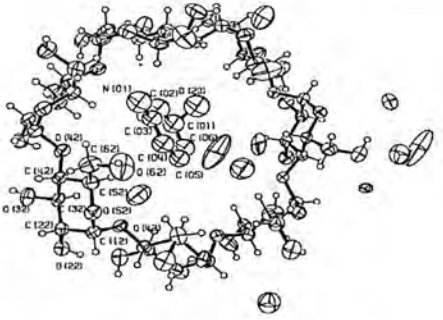

Fig 1. The perspective Drawing of the title Compound

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PHASE TRANSITIONS OF ORGANIC CRYSTALS CAUSED BY CONFORMATIONAL CHANGES OF ALKYL CHAINS

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Organic crystals often show phase transitions coupled with order-disorder transformations of molecular moieties. However, very few studies have been done on the detailed structural changes during transitions, because of the crystal damage and difficulties of intensity measurements for single crystal structure analyses at various temperatures. Recently, temperature-dependent structure analyses became possible through the development of diffractometers with two-dimensional detectors. Crystals of acridin-*N*-oxyl derivatives with a long alkyl chain (C_nH_{2n+1}, n=12, 13) showed that the first order transition occurred at 170 and 259K for n=12 and n=13 derivatives, respectively. In the case of the n=13, the single crystalline states were kept during the transition Structure analyses were carried out during the transition from 264 to 252 K every 2 K and at 295, 280, 273, 244 and 100 K. Crystals of *N*-4-methylpentanoyl-*N'*-ethylurea showed a phase transition at 367K (mp=378 K) and also kept single-crystalline-state during the transition. Structure analyses were performed at 98, 298, 328 K and in the range of 348 ~ 374 K every 2 K. In these crystals a long alkyl chain became disordered at high temperature phase. The detailed mechanism of the phase transition, conformational change of alkyl group induced by the thermal expansion, will be reported.

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A4-21

X-RAY CRYSTAL STRUCTURE ANALYSIS OF 17-OXO-16-(2-PYRIDYLMETHYLENE)ANDROST-5-EN-3β-OL MONOHYDRATE

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Epiandrostene derivatives are known to possess various medicinal and biological activities. The crystal structure analysis of the title compound 17-oxo-16-(2-pyridylmethylene)androst-5-en-3β-ol monohydrate, C_{25} H_{31} N $O_2.H_2O$, has been determined by the x-ray diffraction method. The compound crystallizes in monoclinic space group $P2_1$ and the unit cell dimensions are: a = 6.5376(3)Å b = 11.8766(10)Å c = 13.5312(15)Å, β = 91.197(12)°, $P2_1$, V = 1050.39(15)Å^3 , Z = 2 , μ = 0.64mm^{-1}, radiation Cu kα. The three-dimensional intensity data were collected on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by direct methods using SHELXL-97 using full matrix least square refinement. Final R = 0.0408 and WR = 0.1163 for 1888 observed reflection with I > 2σ(I). In the title compound the outer two six-membered rings are in chair conformations, while the central ring is in an 8β,9α-half-chair conformation. The five membered ring adopts 13,14-half-chair conformation. The pyridylmethylene has an E configuration with respect to the carbonyl at position 17. The structure is stabilized by intermolecular O-H...N and O-H...O hydrogen bonds . The structure and conformational features of the title compound will be discussed.

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SYNTHESES, CRYSTAL STRUCTURES AND LOW TEMPERATURE MAGNETIC STUDY OF TWO METAL-ORGANIC COORDINATION 3D FRAMEWORKS BASED ON MIXED N- AND O-DONOR LIGANDS

Golam Mostafa[a], Tian-Huey Lu[a], Tapas Kr. Maji[b], N. RayChaudhuri[b]. [a]Department of Physics, National Tsing-Hua University, Taiwan, R.O.C., [b]Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032, India.

Currently, scientists have dedicated their efforts to the magneto-structural studies on polynuclear complexes, aimed at understanding the structural and chemical factors that govern the exchange coupling between paramagnetic centers and bridging ligands to develop the magneto-structural correlation enabling the designed synthesis of interesting magnetic material. Research work using flexible malonate dianion is of current interest due to its versatile binding modes. But the work containing this flexible O-donor carboxylate ligand in combination with rigid N-donor based organic spacer is scanty.

We wish to present here the syntheses, structural diversity and low temperature magnetic study of two novel 3D architecture of copper(II), $[\{Cu_2(mal)_2(pyz)\}(H_2O)]_n$ **(1)** and manganese(II), $[Mn_2(mal)_2(4,4'bipy)(H_2O)]_n$ **(2)** [mal = malonate, pyz = pyrazine, 4,4'-bipy = 4,4'-bipyridine]. The low temperature magnetic study of complex **1** shows ferro as well as antiferromagnetic interaction. The ferromagentic interaction ($J=+8.8cm^{-1}$) operates due to syn-anti carboxylate bridging mode of the malonate dianion and antiferromagnetic interaction ($J' = -3.7\ cm^{-1}$) operates between the pyrazine bridging part.

The low temperature magnetic measurement of complex **2** shows the weak anitferromagnetic interaction ($J = -0.19\ cm^{-1}$). Crystal data: (1) Tetragonal, $P\bar{4}2_1c$, a=b=12.5982(12),c=9.1858(12)Å, R=0.0305, wR2=0.0840, S=1.06. (2) Monoclinic, $P2_1/n$, a=7.2974(10), b=18.7715(10), c=7.514(3), β=91.743(12)^0, R=0.0428, wR2=0.1431, S=1.12.

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A4-23

SELECTIVE PRECIPITATION OF POLYOXOMETALATE CLUSTERS BY ORGANIC COUNTERIONS: A SUPRA-MOLECULAR STRATEGY FOR CHEMICAL SYNTHESIS

Herman H-Y. Sung, Xiao-Yuan Li, Li-Rong Cai, Ian D. Williams and Samuel M-F. Lo.Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.

The modification of inorganic frameworks and structures by organic groups is well established in the hydrothermal synthesis of open-framework and microporous solids such as zeolites, in which the organic groups may serve as 'templates'. Polyoxometalate clusters have been receiving increasing attention due to their varied physical, chemical and even biological activity. Herein we attempt to show that organic counter-ions can also serve as selective crystallization tools for these oxides, allowing the isolation of novel cluster anions in high yield and purity. In the molybdenum-vanadium-phosphate system we report several new cluster types. These include the reduced capped Keggin cluster $[Mo_8V_6PO_{42}]^{8-}$ which has been isolated as its piperazinium and 1,4-diammoniocyclohexane salts. This is interesting since the Mo and V sites are chemically ordered and have nominal fractional valence states of +5.5 and +4.5 respectively. Initial studies on the physio-chemical properties and REDOX behavior of these clusters will be discussed, as will aspects of the supra-molecular assembly in the crystal packing which influence the process of selective cluster precipitation.

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THE HYDROTHERMAL CRYSTALLIZATION OF ORGANIC COMPOUNDS

Ian D. Williams, Lo-Ming Lai, Samuel M-F. Lo, Fanny L-Y. Shek and John A. Cha. Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.

The application of hydrothermal and related methodologies to the growth of organic crystals will be discussed. The advantages include enhanced crystal size, quality and high isolated yield. For co-crystals of different molecular species high phase purity and stoichiometric control can also be achieved. In the field of natural product characterization the improvements in modern X-ray diffractometry, combined with such new crystallization strategies, should see X-ray diffraction play an increasing role. We present several examples from this area, including the anti-malarial drug artemesinin and its derivatives.

In the field of crystal engineering, hydrothermal methods can be used to form organic co-crystals between aromatic acids and bases with specific stoichiometries so that molecular crystal 'phase diagrams' can be explored. Stoichiometry control also has important structural consequences and various bipyridines can form both a family of 1:1 neutral molecular adducts with phthalic acid, as well as a 1:2 family of organic salts. The hydrogen bonding in these crystals is under supra-molecular control and give examples of crystals with short single well N-H-O hydrogen bonds, such as 2[4,4'-bipy$H_{0.5}$][C_6H_2-1,2,4,5-$(COO)_4$-H_3]. Crystals suitable for neutron diffraction, including deuterated forms, are readily formed by hydrothermal methods and allow new insights into this important class of hydrogen bond.

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PREPARATION, CHARACTERIZATION AND STRUCTURES OF COPPER(II) AND ZINC(II) COMPLEXES OF AN ASYMMETRIC COENZYME ANALOGUE

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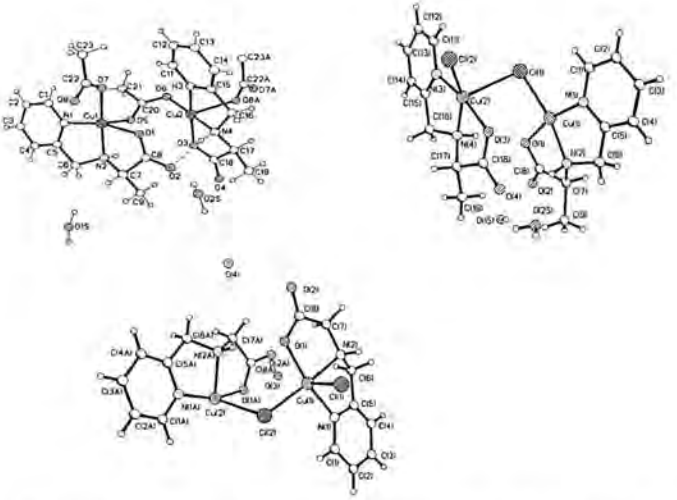
Pyridoxal phosphate is a cofactor required by many enzymes for catalyzing amino acid transformations. The reactions may involve the formation of an intermediate Schiff base. A series of copper(II) and Zn complexes of the ligand N-(2-pyridylmethyl)glycine, and N-(2-pyridylmethyl)-L-alanine, which were regarded as analogues of pyridoxal phosphate have been synthesized and characterized. Five single crystal structures were solved. It is clear that when the anions, which were introduced by the copper(II) or Zn salt coordinated with the metal center, a linear chain structure were obtained.



$[\{Cu(pala)Cl\}_2]_n \cdot 1.5nH_2O$, $[\{Cu(pala)(CH_3COO)\}_2]_n \cdot nH_2O$

$[\{Cu(pgly)Cl\}_2]_n \cdot 2nH_2O$

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EFFECT OF SUBSTITUENTS ON THE SOLID-STATE SUPRAMOLECULAR TRANSFORMATIONS

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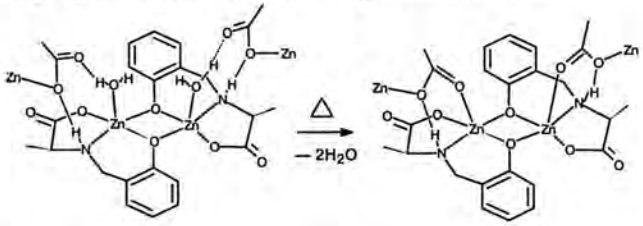
Supramolecules are generally prepared by self-assembly. Transformation of one type of network structure to another is very rare in supramolecular chemistry as well as in crystal engineering. For the first time, we have reported that the dimer $[Zn_2(sala)_2(H_2O)_2]_n.2H_2O$ (sala = N-(2-hydroxybenzyl)-*L*-alanine) with cross-linked hydrogen bonded helical porous honeycomb coordination polymeric network structure, upon removal of water molecules by thermal dehydration resulted in another 3D helical polymer, this time held by covalent bonds.



Thermal dehydration in a similar system, $[Cu_2(sala)_2(H_2O)]_n$ with helical coordination polymeric structure results in the solid state supramolecular conversion to the chiral 3D covalent open network $[Cu_2(sala)_2]_n$. The structure is isotypical to the Zn analogue. X-ray crystallography reveals that hydrogen bonding plays a key role in this process. These are the first examples of a true 'solid-state supramolecular synthesis' from two different precursors with two different metals. We have also investigated the influence of the substituents of the backbone of the ligand N-(2-hydroxybenzyl)-L-aminoacid on the solid state structures, and their dehydrated products. The results will be discussed in the talk.

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SYNTHESIS, CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF THE COMPLEXES OF METAL NITRATES WITH SCHIFF BASE DERIVED FROM 4-AMINOANTIPYRINE AND THENOYLTRIFLUORO ACETONE

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Metal complexes of Schiff base have occupied a central role in the development of coordination chemistry. This is apparent from the large number of publications ranging from the purely synthetic to modern physical and biochemical studies of these complexes.

New tridentate Schiff base ligand L_1 derived from the condensation of thenoyltrifluoro- acetone with 4-aminoantipyrine has been synthesized and characterized on the basis of elemental analyses, IR and X-ray diffraction methods. The structural analysis of this Schiff base ligand by X-ray diffraction indicates that it is a neutral tridentate in the ketoenamine form. Complexes of the type $[M\ (L_1)_m\ (H2O)_n]\ (NO_3)\ s$ (where $M=Ni^{2+}$, Cu^{2+}, Zn^{2+}, m=l,n=l,s=2; when $M=La^{3+}$, Sm^{3+}, Dy^{3+}, Er^{3+}, Nd^{3+}, m=2,n=0,s=3) have been synthesized and characterized on the basis of elemental analyses, IR, DTA. The complexes have been screened for their antibacterial activities against two bacteria.

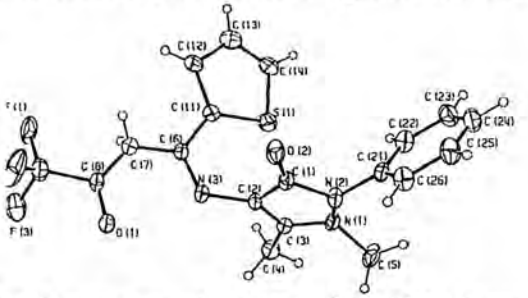

Fig I The Perspective Drawing of the Title Compound

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COORDINATION CHEMISTRY OF SULFONATES: A SYSTEMATIC X-RAY INVESTIGATION OF METAL ARENEDISULFONATES

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The coordination chemistry of metal sulfonates is not well explored and/or rationalized, unlike that of metal phosphates, which are well studied. Owing to the weak coordination strength of the sulfonate oxygen atoms toward the metal ions, only a few structures of transition metal sulfonates with the SO_3^- group that form direct coordination with the metal ions, are available. For the purpose of investigating the coordination chemistry of sulfonates, as well as the possibility of constructing functional inorganic-organic lamellar materials derived from metal disulfonates, the crystal structures of a series of metal arenedisulfonates were investigated.

All the compounds were prepared in aqueous solution. For Group IA and IIA metal 1,5-naphthalenedisulfonates[1], all except Mg^{2+} such as Li^+, Na^+, K^+, Ca^{2+}, Sr^{2+} and Ba^{2+} are coordinated by SO_3^- and similar inorganic-organic layered structures are adopted. For transition metal ions, Co^{3+}, Ni^{2+}, Cu^{2+} and Cd^{2+} form aquametal complex cations segregated with sulfonate anions. However, after incorporating amino ligands to the metal centers, SO_3^- is coordinated to Cu^{2+} [2] and Cd^{2+} [3] in aqueous solution, and 1-dimensional polymers are constructed by the chromophores $[MN_4O_2]^{2+}$ with arenedisulfonates anions as bifunctional spacers.

1. J. Cai et al. Acta Cryst. Section B, **2001,** B57, 520-530; 2. J. Cai et al. J. Chem. Soc. Dalton Trans., **2001**, 1137-1142; 3. J. Cai et al. J. Chem. Soc. Dalton Trans., **2001,** 2370-2375.

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A4-29

CRYSTAL STRUCTURE OF BROMOMETHOXY OSTHOL (7--METHOXY-8 (2-BROMO-3 –METHOXYL 3-METHYL-BUTYL) COUMARIN)

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Coumarins form an important class of widely distributed natural compounds. Most of them are isolated from plants especially from the family Umbelliferea, Rutaceae and leguminosae and also from animals or microorganisms. A wide spectrum of biological activities of coumarins includes -antithrombic effect, vasodilating effect on coronary vessels, reduction in blood pressure, antipastic and photo sensitizing effects. Osthol is a naturally occurring compound isolated from the seeds of Imperatoria Osthruthium. During the process of search for bioactive leads, Bromomethoxy Osthol was prepared by a facile, high yielding reaction of Osthol with Polymer supported per bromide resin. The chemical structure was assigned based on 1D and 2D NMR studies. The crystal study was conducted with an interest to check whether the compound was a racemic mixture or a single isomer and if so to find the absolute configuration. The compound crystallizes in triclinic system with 4 molecules in the unit cell and the cell dimensions were, a=10.280(2)Å, b=10.497(4)Å, c=16.175(4)Å, α = 75.91(2)°, β=80.81(2)°, γ=68.00(3)°. The structure was solved in space group P1.However latter it was found that there is a centrosymmetry between the molecules & hence the origin was shifted to the point of centrosymmetry and the structure was refined with 2 molecules in the asymmetric unit with space group P1.The two molecules differ in their conformations. The other structural details will be presented.

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STRUCTURE OF 1,8-BIS[(3-FORMYL-2-HYDROXY-5-METHYL)BENZYL]-1,4,8,11-TETRA-AZA-5,5,7,12, 12,14-HEXAMETHYLCYCLOTETRADECANE, A MACROCYCLIC LIGAND

G. Senthil Kumar[a], N. Sengottuvelan[b], D. Saravanakumar[b], M. Kandasamy[b], K.Chinnakali[a], Suchada Chantrapromma[c] and H-K. Fun[c], [a]Department of Physics, Anna University, Chennai 600025, India; [b]Department of Inorganic Chemistry, University of Madras, Chennai 600025, India and [c]School of Physics, Universiti Sains Malaysia, 11800USM, Penang, Malaysia.

Most of the naturally occurring enzymes been found to contain one or more metal atoms in their active sites, which tremendously influence their biological activities. As it is very difficult to study the biological activities of the naturally occurring bimolecules, synthetic models of various systems have been prepared to mimic the dexterous biological behaviour of the metal centers. The chemistry of polymacrocycles with coordinating side arms has attracted increasing interest during the last decade due to their abilities as coordinating ligands. For example, the synthesis of hexamethylated cyclam(1,4,8,11-tetraazacyclotetradecane) derivatives N-substituted by donor groups has been widely investigated. In fact such a N-substitution onto a macrocycle may increase its selectivity towards metal sequestration as well as the stability of the formed complexes. Moreover it is well known that the trans substituted hexamethylated cyclam can lead to hexa-coordinated complexes. The complexes may allow magnetic interaction or electron transfer studies depending on the nature of the encapsulated cations. Conversely, N,N'-disubstituted cyclams were far less studied due to their rather difficult synthesis. Hence a new building block for the complexation which contains N,N'-disubstituted (3-formyl-2-hydroxy-5-methyl)benzyl group in the cyclam has been devised[1]. This system is found to contain both phenolic oxygen and imine nitrogen group as donor centers, which have robust ligating nature for metal coordination. The crystal of the above compound contains two half-molecules in the asymmetric unit with the other half generated by a center of symmetry. The two phenolic oxygen atoms lie on either side of the planar part of the macrocycle at 2.321Å. The structure is stabilized by N-H...O and C-H...O hydrogen bonds.

[1]N.Sengottuvelan, D.Saravanakumar & M.Kandasamy (2001). Under preparation.

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AGGREGATION-CONTROLLED PROTON TAUTOMERIZATION

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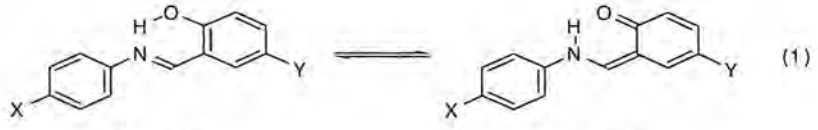
Compounds that undergo proton tautomerization can be thermochromic, because the tautomerization involves a proton transfer that accompanies a reorganization of the relevant π-conjugated system. Salicylideneaniline (**1**) and its analogs belong to a class of such compounds. In salicylideneanilines, the OH form is usually much more stable than the NH form [equation (1)] and the population change of the two tautomers with variation of temperature has been regarded as the cause for thermochromism. We found that in the crystals of **2**, NH form is predominantly zwitterionic and is considerably stabilized by intermolecular hydrogen bondings and electrostatic intermolecular interactions. The results indicate that the association of molecules is essential for the stabilization of the NH form.



(1)

OH form **NH form**

1 : X = Y = H **2** : X = OH, Y=Cl

We discovered that, a major stabilization of the NH form generally occurs even in a fluid solution, when molecules form an aggregate. At 297 K, the OH form is exclusively present. When temperature is lowered, the OH form decreases in population and the NH form emerges. At 77 K, the NH form is exclusively present. This phenomenon strongly depends on the concentration of the solution. The results indicate the formation of aggregates at low temperature and the stabilization of the NH form in the aggregate. Thus, the proton tautomerization is controlled by the aggregation of molecules.

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A4-32

CRYSTAL STRUCTURE OF 2-N-BUTYL-4-CHLORO-1[(2'-CYANOBIPHENYL-4-YL)METHYL]-5-HYDROXYMETHYL IMIDAZOLE

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The title compound is a white crystalline solid and serves as an important key intermediate for preparing the antihypertensive drug Losartan potassium. Imidazole part of losartan carrying substituents is the prime cause for the antihypertensive property. It has melting point of 154°C, soluble in chloroform, tetrahydrofuran, acetone, etc. The compound ($C_{22}H_{22}ON_3Cl$) crystallized in triclinic space group P1 with a=8.198(2), b=10.997(3), c=11.524(2)Å, α=90.83(2), β=94.31(2), γ=109.45(2)° and Z=2. The structure was solved by direct methods and the final refinement was carried out with anisotropic thermal parameters using full-matrix least-squares for all non – hydrogen atoms to a final R-value of 0.0813 for 3827 unique reflections at I>2 (I) collected using Enraf-Nonius CAD-4 diffractometer with CuKα radiation. The benzene ring containing C19 atom in this structure is approximately perpendicular to the imidazole ring. The structure is stabilized by O-H...N, C-H...N and C-H...O types of intermolecular hydrogen bonds in addition to the van der Waals forces. The structure and conformational features will be discussed in detail.

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CRYSTAL STRUCTURE ANALYSIS OF 4-CHLORO-3-METHYL-6[(N-2-PICOLYL)-1'-IMINOMETHYL]PHENOLATO COPPER(II)PERCHLORATE

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Copper is the third most abundant element among the transition metal ions found to be involved in biological processes. The synthesis of mononuclear copper complexes has been stimulated by a desire to 'mimic' the active sites of metalloproteins. The mononuclear Cu complex crystallizes in monoclinic space group $P2_1/n$ with cell parameters a = 7.295(4), b = 19.627(5), c = 12.770(4)Å and β = 101.25(4)°. The structure was solved by Patterson's method by SHELXS97 program and refined by full-matrix least-squares technique using SHELXL97 program. The final R value is 0.0387 for 2906 unique reflection in the $I > 2\sigma(I)$ cut off range. The copper atom coordinated to oxygen and nitrogen atoms found to have a slight distorted square planar geometry. The six membered ring containing Cu and O16, atoms assume sofa conformation and the five membered ring containing Cu and N15 is planar and lie in the same plane with the picolyl ring. The negative charge in the perchlorate molecule is neutralized by protonation in the methoxy group. The molecules are packed in a discrete fashion with and O-H...O and C-H...O types of intermolecular interactions playing a major role in stabilizing the molecules.

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CRYSTAL STRUCTURE OF TRICOSANE-1, 23-DIOL

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The crystal structure analysis of tricosane-1, 23-diol, HO–$(CH_2)_{23}$–OH, was carried out by single crystal X-ray diffraction method. All measurements were made on a Rigaku AFC-5R diffractometer with graphite monochromatized Cu Kα radiation. The crystal structure is an orthorhombic system (a=7.230(6)Å, b=63.045(5)Å, c=5.041(4)Å, Z=4) with a space group $P2_12_12_1$. All calculations were performed using *TEXSAN*. The structure was solved by direct methods with *SAPI* 91. The methylene H atoms were located at idealized positions, and were allowed to ride on the parent C atoms (C–H=0.95Å). The hydroxy H atoms were located from a difference Fourier map, and were allowed to refine isotropically for the final refinements. All H-atoms isotropic displacement parameters were fixed at $1.2U_{eq}$ of the parent atom. The final cycle of full-matrix least-squares refinement was based on 2491 observed reflections (F^2>-3σ(F^2)). The refinement was concluded with final reliability factors $R(F^2>2\sigma(F^2))$=0.047, $wR(F^2)$=0.176. In the molecular structure of the title compound, one of the hydroxy groups has a *gauche* conformation with respect to the hydrocarbon skeleton, whereas the other has a *trans* conformation. The molecules arranged along the longest axis, b, form layers which are similar to those of the smectic A liquid crystals.

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CRYSTAL AND MOLECULAR STRUCTURE OF 2,6, -DI (2,3,4,- TRIMETHOXY) BENZYLIDENE CYCLOXANONE

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The title campound C_{26} H_{30} O_7 is a new chalcone and it will be used as starting material for the synthesis of novel derivatives of 1,3–thiazines. These are important class of hetrocyclic compounds having diverse biological activities such as antibacterial, antifungal, insecticidal, anthelmintic and anticonvulsant

The title compound crystallises in orthorhombic system, space group Abm2 with a=8.704(1), b=38.140(7), c=6.945(3)A^0, V=2305A^{03} Z=4, T=293K, λ =0.71073A^0, μ =0.095mm^{-1}, F(000)=968, D_c=1.309mg/m^3 . The intensity data were collected from the Enraf-Nonius CAD-4 diffractometer. The structure was solved by direct methods and refined by full matrix least squares on F^2 to a final R value of 0.0377 and WR_2 value of 0.1105 for 1037 reflection with I > 2 sigma (I). The structure is stabilized by hydrogen bonds in crystal packing. The structural aspects of the molecule will be discussed in detail.

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CRYSTAL STRUCTURE OF N (3', 4', 5'-TRIMETHOXY BENZYLIDENE)-3-CHLORO-4-FLUOROANILINE N-OXIDE

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The title compound crystallises in monoclinic space group $P2_1/n$, with a=7.0843(6), b=8.3236(6), c=26.1306(6) Å, β=91.253(5)°, Z=4, V=1540.47(9) Å^3, T=293(2) K, λ = 1.5418Å, μ =2.463mm-1, F(000)=680, Dx=1.413mg/m3, R=0.0517, Rw=0.1614 for 2487 reflections, with I>4 (I). The 3d-intensity data were collected from the CAD4 diffractometer and the structure was solved by direct methods and refined by full matrix least squares method using SHELXL-97 program. The three methoxy groups attached to the other phenyl ring have large deviations from the mean plane of the ring making the molecule on the whole non-planar. There are no inter molecular hydrogen bonds and the structure is stabilised by van der Waals interactions.

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X-RAY CRYSTAL STRUCTURE OF TRIPHENYLPHOSPHINE OXIDE *M*-CHLOROBENZOIC ACID

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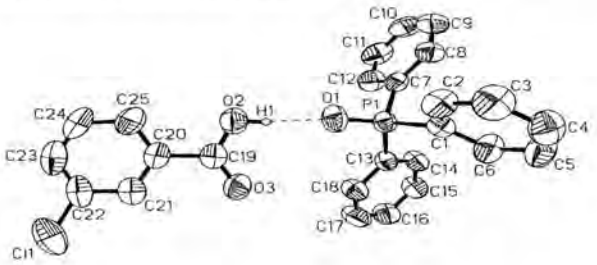
Hydrogen bonds play an important role in many systems. This is mainly due to their strong directional interaction compared to other intermolecular forces. Such hydrogen bonding property has been utilized in molecular recognition and crystal structure engineering. Triphenylphosphine oxide (TPPO) has a great conformational flexibility and hydrogen bond formation ability, which makes it a versatile molecule for cocrystallization. As part of our research interest in the above system, X-ray crystal structure of the title compound has been investigated.

$C_{25}H_{20}ClO_3P$, M_r 434.83, Monoclinic ($P2_1/n$); a = 8.845(1), b = *16*.101(1), c = *16*.029(2) Å, β = 103.97(1)°, V = 2215.3(4) Å^3, Z = 4, $D_{calc.}$ = 1.304 g cm^{-3}, λ(Mo-K_α) = 0.71073 Å, μ = 0.268 (mm^{-1}), R = 0.042 for 3334 reflections and 280 parameters.

In our contribution, details of the crystal structure will be reported and the type of hydrogen bond and its effect on



TPPO conformation will be discussed.

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NOVEL COORDINATION POLYMERS CONSTRUCTED FROM 4,4'-BIPYRIDINE AND PHOSPHATE

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The synthesis of open-framework metal phosphates has been a subject of intense research owing to their interesting structural chemistry and potential applications in catalysis. Recently, many research activities have focused on the synthesis of inorganic-organic hybrid frameworks. A study of the literature about transition metal supramolecular architectures shows that the most extensively studied bridging organic ligand is 4,4'-bipyridine. The results presented here concern several novel compounds in the metal-phosphate-4,4'-bpy system. For example, the structure of (4,4'-H_2bpy)[V_2(4,4'-bpy)$_2$(HPO_4)$_4$] consists of phosphate-bridged vanadium(III) chains, which are linked through 4,4'-bpy ligands to form anionic sheets with the charge compensating uncoordinated (4,4'-H_2bpy)$^{2+}$ cations between the sheets. [Ni(4,4'-bpy)$_2$(H_2PO_4)$_2$]·C_4H_9OH·H_2O exhibits a new type of interpenetration involving a 2D square net and a 3D $CdSO_4$-type framework of the same chemical composition. The structure of [(VO_2)$_2$(4,4'-bpy)$_{0.5}$(4,4'-Hbpy)(PO_4)]·H_2O consists of phosphate-bridged vanadium(V) double chains linked through 4,4'-bpy ligands to form a sheet with the monoprotonated 4,4'-Hbpy$^+$ ligand being coordinated to the metal atom as a pendent group. The synthesis and crystal structures of these novel compounds will be presented.

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FROM 5,1'-DICYCLOPENTADIENE SKELETON TO SPIRO[4,5]DECA-1,6,8-TRIENE SKELETON

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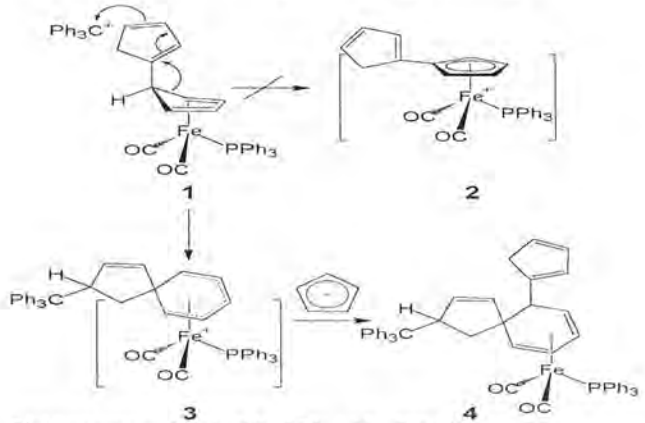
Utilizing a strategy of electron-transfer chain catalysis followed by nucleophilic alkylation, (η^4-*exo*-5-(C_5H_5)C_5H_5)Fe(CO)$_2$PPh$_3$ (**1**) was obtained in 60% isolated yield starting from (η^5-C_5H_5)Fe(CO)$_2$I, PPh_3, and C_5H_5Li. Normally the *endo* hydride of similar compounds could easily be abstracted by Lewis acid [Ph_3C^+] or protic acid HBF_4 and accordingly a treatment of [Ph_3C^+] on **1** was expected to result in [(η^5-(C_5H_5)C_5H_4)Fe(CO)$_2$PPh$_3^+$] (**2**). However, the reaction with [Ph_3C^+] didn't give **2** but [(η^5-spiro[4.5]decatrienyl)Fe(CO)$_2$PPh$_3^+$] (**3**). Cation **3**, upon a nucleophilic attack by C_5H_5Li, gave a (C_5H_5)-derived (η^4-



spiro[4,5]decatriene)Fe(CO)$_2$PPh$_3$ (**4**, 82%).

The X-ray structure analysis of **4** gave clearly the molecular connectivity that retrochemically suggested an unprecedented transformation from 5,1'-di-cyclopentadiene skeleton to spiro[4,5]deca-1,6,8-triene skeleton.

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A4-40

INTERMOLECULAR INTERACTIONS EXAMINED BY STRUCTURAL CHANGES OF MIXED CRYSTALS.

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It has been revealed that crystals of 4-(4-X-Ph-CH=N)-TEMPO radicals (X = Cl, Br and Me) were crystallized into different forms and showed different magnetic interactions. Crystals of the Br-derivative showed polymorphism with Cl- and Br-forms. To examine the role of the substituents on the crystal packing-mode, we prepared two-component mixed crystals (Cl-Br, Cl-Me, and Br-Me) and compared structural changes as the ratios of the components. Crystal structures of the mixed crystals are isomorphous with those of either pure component. For Br-Me system, mixed crystals of Me-, Br-, and Cl-forms were obtained. From the changes of the intermolecular interactions and the comparison of the polymorphic forms of the Br derivative, it was suggested that an intermolecular Br···Br interaction is very important for the crystal packing. The electrostatic interactions of the substituents and π–π interactions of phenyl rings are also important for the packing mode. Intermolecular energies were calculated using simple force-field potentials for the X···Y (X, Y=Cl, Br, Me) molecular pairs and Aryl-Aryl stacking pairs in the mixed crystals of Br- and Cl-forms. These calculations partly support the observed ratios of components.

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SYNTHESIS AND STRUCTURE OF 4,4,4-TRIFLUORO- 1-(2-THIOPHENE-2, 3-BUTANEDIONE-AMINO- ANTIPYRINE SCHIFF BASE

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Schiff base compounds derived from large numbers of carbonyl and amine compounds have been investigated, since they are becoming increasingly important as biochemical, analytical and antimicrobial reagents. The crystal data of the title compound is as follows: a= 10.964(3), b = 12.570(3), c = 13.840(4), β = 96.822(5)°, monoclinic, space group $P2_1/c$, Z = 4, F (000) =864. D_c = 1.478 g cm^{-3}, μ =0.226 mm^{-1}. The final refinement converges to R = 0.0546 on F^2, with the goodness - fit - of 1.046. The highest and lowest electron densities in the final difference Fourier map were 0.499 and -0.388e $Å^{-3}$.

The molecule consists of the pyrazolone, thioplene, phenyl rings and trifluoropropane- dicarbonyl moiety (see Fig 1). The bond lengths of C (6)-N (3), C (8)-O (1) and C (7)-O (8) are 1.274(4), 1.219(3) and 1.204(3) Å, respectively, corresponding to the -C=N and -C=0 bond lengths. but the bond lengths of C (6)-C (7) and C (7)-C (8) are 1.534(3) and 1.529(3) Å respectively. corresponding to the single C-C bond length, pointing to no extensive electron delocalization over the moiety.

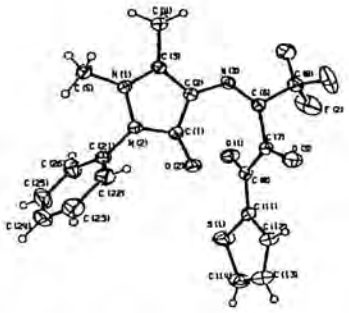

Fig 1 The Perspective Drawing of the Title Compound

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ROLE OF HALOGEN BONDING IN FORMATION OF STABLE INCLUSION COMPLEXES: X-RAY STRUCTURES OF *MYO*-INOSITOL DERIVATIVES WITH DIHALOMETHANES (CH2X2, X = Cl, Br)

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Inclusion complexes with high selectivity for guests is a frontier research area because of its applications in molecular selectivity and separations. However, designing a host that exhibits a specific molecular recognition capability is a challenging task. In a serendipitous discovery, a spontaneous crystallization of racemic 1,2,3,4,5 penta-O-benzoyl-6-O-tosyl myo-inositol (1) derivative yielding highly stable inclusion crystals was observed only with dihalomethanes (CH2X2, X=Cl., Br) whereas other common solvents failed to give crystals. X-ray structures revealed that the guests were held essentially by short C-X...O contacts and C-H...O interactions (Fig. 1).[1] In order to assess the role of former interaction termed as halogen bonding[2] in stabilizing host-guest complexes, a few more *myo*-inositol derivatives were synthesized . In this paper, we report two structures of hexa-O-benzoyl-*myo*-inositol (2) with dihalomethane guests (CH2X2, X=Cl., Br). Packing of molecules show (Fig. 2) two different types of open channels each containing molecules of CH_2X_2. Guest molecules in one of the channels make essentially strong C-H...O contacts while those in the other make X...O contacts with the host which are weaker than those observed in (1)[1] . But remarkably, here again, the spontaneous crystallization of (2) occures only with CH_2X_2, although the inclusion crystals of (2) are highly unstable to open atmosphere compared to the stable crystals of (1). The role of C-X...O interactions in the formation of guest specific stable inclusion complexes will be discussed with reference to the above crystal structures and others analyzed from the Cambridge Crystallographic Data Base.

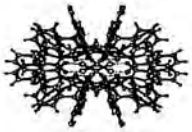

Fig. 1

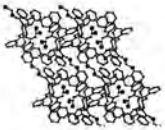

Fig. 2 (for CH2Cl2)

Reference:
[1] K. M. Sureshan, R.G. Gonnade, V. G. Puranik, M. S. Shashidhar and M. M. Bhadbhade, Chem.Commun., 2001, 881.
[2] E. Corradi, S. V. Meille, M. T. Messina, P. Metrangolo and G. Resnati, Angew. Chem. Int. Ed. 2000, 39, 1782.

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A4-43

STRUCTURAL INVESTIGATIONS ON METAL PHOSPHONATES

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Interest in transition metal phosphonate chemistry has accelerated in the recent years owing to their potential utility as sorbents and catalysts. We have recently synthesized some metal phosphonates using cyclohexyl phosphonic acid ($CyPO_3H_2$). The reaction when carried out in different conditions such as, hydrothermal, microwave as well as by slow crystallization, resulted in the same divalent phosphonates having a general formula of $M^{II}(O_3PR).H_2O$, (R= cyclohexyl). Analytically pure products were obtained in each case and were characterized by IR, DRUV, TGA/DTA, microscopy, and powder XRD methods. Representative examples were also studied by single crystal X-ray diffraction studies. The thermal analysis shows the removal of a water molecule and finally the formation of metal phosphate materials. The details of this investigation will be discussed in this presentation.

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CRYSTAL STRUCTURES OF 6-SUBSTITUTED DIBENZO[d,g][1,3,6,2] DIOXATHIO PHOSPHOCIN DERIVATIVES CONFORMATION OF HETEROCYCLIC RING.

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Organophosphorus heterocycles containing suitably substituted Phosphoryl unit exhibit significant Physiological activity depending on their size, the magnitude of the electrophilic character of phosphorus atom, the strength of the bond p-x and steoric nature of the substitutents. These compounds find very wide applications as pesticides, insecticides, nerve gases, antioxidants and as stabilizers in polymer and oil industries. The structural investigations of four 6 substituted dibenzo[d,g][1,3,6,2] dioxathiaphosphocin derivatives have been studies to understand the influence of the substituents on the conformation and identity the biological active phosphorus activities.

Crystal data:
I. C20 H15 Cl2O3PS2, monoclinic P21/c, a=13.272(2), b=9.225(1), c=17.257(1)Å (=90.39(1)°, Z=4, F(000)=960, dc=1.47Mg.m-3 , R=0.035 and Rw=0.083 for 2874 observed and 3153 collected reflections.
II. C20H15Cl2O3 PS2, triclinic, P-1, a=7.845(3), b=11.720(2), c=11.871(2)Å (=88.85(1), (=73.61(2), (=89.08(2)°, Z=2, F(000)=480, dc=1.489Mgm-3, R=0.0345 and Rw=0.0835 for 2701 observed and 2896 measured reflections.
III. C16H14Cl4O3 PSN, monoclinic, P21/c, a=9.188(2), b=20.588(5), c=10.861(3)Å, (=102.55(2)°, Z=4,, F(000)=960, dc=1.567Mgm-3, R=0.0343 and Rw=0.0875 for 3137 significant reflections.
IV. C13H15O3 PS, monoclinic, P21/n, a=11.624(7), b=11.091(3), c=14.407(4)Å, (=107.88(3)°, Z=4, F(000)=896, dc=1.70 Mgm-3, R=0.045 and Rw=0.109 for 2525 reflections.

All the structures are solved by direct methods and refined by full matrix least squares method. In the first three structures, the 8-membered dioxathia phosphocin ring adopts a boat-chair (BC) conformation and the substituents are in axial and equatorial positions at P, whereas, in the fourth structure, the heterocyclic ring exhibits a twist boat (TB) conformation. The geometrical parameters and orientations of the substituents at P will be discussed.

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A4-45

IN SITU OBSERVATION OF FLIP MOTION OF VINYL GROUP IN STYRENE DERIVATIVE CRYSTALS

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Styrene is one of the most widely used materials in synthetic polymer science. Its structure has been studied widely by theoretical calculations, but no crystal structure has been reported so far. However, a crystal structure of styrene would be very useful to understand its chemical properties and would also enable a comparision with the theoretically derived structure.

Single crystals of styrene (C_8H_8: m.p.242.5 K) and 2,4,6-trimethylstyrene ($C_{11}H_{14}$: m.p.236.2 K) have been made by *in situ* crystallization method, and their structures were determined by single crystal X-ray diffraction analyses at several temperatures. For comparison, crystal structures four other styrene derivatives, which are solid at room temperature, were also determined. In styrene 2,4,6-trimethylstyrene and 4-vinylbenzoicacid ($C_9H_8O_2$), a disorder where the vinyl group was fliped to the opposite direction was observed. As the occupancy factor changes with temperature, this flipping disorder was found to be the dynamical thermal motion. In 2,4,6-trimethylstyrene, space group was changed from $C2/c$ to $P2_1/c$ between 173K and 153K.

By comparing crystal structures of disordered and ordered styrene derivatives, the nature of the flipping motion of vinyl group can be clearly explained in terms of the environment around vinyl group, *i.e.* shape and volume of space occupied by vinyl group.

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MOLECULAR STRUCTURE OF DI-NUCLEAR Ni-COMPLEXES AS THE MODEL OF UREASE ACIVE SITE

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Urease catalyzes the hydrolysis of urea, an abundant end product of metabolism, to form ammonia and carbon dioxide. So far, so many investigations of the activity of urease and structural studies of the complex relevant to urease active site have been under taken to elucidate the mechanism of urease catalysis. It has been reported that for the activity of ap-urease, the adoption of carbon dioxide is essential in the presence of Ni ions, and that two Ni ions are 3.5 Å apart.

We carried out the X-ray structural analysis of di-nuclear Ni-complexes; $[Ni_2(L\text{-}Et)(CHF_2COO)(CH_3OH)_2](ClO_4)_2$ (**1**) and $[Ni_2(L\text{-}Et)(CF_3COO)(H_2O)_2](ClO_4)_2$ (**2**) (HL-Et = *N*, *N*, *N'*, *N'*-tetrakis[1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1, 3-diaminopropane) as the model of urease active site, to study the urease catalysis in more detail. Complexes **1** and **2** are isostructural. For **1** and **2**, each nickel center has an octahedral geometry with an N_3O_3 donor set from a bridging difuluoroacetato (for **2**, trifuluoroacetato), alkoxo of L-Et, methanol molecule (for **2**, H_2O molecule), tertiary amino nitrogen and two imidazolyl nitrogens of L-Et. The alkoxo oxygen atom bridges the corner of the two octahedrons. The Ni---Ni distances are 3.542(2) Å and 3.545(1) Å for **1** and **2**, respectively.

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CRYSTAL AND MOLECULAR STRUCTURE OF A COMPLEX: RHODIUM(111)-(1,10-PHENANTHROLINE)-(1,3-bis(BENZIMIDAZOLYL) BENZENE.

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N-heterocycles undergo cyclometallation to give five membered metallocycles. Cyclometallated complexes are used in organic synthesis, asymmetric synthesis, homogeneous catalysis, liquid crystals and photochemistry.

X-ray crystal structure of the title compound has been determined. The compound crystallizes in monoclinic spacegroup $P2_1/n$ with cell parameters a =16.165(2) Å, b =11.377(2) Å, c =16.998(2) Å, β=92.35(1)^0, z =2 and V=3123.46Å^3. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least- squares method using SHELXL-97 program. The final R-value is 0.0268 for unique 4365 reflections with $I>2\sigma(I)$ collected using Siemens P4 diffractometer.

The 2D NMR experiments on the above complex showed unidentate binding nature of O-phenanthroline. However, such a possibility was ruled out from the crystal structure analysis as it has established the bidentate binding mode of O-phenanthroline.The details of the crystal structure will be discussed.

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CRYSTAL AND MOLECULAR STRUCTURE.OF 2-(2[1]-N-O-PYRIDYLIDINE-PHENYL)BENZIMIDAZOLE

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X-ray crystal structure analysis of the title compound has been determined. The compound crystallizes in monoclinic spacegroup $P2_1/c$ with cell parameters a =8.6966(85)Å b =13.0455(95)Å, c =13.2707(41)Å, β=97.3822(44)^0. Z =2 and V=1493.10Å^3 . The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least- squares method using SHELXL-97 program. The final R- value is 0.1505 for unique 2047 reflections with I>2σ(I) collected using Rigaku AFC7S diffractometer with MoKα radiation.Further refinement is under progress.The details of the crystal structure will be discussed

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CRYSTAL STRUCTURE-REACTIVITY CORRELATION METHOD: SOLID STATE PHOTOCHEMISTRY AND X-RAY CRYSTALLOGRAPHY OF 6-HYDROXY CYCLODECANONE

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Solid state irradiation of 6-hydroxycyclodecanone (**1**) leads to a major photoproduct, namely trans-9,10-decanediol (**2**) and its diastereomer, cis-9,10-decanediol (**3**) (minor product). X-ray structural investigations of (**1**) and (**2**) were undertaken to understand the product formation and the role of the specific crystal packing that leads to the observed photoproducts. Crystal data: (**1**), Monoclinic, $P2_1$, a=7.169(1), b=5.331(1), c=12.509(1)Å, β=92.02(1)°, Z=2, R=0.0302 for 936 observed reflections [I>2σ(I)]. Crystal structure analysis reveals that there are two possible hydrogens at γ-positions that may be abstracted, but the product formed is due to ω-hydrogen abstraction. However the geometrical requirement for this hydrogen to be abstracted is very severe. The product formation may be rationalized on the basis of a 1,4-biradical formation due to γ-hydrogen abstraction and its rearrangement to 1,6-biradical that collapses to the photoproducts. Details of the structure, reactivity and packing will be presented.

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SUBSTITUENT EFFECT ON THE CONFORMATION OF 1,5-BENZOTHIAZEPINE DERIVATIVES: CRYSTAL AND MOLECULAR STRUCTURE OF 2,3,4,5-TETRAHYDRO-*R*-2, *C*-4-DIPHENYL-1,5-BENZOTHIAZEPINE(1) AND *N*-NITROSO-2,3,4,5-TETRAHYDRO-2,2',4-TRIMETHYL-1,5-BENZOTHIAZEPINE(2).

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As confirmed by X-ray analysis, the molecule 1 adopts a twist boat conformation with the pairs of atoms N5, C11 and S1, C10 are oppositely oriented with respect to the C2-C3-C4 plane. The conformation of the molecule of 2 is best described as a boat with the four atoms, C2, S1, C4 and N5 lying on a plane. The torsion angles of the bonds of the seven membered ring also suggest a boat conformation in 2, with significant torsional distortion around S1-C2 bond. The S1···N5 intramolecular distances in 1 and 2 are found to be 3.220(2)Å and 3.007(3)Å, respectively. There is a significant intramolecular C-H···O interaction involving the atoms, C4 and O13 in 2, which may favor the *syn* orientation of the nitroso group with respect to the N5-C4 bond. The equatorial orientations of the two phenyl groups and the C4-methyl group in 1 and 2, respectively, are deduced from the corresponding torsion angles. The diequatorial orientations of the two phenyl groups in 1 confirm their *cis* configurational dispositions. The presence of the nitroso group in the predominant polarized form in 2 is evident from the N5-N12 and N12-O13 bond lengths with the N-N=O moiety being non-coplanar with the fused benzene ring.

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EXTENDED METAL-ORGANIC NETWORKS: A DETAILED X-RAY STRUCTURAL INVESTIGATION

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There has been a recent upsurge in the synthesis of coordination polymers, which are based on multifunctional ligands because of the ability of some of these polymeric materials to form open framework metal-organic microporous materials. Especially, recent studies have shown the use of divalent transition metal ions and benzene di-, and tricarboxylic acids as modular precursors in designing numerous metal-organic polymeric solids with desired topologies. Particularly interesting are the complexes formed by H_2BDC and H_3BTC having one-dimensional polymeric chain or brick-wall structures and their selective guest binding abilities. We recently investigated the extended solid forming ability of both H_3BTC and H_4BTEC towards divalent first row transition metal ions, such as Co^{2+}, Ni^{2+} and Zn^{2+} in the presence of a donor amine. The results obtained by single crystal X-ray diffraction studies on the products of these reactions will be described in this presentation. In addition, structural studies on the interaction of alkaline earth metal ions with aromatic amino carboxylic acids will also be discussed.

H_2BDC H_3BTC H_4BTEC

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A4-52

CRYSTAL ENGINEERING DESIGN OF NEW CLATHRATE COMPOUNDS

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Clathrate compounds arise from multiple interactions between two different types of molecules packed together in a crystal lattice. We have devised a modular method, which permits simple syntheses of new clathrate hosts from readily available precursor molecules. The crystal engineering concepts behind this synthetic approach will be explained. Families of new inclusion hosts have been obtained successfully through variation of the molecular building blocks. In the resulting inclusion compounds host, and guest molecules interact through a combination of weak intermolecular contacts such as aromatic face-face, aromatic edge-face, halogen-halogen, and C-H...N hydrogen bonds. Since the molecules are allowed to select the best combination of these weak interactions a wide range of inclusion structures is obtained. The X-ray structures of a number of these compounds will be presented. These will be described in terms of the design concept and the intermolecular contacts of most importance in determining the clathrate structures.

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A4-53

CRYSTAL STRUCTURE OF A TRIDENTATE LIGAND

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Ligand design and construction are important aspects in controlling the structure and reactivity in coordination chemistry. The different ligands containing metallic centers are used as catalysts in the growth and development of metal-cluster chemistry. The development of these ligands has led to the successful synthesis of homo and hetero nuclear metal complexes, which have found applications in the area of biomimicry. The compound bis[(3,5-dimethyl,2-hydroxy)-2'-hydroxy-5'-bromo]benzylmethylamine crystallizes in triclinic space group, P1 with cell parameters a = 5.228(1), b = 12.364(1), c = 13.234(1)Å, α = 94.04(1), β = 95.72(1) and γ = 95.90(1)°. The structure was solved by direct methods using SHELXS97 and refined by full-matrix least-squares methods using SHELXL97 program to a final R-value of 0.0508 for 3810 unique reflections. The two phenyl rings are planar and orients at an angle of 53.9(2)° with each other. The nitrogen atom shows pyramidal character. In the ligand O-H...N and O-H...O types of hydrogen bondings are useful in stabilizing the molecules in the unit cell in addition to van der Waals forces. An intramolecular O-H...N type of hydrogen bond is observed between the atoms O17 and N8. Packing shows that the symmetry-related molecules are built up with respect to the symmetry axis and two molecules interact to form a closed ring.

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CRYSTAL STRUCTURE OF A DIMERIC MONONUCLEAR COPPER COMPLEX

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The behavior of multimetallic proteins and the metal-metal cooperativity lead to distinct reactive patterns. The development of the chemistry of binuclear metal complexes has been stimulated to investigate the mutual influence of two metal centers in terms of cooperative effect on the electronic, magnetic and redox properties of such systems. The present study aims to bring out the structural and conformational features of N-[(2-hydroxylato-5-methyl)benzyl-(2'-hydroxylato-3',5'-dimethylbenzyl)]ethylamine dicopper(II) by using crystallographic methods. The Cu complex crystallizes in Monoclinic space group C2/c with cell parameters a = 21.404(2), b = 13.962(1), c = 17.917(1)Å and β = 124.394(2)°. The structure was solved by patterson method and refined by full-matrix least-squares technique using SHELX97 package. The final R factor is 0.0882 for 5253 unique reflection at $I > 2\sigma(I)$ cut off. In the complex, only one half molecule is present in the asymmetric unit and the unit cell contains four molecules in dimeric form. The complex has two solvent molecule, methanol and water, where the oxygen of water molecule occupies a special position and acts as an inversion center. The copper atom has a slight distorted square planar geometry. The two six membered rings containing the Cu atom assume distorted sofa conformation. The copper nuclei are bridged by phenolic oxygen atom in a symmetrical manner. The molecules in the structure are packed in discrete fashion with C-H...O type of intermolecular interactions playing a major role in stabilizing the molecules in addition to van der Waals interactions.

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WATER - CHLORINE HYDROGEN BOND NETWORK IN A CRYSTAL STRUCTURE OF NICKEL COMPLEX

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Nickel enters the cell only by chronic exposure and Ni compounds containing piperidine rings are strong carcinogens. Nickel (II) has been found to inhibit the DNA repair mechanisms by interfering with enzymes or proteins involved in DNA replication and/or DNA repair but the underlying mechanisms are unclear. In order to understand this, the complex {4,4'-Dimethyl-6,6'-bis(piperidinomethyl)-2,2'-[1,3-propanediyl bis (nitrilomethylidene)] diphenolato-O,N,N',O'}-nickel(II)dichloro hexahydrate was synthesized and there structural studies carried out. The Ni complex crystallizes in monoclinic space group $P2_1/c$ with cell parameters a = 9.5966(1), b = 24.9070(1), c = 15.2625(2) Å and β = 93.911(1)°. The structure was solved by Patterson method using SHELXS97 program and refined using full-matrix least-squares method to a final R-value of 0.0661 by SHELXL97 program. There are two chlorine ions in the lattice in order to neutralize the two positive charges of the complex and in addition, there are six water molecules. The study of molecular features in the structure reveals an interesting hydrogen bonding network between the six water molecules and the two chlorine ions.

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CRYSTAL STRUCTURE OF AN ALKENE MONOMER

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The crystal and molecular structure of the mesomorphic hydrocarbon monomer 3-[4-(4'-Ethylbiphenyl)]-1-propene has been determined from X-ray diffraction analysis at 293 (2) K. The compound crystallizes in the form of a non - centrosymmetric monoclinic system, space group Pc, with two molecules per cell. The cell parameters are a = 13.90 (5) Å, b= 5.75 (1) Å, c = 9.54(5) Å and β = 116.1(3)°. In this solution some constraints must be introduced and the atoms have high thermal parameters but no evidence of disorder is present. The two phenyl rings are nearly coplanar with a dihedral angle of 1.49 (4)°. Both of them adopt boat conformations. The molecules are organised with their longest extension in parallel sheets as observed from the packing in the unit cell. This type of layered structure clearly indicates the smectic B phase of the title compound. Since the compound does not contain any polar groups, the arrangement in the crystalline state is strongly dominated by repulsion potentials. The length of the molecule in the crystalline state is 12.45 Å. The layer spacing in the mesophase has been obtained from X-ray diffraction pattern and was found to be 12.6 Å. The layer spacing, comparable to the calculated length of the molecule, shows that the molecules form smecticB-like arrangement within the layers.

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STRUCTURE AND CONFORMATION OF 1-(4-METHOXYBENZENE SULFONYL)-5-OXO-PYRROLIDINE-2-CARBOXAMIDE

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Oxo-pyrrolidine derivatives display biological activity as possible antineoplastic and therapeutic agents. The structure and conformation of the title compound, a novel biologically active system containing an oxo-pyrrolidine moiety, has been studied by X-ray analysis and AM1 molecular orbital calculations. The compound, $C_{12}H_{14}O_5N_2S$, crystallizes in the monoclinic system, space group $P2_1$ with a=9.661(4)Å, b=7.246(3)Å, c=11.378(5)Å, β=113.42(2)°, V=730.88(6)Å^3, Z=2. The crystal structure has been solved by direct methods and refined by full-matrix least-squares, on F^2,to R=0.044 for 1721 observed reflections with $I>2\sigma(I)$.

The crystal structure consists of an essentially planar methoxyphenyl ring linked to a 2-carboxamide substituted oxo-pyrrolidine moiety via a sulfonyl group and a lattice water molecule. The oxo-pyrrolidine group has an envelope geometry. The conformational analysis of the title compound investigated by semi-empirical quantum mechanical AM1 calculations shows a good agreement with the X-ray structure excepting the carboxamide orientation. The results of X-ray structure analysis revealed a rotation of the carboxamide moiety with respect to the AM1 optimised geometry by ~60° about the C(oxo-pyrrolidine)-C(carboxamide) bond. The molecular conformation and crystal packing of the title compound are influenced by different types of hydrogen bonds. In the solid state, the molecules translated in the b-direction are linked through N-H·····O intermolecular hydrogen bonds to form an infinite one-dimensional chain.

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SYNTHESIS, CRYSTAL STRUCTURE AND THERMAL PROPERTY OF TRIHYDRAZINIUM MONOAQUOTETRA (PYRAZINE-2-CARBOXYLATO) NEODYMIUM(III) DINITRATE, $(N_2H_5)_3[ND(PC)_4(H_2O)](NO_3)_2$

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Trihydrazinum monoaquotetra (pyrazine-2-carboxylato) neodymium (III) dinitrate, $(N_2H_5)_3[Nd(pc)_4(H_2O)](NO_3)_2$,where pc = pyrazine-2-carboxylate, crystallizes in the monoclinic space group C2/c, with a = 10.7176(7), b = 21.7630(13), c = 14.9608(9) Å, β = 104.468(4)° and Z=4. The structure was solved by heavy atom method and refined by Full-matrix least-squares method to an R value of 0.0272(λ = 0.71073 Å) for 4911 independent reflections. The crystal consists of discrete $N_2H_5^+$, $Nd(pc)_4(H_2O)$ and NO_3 ions. The structure contain monomeric molecules, in which the neodymium ion has nine coordination, formed by four oxygen atoms from monodendate carboxylic groups of four pyrazinic acids (mean Nd-O=2.4180 Å), four heteroring nitrogen atoms located next to the carboxylic groups (mean Nd-N = 2.6744Å) and one oxygen atom from water molecule (Nd-O = 2.490 Å). The simultaneous TG-DTA of the compound shows a broad endotherm at 216°C corresponding to the loss of a water molecule, indicating its coordination to the metal ion. A network of hydrogen bonds operating via the coordinated water molecule, nitrate, carboxylate and hydrazinium ions maintain the stability of the crystal.

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CRYSTAL STRUCTURE OF ω-[4-(4-METHOXYPHENOXYCARBONYL) PHENOXYCARBON-YL] PENTYL 4-FERROCENYLBENZOATE

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The structure of a monosubstituted ferrocene derivative, $C_{37}H_{34}O_7Fe$, was determined by the X-ray diffraction method. The single crystal of the title compound was obtained from a solution with a mixed solvent of ethyl acetate and ethanol (1:3) by the slow evaporation method. All measurements were made on a Rigaku AFC-5*R* diffractometer with graphite monochromatized Cu-$K\alpha$ radiation. The crystals belong to monoclinic system, space group $P2_1$, a=8.860(3)Å, b=9.955(4)Å, c=36.092(3)Å and β=97.01(2)°. All calculations were performed using the *TEXSAN* crystallographic software package. The structure was solved by direct methods (*MULTAN*88) and expanded using the Fourier Technique. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were introduced at their theoretical positions and allowed to ride with the carbon atoms to which they are attached. The final refinement was made by full-matrix least-squares based on 6084 observed reflections (F^2>-3.00$\sigma(F^2)$). The refinement was concluded with final reliability factors $R(F^2>-3.00\sigma(F^2))$=0.039, $\omega R(F^2)$=0.129. The molecular feature is a rod-like one and cyclopentadienyl rings exhibit an eclipsed conformation rather than a staggered one. The unit cell of the crystal contained two crystallographically unequivalent molecules *A* and *B*.

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DIRECT OBSERVATION OF PHOTO-INDUCED PHENYLNITRENES BY X-RAY CRYSTALLOGRAPHY

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Phenylnitrene is important as an intermediate of the chemical reaction of phenylazide, that is an archetype for many photoaffinity labeling approaches and 'photoresist' technologies. From the spectroscopic studies, it has been reported that the powdered samples of phenylazide derivatives produced phenylnitrenes upon photo-irradiation. However, crystal structure of phenylnitrens is not reported so far because of its high reactivity. In this study, the structure of phenylnitrenes, generated in a single crystal by photo-irradiation at 80K, was investigated by X-ray crystallography.

2-azidobiphenyl (1) was synthesized by diazotization of 2-aminobiphenyl and crystallized from toluene. Single crystal of 1 was irradiated by ultra high-pressure mercury lamp (λ> 420nm) at 80K, then X-ray diffraction data of the crystal was collected on a SMART CCD diffractometer. On irradiation, the crystal turned from colorless to brown, and cell lengths were significantly changed. Successfully, the structure of photo-induced 2-nitrenobiphenyl (2) in the crystal was revealed by X-ray diffraction analysis. The occupancy of 2 was 21.8%. Existence of 2 was also confirmed by cryogenic IR spectroscopy and theoretical calculation. Other phenylnitrenes are now investigated by a similar method.

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CYCLIC OXOCARBON DIANIONS AS HUBS IN THE SELF-ASSEMBLY OF SUPRAMOLECULAR STRUCTURES

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In the course of our systematic investigation on novel inclusion compounds of urea/thiourea/selenourea with quaternary ammonium salts,[1] we found that an elusive species such as allophanate $NH_2CONHCO_2^-$ [2] or dihydrogen borate $BO(OH)_2^-$ [3] can be generated in situ and stabilized in a hydrogen-bonded urea/thiourea/selenourea-anion host framework. The non-benzenoid aromatic dianions $C_nO_n^{2-}$ (n = 3, deltate; n = 4, squarate; n = 5, croconate; n = 6, rhodizonate) are each a potentially effective divergent multi-site hydrogen-bond acceptor for supramolecular assembly. Following our initial studies on the squarate ion,[4] we have extended our investigation to the croconate and relatively unstable rhodizonate species, and recent results will be presented. This work is supported by Hong Kong Research Grants Council Earmarked Grant CUHK 4206/99P.

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NOVEL COORDINATION AND SUPRAMOLECULAR POLYMERIC NETWORKS OF CADMIUM USING SELENOCYANATE AS A BUILDING BLOCK

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The molecular self assembly of coordination polymers and supramolecules is a promising route to novel molecular materials. These materials not only generate new insights into structural diversity but also exhibit potential applications. The versatility of an ambidentate selenocyanate ligand as an effective building block is rare in the literature, which can provide much controlled synthesis due to hard (N) and soft (Se) combination. Controlled assembly of donor and acceptor building blocks to generate an entirely supramolecular coordination architecture is our ultimate aim, using the potential bridging ability of SeCN with a cadmium metal centre, which can permit a wide number of geometries and coordination numbers.

We wish to present the syntheses and structural diversity of four novel selenocyanate bridged networks of cadmium,$[Cd_2(ibn)(SeCN)_4]_n$ **(1)**, $[Cd_2(iprdien)(SeCN)_4]_n$ **(2)**, $[Cd_2(medien)(SeCN)_4]_n$ **(3)** and $[Cd_2(pyz)(SeCN)_4]_n$ and **(4)**[ibn=1,2-diamine-2-methylpropane,iprdien=N1-isopropyldiethyelentriamine, medien=bis-(2-aminethyl) methylamine and pyz=pyrazine]. Complexes **(1)** and **(2)** are 1D and 2D coordination polymers respectively, with alternating arrays of octahedral and tetrahedral cadmium centres and each of them show 'symbiosis' following Jorgenson principle. Complex **(3)** is a 1D coordination polymer forming a 2D supramolecular polymeric network by noncovalent interaction. Complex **(4)** is a 2D architecture of cadmium bridging simultaneously through SeCN and pyrazine creating a square type molecular box.

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A GLANCE AT THE RECENT DEVELOPMENTS IN THE SUPRAMOLECULAR CHEMISTRY

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Supramolecular chemistry – chemistry beyond the molecule as defined by Lehn[1] has evolved as a multidisciplinary area extending its roots into various branches of science; biology to computing areas. The simplicity in the synthesis, rationalistic approach in the design strategies, developments in the characterization techniques such as NMR and X-ray, and above all, the applications of the materials thus synthesized to meet the needs of 21st century made the supramolecular chemistry as one of the frontier research areas of this century. Although, it has started with the synthesis of crown ethers incorporating guest molecules in the cavities,[2] the process indeed is well known in biology much earlier in the form of molecular recognition between protein/DNA and small molecules through non-covalent bonds such as hydrogen bonds.[3] This is the knowledge that has stimulated the design of variety of assemblies employing small organic molecules connected by noncovalent bonds, for example, O-H···O, N-H···O, N-H···N, C-H···O etc.[4] In this process, noncovalents bonds of several types have been either explored or reinvestigated determining their properties unambiguously. Although, the assemblies constructed by non-covalent bonds are often unstable, the rigidity of the metal-ligand linkages in the form of dative bonds in the coordination polymers added a new dimension to the supramolecular chemistry by facilitating the formation of variety of supramolecular architectures with high degree of stability.[5] The salient features of these assemblies (hydrogen-bonded and metal-ligand structures) will be presented along with the results evolved from our laboratory in the last few years.

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FORMATION OF SHEET TYPE STRUCTURE FROM CASHEW NET SHELL LIQUID USED AS A MONOMER FOR POLYESTER SYNTHESIS

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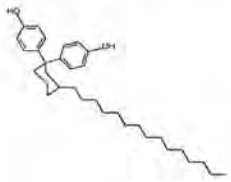
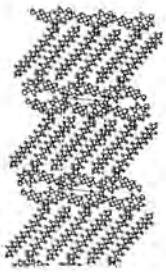
A new bisphenol (a), has been synthesized from the cashewnet shell liquid (CNSL). Its preparation and use for polycarbonate synthesis has been patented[1]. Crystals of $C_{33}H_{50}O_2$ belong to the triclinic space group P-1, a = 6.938 (1), b = 9.907(1), c = 21.841(3) Å, α = 87.982 (3)°, β = 83.377 (3)°, γ = 84.644(3)°, V = 1483.9(6)Å^3. Data were collected on Bruker SMART APEX CCD Single Crystal X-ray Diffractometer using Mo-K_α radiation. The structure was solved and refined using SHELX^{TL} Present R = 0.079, for 1236 unique observed reflections. Crystal structure shows a long alkyl chain (b) of 15 carbon atoms. The alkyl substituents from adjacent H-bonded chain interdigitate and crystallize to form a sheet. Between the polar groups, net work of O-H...O hydrogen bonds are seen along with C-H...π interactions. The long non-polar C15



(a)

(b)



(c)

alkyl chain interacts with the chains from above and below to form sheets through weak vander Waals forces (c).

Reference: [1]US Patent No. 6255,439 (2001).

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ABSOLUTE CONFIGURATION OF SPIRO β-LACTAM: CRYSTAL STRUCTURE OF N(4-METHOXYPHENYL)-3-(SPIRO 1,3 OXATHIANE)-4-PHENYL-AZETIDINE-2-ONE

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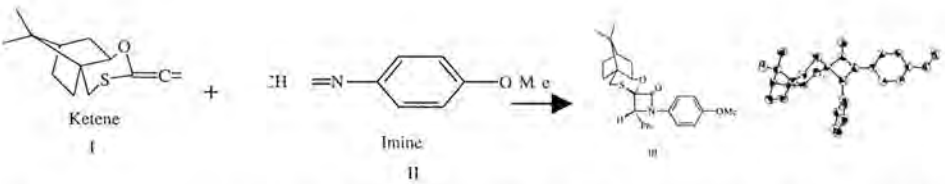
The spiro β-lactam **III**, N (4-methoxyphenyl)-3-(spiro 1,3 oxathiane)-4-Phenyl-azetidine-2-one, was synthesised via ketene imine cycloaddition reaction (Staudinger Reaction). Deprotection of the oxathiolane group will give 3-oxo-β-lactam, which is an important intermediate for the synthesis of various biologically important compounds which show β-lactamase inhibitor activity[1]. They are also precursors for the 3-hydroxy-4-aryl-β-lactams of which 4-phenyl isomer



is used as a synthon for the Taxol side chain[2]. Crystals of $C_{26}H_{29}NO_3S$ belong to orthorhombic, space group $P2_12_12_1$, a= 6.442(4), b = 18.091(1), c = 19.393(1) Å, V= 2260.1(3) Å^3. Data were collected on Bruker SMART APEX CCD Single Crystal X-ray Diffractometer using Mo-K_α radiation. The structure was solved and refined using SHELX^{TL}. Least squares refinement of scale, positional and anisotropic thermal parameters converged to R = 0.042, R_w = 0.094 for 5355 unique observed reflections. Molecular structure shows that the approach of imine is from the opposite side of gem- dimethylmethylene bridge.

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STRUCTURAL AND CHEMICAL PROPERTIES OF NITRIDO AND NITRENE CARBONYL CLUSTERS OF RUTHENIUM

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Nitrido and nitrene clusters are members of a potentially vast class of mixed transition metal-main group compounds. Such molecules are currently of structural and chemical interest since they offer opportunities to evaluate the validity of current models of bonding for mixed polynuclear systems and to improve on the degradative instability of homonuclear metal compounds. Metal surface-bound nitrido and nitrene species are believed to be an integral part in a number of heterogeneously catalyzed chemical processes such as nitrogen oxide reduction, the Haber process and hydrazine decomposition. In light of the metal cluster-metal surface analogy, the low-valent nitrido and nitrene are particularly interesting. In several surface reactions involving NO or N_2, adsorbed nitrogen atoms are known to be key intermediates. To enhance our understanding in these systems, we have developed some synthetic routes to tetranuclear ruthenium and ruthenium-cobalt carbonyl clusters containing nitrido or nitrene ligands. Their structural and chemical properties have been investigated. These clusters display novel metal-nitrene core structures and their electrochemical properties together with the 15-N NMR spectroscopic studies have been investigated. The magnetic nuclear deshielding of nitrene N-atoms increases with the nuclearity and electron-accepting ability of the organic substituent bonded, while the chemical shift of an interstitial nitride increases with compression of the interstitial nitrogen in a metal cluster.

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CRYSTAL STRUCTURE OF THE NOVEL CU (II) POLYNUCLEAR NET-STYLE COMPLEX OF N, N-BIS (BENZIMIDAZOL-2-YLMETHYL) AMINE

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A novel Cu(II) polynuclear net-style complex of N, N-bis(benzimidazol-2-ylmethyl)amine was synthesized and its crystal structure was determined by X-ray diffraction method. The crystallographic data is as follows: $C_{42}H_{40}N_{12}O_{17}Cl_4Cu_2$, m_r=1253.74, monoclinic system, space group Cc, a=2.771(4), b=0.9432(11), c=2.501(3) nm, β=120.17(5)°, V=5.652(13) nm^3, Dc=1.473 Mg/m^3, Z=4, F(000)=2552, μ=1.017 mm^{-1}, R=0.0661, wR=0.1462, S=0.971. The crystal structure shows that one stoichemistry molecule composed of two Cu(II) ions, two N, N-bis (benzimidazol-2-ylmethyl) amine, one 4, 4-bipyridyl as bridge, one water and four ClO^{4-}. A lot of stoichemistry molecules are linked by ClO^{4-} to form one layer of net-style structure (see figure 1).

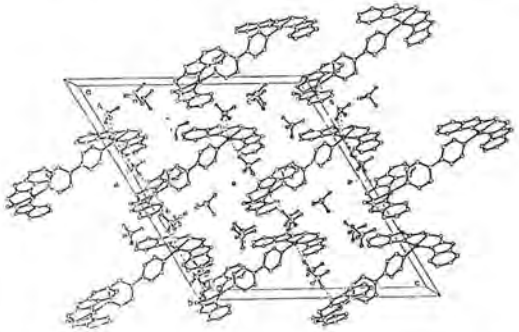

Figure 1 One layer of net-style structure of the complex of $C_{42}H_{40}N_{12}O_{17}Cl_4Cu_2$

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STRUCTURAL STUDIES OF NEW DIORGANOTIN DITHIOCARBAMATES

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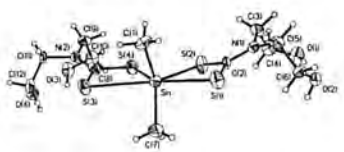
Dithiocarbamates and organotins have been cited in the literature as compounds that can show biological activity. Some dithiocarbamates such as imuthiol (sodium diethydithiocarbamate) has been utilised in the pharmaceutical industry while the organotins have been investigated for its anti-tumour activity. The new organotin(IV) dithiocarbamates derived from various secondary amines were synthesised using a method where the ligands were generated *in situ* and reacted directly with the diorganotin(IV) moieties. Two crystals I and II were derived from the reaction involving 2-(2-hydroxy-ethylamino)-ethanol, while that with 2-methylamino-ethanol and di-*iso*-propyl-amine afforded III and IV respectively.

I II



III IV

The crystal structures of I, II, III and IV showed that the tin atom formed a six co-ordinate *cis* bis-chelated complex. The dithiocarbamate ligands chelated anisobidentically with a distinct short and long Sn-S bond distances in I and IV, while II and III demonstrated both anisobidentate and isobidentate chelations. The angle subtended at the tin atom by the two alkly groups is bigger than that by the two aryl groups due to steric requirements. The same trend was reported by Lindley and Carr (1974). The geometry around the tin centre was not affected by the presence of hydroxy groups, which gave rise to intermolecular and intramolecular hydrogen bonding in the crystal lattice.

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THE NOVEL LINEAR NONANICKEL METAL STRING $[Ni_9(\mu_9\text{-PEPTEA})_4(X)(Y)]$ COMPLEXES X=Y=SCN$^-$ AND X=$CF_3SO_3^-$,Y=CH_3O^-

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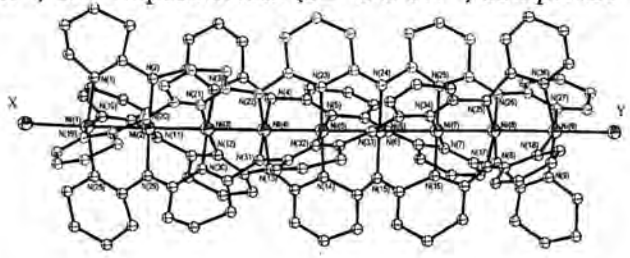
The synthesis, structure and properties of $[Ni_9(peptea)_4(X)(Y)]$, X=Y=Cl^-, X=Y=SCN^- and X=$CF_3SO_3^-$, Y=CH_3O^-,($pepteaH_4$ = pentapyridyltetraamine) metal string complexes are reported. The nonanickel unit is essentially in a linear arrangement and is helically wrapped by four all-syn type $peptea^{4-}$ ligands. There are two axial ligands (X and Y) attached at terminal nickel ions. According to the structural, analysis the complex exhibits D_4 symmetry and there are four sets of Ni-Ni distance, which are 2.364(2), 2.283(2), 2.243(2), 2.227(2) for X=Y=SCN^- from outer to inner, respectively. For these complexes, the average bond distance of Ni_{inner}-N are short, consistent with a square planar, low spin arrangement of nickel(II) ions. The termianl Ni^{II} ions ,Ni(1) and Ni(9), are in a square-pyramidal form with long Ni-N distance and high-spin state. A temperature–dependent magnetic study of these complexes, X=Y=Cl^-, X=Y=SCN^- and X=$CF_3SO_3^-$, Y=CH_3O^-, indicate that there is a weak antiferromagnetic interaction between the two terminal high-spin nickel(II) ions with J = -2.1cm^{-1}, -0.2 cm^{-1} and –0.9 cm^{-1}, respectively. This interaction is smaller than those of similar trinuclear (J= -99 cm^{-1}), pentanuclear (J= -8.3 cm^{-1}) and heptanuclear (J= -3.8 cm^{-1}) complexes.



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CRYSTAL STRUCTURE OF CHOLESTERYL 2,4-DICHLOROBENZOATE

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Crystal of 2,4-dichlorobenzoate($C_{34}H_{48}O_2Cl_2$), a cholesterol derivative, are orthorhombic, space group $P2_12_12_1$, $Z=4$, $a=9.283(2)$, $b=13.462(3)$, $c=24.706(4)$Å, $Dc=1.20$ g/cm^3. The intensity data were collected on a Nonius CAD-4 diffractometer with a graphite-monochromatized Mo-Kα radiation to a maximum 2θ value of 52°.

The structure is solved by direct methods and refined by Fourier and full matrix least-squares methods. The present R factor is 0.099 for 1542 observed reflections.

Compared with other cholesterol derivatives, the cholesteryl ring and tail region of the molecule are normal. The structure of cholesteryl 2,4-dichlorobenzoate molecules, have their tetracyclic systems almost parallel to each other. The molecular long axes are parallel to the c-axis and these molecules stack along 2_1 screw axes. Cholesteryl 2,4-dichlorobenzoate belongs to the layer type crystal structure as in most cholesteryl esters and cholesteryl carbonates.

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STRUCTURE ANALYSIS OF UNSTABLE SPECIES PRODUCED BY PHOTO IRRADIATION

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Many organic reactions proceed by multi-step processes in which intermediate molecular species are involved in the conversion from one molecule to another. Such intermediate molecules, in general, are so unstable at room temperature that the structure analysis has been considered to be very difficult. However, the unstable species produced by photo irradiation may be trapped in the crystalline lattice at low temperatures and the structures can be analyzed by X-ray technique. Recently we analyzed the structures of a triplet carbene and a nitrene produced in crystalline lattice by X-rays when the reactant crystal was irradiated with UV or visible light at 80 K. Another example is the photo-excited structure of the platinum complex, $[Bu_4N]_4[Pt_2H_2(pop)_4]$ (pop = $[P_2O_5H_2]^{2-}$). Two Pt atoms are linked by four pop ligands in the anion. The unit-cell volume decreased when the crystal was irradiated with visible light and returned to the original cell when the light was off. The three-dimensional intensity data were collected with the light on and off at low temperatures. The significant difference in molecular structure was observed between the structures at light-on and -off states; the Pt-Pt distance significantly decreased at the light-on state. The shortening of the Pt-Pt distance well explains the excited state of the Pt-Pt orbital of the anion assumed so far.

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A5 : Crystallography in materials science

A5 : Crystallography in materials science

A5-1

STRUCTURE OF THE MORPHOTROPIC PHASE BOUNDARY (MPB) PHASE IN (1-x) [Pb ($Mg_{1/3}Nb_{2/3}$)O_3]-x$PbTiO_3$ (PMN-PT) CERAMICS

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PMN-PT ceramics possess excellent electromechanical properties useful for piezoelectric transducer and actuator applications. The phase diagram of this system exhibits an MPB which separates tetragonal (T) and rhombohedral (R) phase fields similar to that in the well known $Pb(Zr_xTi_{1-x})O_3$ (PZT) system. The T and R phases are believed to co-exist in the MPB region. Different workers have reported different compositional widths of the coexistence region depending upon synthesis route adopted [Kelly *et al.* J.Am.Ceram.Soc. 80, 957, 1997, Shrout *et al.* Ferroelectrics Lett.12, 63 1990].

In this work we have used a new method of synthesis and shown that the width of the coexistence region is about $\Delta x \approx 0.05$ which is an order of magnitude smaller than that reported by Kelly *et al.* Further by using Rietveld refinement of x-ray powder diffraction data, we have shown that the structure of PMN-PT in the MPB region is monoclinic with space group Pm and not the mixture of T and R phases, hitherto believed. The lattice parameters of the monoclinic cell (x=0.34) are found to be a_M=4.03Å, b_M=4.00Å, c_M=4.01Å and β=89.86 degrees. This structure is different from the monoclinic structure with space group Cm reported recently for PZT.

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A5-2

MICROTOPOGRAPHIC STUDY OF DOPED CRYSTALS OF LEAD IODIDE

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Both undoped and doped crystals of lead iodide have been grown by the Vapour technique. Growth features on the basal (0001)surface of the undoped and doped crystals were studied by optical and scanning electron microscopy. The most frequently observed growth feature has been the existence unevenly spaced hexagonal/trigonal parallel growth steps. The steps presumably arise from layer by layer growth mechanism as confirmed by calculation of Jackson's interface roughning factor.The micrographs of the doped crystals display the familiar phenomenon of bunching of growth steps to a smaller or larger degree. The "bunched" step is built up, because the individual small steps slow down as they move across the crystal surface, thus allowing the succeeding layers to catch up with front layers. This slowing down is caused by the impurities on the surface. When doped crystals were left over-night in the furnance ,they developed large number of thermal hexagonal etch pits formed by the evaporation of the material on the surface in a manner reverse to that of crystal growth .They presumably form at impurity – contained locations or at impurity aggregates

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A5-3

RELAXOR FERROELECTRIC PHASE TRANSITION IN $Pb_{0.50}Ca_{0.50}TiO_3$: STRUCTURAL AND DIELECTRIC STUDIES

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Studies on $Pb_{1-x}Ca_xTiO_3$ (PCT) have attracted enormous attention. While the effect of low Ca^{2+} content ($x<0.40$) on the structure and phase transition behaviour of PCT is well understood, there are several conflicting reports for $x>0.40$ and especially for the composition $x=0.50$. Sawaguchi and Charters (J. Am. Ceram. Soc., 42, 158, 1959) reported that the temperature variation of dielectric constant ($\varepsilon'(T)$) in PCT50 ceramics prepared by conventional solid state route exhibit two peaks while Ganesh *et al* (J. Am. Ceram. Soc., 80, 653, 1997) have observed only a single peak. Ranjan *et al* (Appl. Phys. Lett., 70, 3221, 1997) have reported relaxor ferroelectric transition in PCT50 samples prepared by a semiwet route.

Rietveld analysis of powder x-ray diffraction data on PCT50 samples obtained by conventional solid state route reveals the presence of two phases with P4mm and Pbnm space groups due to limitations of the solid state route. $\varepsilon'(T)$ measurements also reveal two peaks in $\varepsilon^*(T)$ corresponding to a ferroelectric and a relaxor ferroelectric phase. Following Ranjan *et al*, we propose that the orthorhombic phase is the relaxor ferroelectric phase and it has got tilted octahedral structure similar to $CaTiO_3$. We have also studied the effect of sintering temperature on the relative proportions of these two phases.

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INVESTIGATION ON SYNTHESIS ,CHARACTERISATION AND EFFECT OF Ag DOPING ON THE TRANSITION TEMPERATURE AND CRITICAL CURRENT DENSITY OF $Hg_{1-x}Pb_xBa_2Ca_2Cu_3O_{8+\delta}$ ($0.1 \leq x \leq 0.5$) HTSC TAPES

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Pb-doped Hg1223 HTSC tapes have been synthesized by annealing the precursor tape (fabricated by doctor blade tape casting technique) in the environment of Hg(Pb) vapour in an evacuated sealed quartz tube at 870^0C for 8 h. The HTSC tapes with x ranging between 0.1 and 0.5 exhibit high temperature superconductivity at temperatures falling in the range of 110-119 K. The tape sample with optimum doping of $Pb_{0.35}$ has a highest T_c of ~119K and $5.1x10^3$ A/cm^2. Gross structural characterisation of as-synthesised Hg(Pb) HTSC tape sample shows the dominant presence of Hg(Pb)-1223 tetragonal phase. As-synthesised $Hg(Pb)Ba_2Ca_2Cu_3O_{8+\delta}$ HTSC observed under transmission electron microscope also confirmed the dominant presence of Hg(Pb) 1223 tetragonal phase.With the slight addition of Ag into optimally Pb doped Hg-1223 tape sample, T_c has been found to increase slightly but there is significant enhancement of J_c up to a optimum concentration of Ag. The highest T_c of ~123 K and highest J_c of ~2.5 $x10^4$ A/cm^2 is obtained for the tape sample having Ag concentration of 0.2 i.e., ($Ag_{0.2}$) being an order of magnitude higher than the J_c of Ag free optimally Pb-doped Hg-1223 tape samples. The surface microstructural characterisation of the optimally Pb doped HTSC tape sample show quite uniform platelet like grain stucture.

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A5-5

INFLUENCE OF THE PARAMETERS T AND $t_{cum}(T)$ ON THE CRYSTAL STRUCTURAL CHARACTERISTICS OF POLYMERS

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Thermally induced changes in the crystal structural characteristics are often associated with lattice expansion, contraction, phase transformations etc. These effects are generally identified by the parameter, temperature(T), at which they are found to occur. Detailed investigations on the crystal structural characteristics of thermally aged polymers have shown that in addition to the parameter T, the duration of cumulative exposure to a constant temperature, $t_{cum}(T)$, also introduces changes in the crystal structural characteristics, very similar to the influence of T. The combined role of the parameters T and $t_{cum}(T)$ has led to the identification of a (T, $t_{cum}(T)$) effect on the crystal structural characteristics viz., changes introduced at temperature T_2 can recur at temperature T_1 ($< T_2$) also, if the exposure to the latter is long enough. Details of the observations based on the 2θ, intensity, half width and azimuthal spread of reflections from various thermally aged polymers will be presented in this paper.

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PRELIMENARY X - RAY STUDIES OF THE MESOGEN TRANS, TRANS – 4 – N – PROPYLBICYCLOHEXYL–4'–CARBONITRITE AS A FUNCTION OF TEMPERATURE

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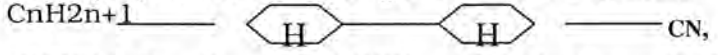
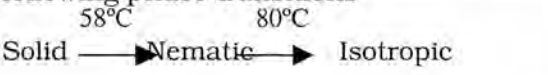
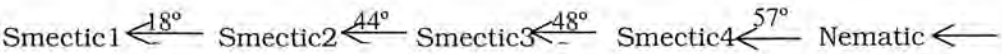
The compound trans, trans – 4 - n – propylbicyclohexyl – 4' – carbonitrite (abbreviated to CCH_3) is a member of the homologous mesogenic series of cyanocyclohexyl cyclohexanes having the structural formula



(n=3 for CCH3). The Compound CCH_3 (molecular formula $C_{16}H_{27}N$) exhibits the following phase transitions





Though much work has been done on the compound and other members of the series including its crystal structure determination [1] in the solid phase, not all the smectic phases have been identified. Also the intermolecular separation 'd_1' and apparent molecular length/ layer thickness 'd_2' and their variation with temperature over the various mesophases have been studied with a view to determining d_1 and d_2. X-ray photographs have been taken and d_1, d_2 calculated from the radii of the rings obtained on the photographic plates at various temperatures. Correlation is sought between the solid state cell parameters [1] and the parameters d_1 and d_2 in the liquid crystalline phase.

References :

[1] W. Hasse and H.Paulus, Mol. Cryst. 100, 111 – 126 (1983)

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A5-7

CHARACTERIZATION OF STABILIZED YTRRIA-ZIRCONIA PRODUCED BY COOPRECIPITATION METHOD

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The Coo precipitation method was used to produce stabilized ytrya-Zyrconia ceramic. The samples were synthesized from $ZrOCl.8H_2O$ and Y-acetate, with purity better than 99%, available commercially from E-Merck and Aldrich respectively. The content of Ytrya was 7%, 9%, and 11% mole. The produced precipitate was calcined at 500 °C. Two kinds of particle size *i.e.* 0.5 μm and 5 μm obtained from milling were pelletized under 5 ton pressure and then sintered at temperature: 1100 °C, 1200 °C, 1300 °C, and 1400 °C for 2 hours. Structural analysis shows that the crystal structure is monoclinic. Particle size and sintering temperature influenced greatly on electrical properties as well as its microstructure, but it did not influence to crystal phase. Samples with size 0.5 μm have densification = (93 -95) %, porosity < 2%, hardness Vickers = (13- 15) Gpa, coefficients of thermal expansion = (16- 20) x 10^{-6} /°C. Samples with size 5 μm have densification = (83 -84) %' porosity = (14 -17) %, hardness Vickers = (10 -12) Gpa, electrical conductivity at 100 °C < 0.01 (Ohm cm) $^{-1}$, and coef. of thermal expansion = (15- 18) x 10^{-6} /°C.

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A5-8

HARDNESS, FRACTURE MECHANICS AND CRACK PROPAGATION STUDIES ON MELT GROWN DOPED $KMgF_3$ CRYSTALS.

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Fresh (100) cleavages of melt grown doped $KMgF_3$ crystals, grown by Czochralski pulling technique with 5% doping of NiF_2, were subjected to indentation induced hardness testing studies using Vicker's micro hardness tester mhp – 100 attached to Neophot-2 of Carl Zeiss, Germany. The Vicker's micro hardness value (H_v) ranges from (4.65-2.72) x 10^2 Kg/ mm^2 in the load range of 10-100 g respectively. The variation of micro hardness with load is best explained by Hays and Kendall's law and the value of Newtonian resistance pressure (W) offered by the sample is found to be 19.59 x 10^{-3} Kg. The fracture toughness (K_c) determines how much fracture stress is applied under uniform loading and its value is found to vary between (0.0720-0.0602) x10^{-3} Kg/$\mu m^{3/2}$ in the load range 20-100 g respectively. The brittleness index (B_i) and yield strength (σ_y) are reported to lie in the range (5.98-4.52) x $\mu m^{-1/2}$ and (143.52-90.78). From the ratio of crack length to half diagonal length (c/a), it is indicated that these crystals exhibit only median types of cracks and brittleness of 1~ 4 standard.

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THE RELATIONSHIP BETWEEN STRUCTURE AND NONLINEAR PROPERTIES OF $Bi_2B_8O_{15}$ SINGLE CRYSTALS*

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The borate family of crystals plays a very important role in the field of nonlinear optics. A large number of borate crystals, including β-BaB_2O_4 (BBO), LiB_3O_5 (LBO), $RECa_4(BO_3)_3O$(RECOB, RE= Y, Gd, Nd, Sm) and BiB_3O_6(BIBO), have been studied or some are useful NLO crystals.

$Bi_2B_8O_{15}$ melts congruently at 715 °C. It has two modifications, i.e. a high temperature phase (α) and a low temperature phase (β). The structure of β-form $Bi_2B_8O_{15}$ was determined for the first time by BRUKER-P4 four-circle diffractometer. It is monoclinic with a noncentrosymmetric structure, where $[B_3O_6]$ rings and $[BiO_6]$ octahedra in which the bismuth cation with a lone-pair electron are located. Similar to BBO, the NLO-active clusters in a $Bi_2B_8O_{15}$ crystals are $[B_3O_6]$ rings. According to the anionic group theory, the anionic groups $[B_3O_6]$ with the distortions of the idealized structures have the microscopic contributions to the second-order susceptibility of the group. In addition, $[BiO_6]$ octahedra with a lone-pair electron in Bi do contributes to the NLO effect. The above structure factors show that $Bi_2B_8O_{15}$ is a potential NLO crystal.

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A5-10

STRUCTURAL INVESTIGATIONS OF La-2125 MIXED OXIDE SUPERCONDUCTING SYSTEM

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Crystallographic studies on the $(La_{2-x}Nd_x)Ca_yBa_2Cu_{4+y}O_z$ [y = 2x; 0.0<x<0.5] samples are carried out using neutron diffraction technique. The analysis of the neutron diffraction patterns for the series of samples with $0.0 < x < 0.5$ was done using Rietveld fitting program. The $La_2Ba_2Cu_4O_z$ (La-224, x = 0.0) exhibits tetragonal phase and is a non-superconductor which becomes superconducting on addition of a '$CaCuO_2$' rock salt like layer with maximum T_c of 78K. It is important to note the significant role played by Ca-doping in improvising the superconducting properties. Analysis of the structural data reveals that, as Ca-concentration increases, the unit cell volume decreases while T_c increases with a maximum value of $T_c \sim 78K$ for x = 0.5. The detailed crystal structure for LaNdCaBCO series of samples has been studied in the light of changes in bond lengths and bond angles with increase in Ca-concentration and it's role in 'turning on' the superconductivity.

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A5-11

RECENT DEVELOPMENTS IN STRUCTURAL AND PHASE TRANSITION STUDIES ON $Pb(Zr_xTi_{1-x})O_3$ CERAMICS

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We report the results of structural, dielectric and piezoelectric investigations on highly homogeneous $Pb(Ti_{1-x}Zr_x)O_3$ (PZT) ceramics prepared by a novel semi-wet route. Careful analysis of the x-ray diffraction profiles have revealed that the structure of PZT on the Zr rich side ($x \geq 0.530$) of the morphotropic phase boundary (MPB) is not rhombohedral, as hitherto believed for decades, but is monoclinic. Results of the Rietveld analysis of the room temperature powder XRD data are presented for $0.515 \leq x \leq 0.530$. We show that the co-existence of monoclinic (F_M^{HT}) and tetragonal (F_T) phases for x=0.520 and 0.525 is due to a first order phase transition. Piezoelectric and dielectric measurements as a function of temperature for $0.515 \leq x < 0.550$ have revealed two anomalies corresponding to F_T to F_M^{HT} and F_M^{HT} to F_M^{LT} transitions discovered by Noheda *et al* [Phys. Rev. B 61(2000) 8687] and Ragini *et al* [Phys. Rev. B 64 (2001) 054101], respectively. Neutron diffraction data is presented to show that the F_M^{HT} to F_M^{LT} transition is an antiferrodistortive cell doubling transition associated with phonon instability at the R-point of the cubic Brillouin zone. We show that the space group of the F_M^{LT} phase is Pc which is different from the Cm space group proposed by Noheda *et al* for the F_M^{HT} phase.

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A5-12

SMALL ANGLE X-RAY SCATTERING OF MESOPOROUS ZrO_2 XEROGEL

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ZrO_2 xerogel was prepared using sol-gel process from the mixture of $Zr(OC_3H_7)_4$:$3H_2O$:$3O(C_2H_4OH)_2$:$0.1AEO_9$:$65C_2H_5OH$; then the mixture was transferred into a stainless autoclave lined with Teflon for the thermal treatment at 230°C for 72h; at last the resulted precipitation was filtered, washed and dried at 50°C for overnight. So produced sample possessed mesoporous structure as N_2 adsorption-desorption measurement has indicated. Small angle X-ray scattering (SAXS) using synchrotron radiation as X-ray source with a long-slit collimation system at Beijing Synchrotron Radiation Laboratory was used to study the structure of the mesoporous ZrO_2 xerogel. It is seen that the Debye plot of $J_{obs}(q)^{-2/3}$ *versus* q^2 deduced from the original measured scattering data is not linear but presents a downward concave curve. It is obvious that the scattering does not obey Debye's theory but shows a positive deviation from Debye's theory, suggesting that the sample is not an ideal two-phase system and there exists micro-inhomogeneity of electron density within the solid phase of ZrO_2 xerogel. This is probably due to the crystallization under 230°C is not being full and the amorphous matter existing in the skeleton, i.e. the sample is in semicrystalline state as confirmed by XRD pattern. Here, we extend Debye's equation from ideal two-phase system to non-ideal two-phase system that shows a positive deviation from Debye's theory; and then we correct the deviation from Debye's theory and give information on the microstructure of the mesoporous ZrO2 xerogel.

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STRUCTURE OF (n=4) FERROELECTRIC AURIVILLIUS PHASES: $ABi_4Ti_4O_{15}$ (A = Ba,Sr and Pb)

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The room temperature structure of three ferroelectric compounds belonging to the Aurivillius family (n=4), ABi4Ti4O15(A=Ba,Sr and Pb) have been analyzed using high resolution powder X-ray diffraction methods. BaBi4Ti4O15 crystallizes in I4/mmm space group with a=3.8566(1) and c=41.8457(14)Å. The structure has been refined by Rietveld method to R_p=5.40%, R_{wp}=7.16% and $R_{(I, hkl)}$=10.49%. On the other hand $SrBi_4Ti_4O_{15}$ and $PbBi_4Ti_4O_{15}$ crystallize in (nearly isomorphous) space group $A2_1am$ with a=5.4510(4), b=5.4410(4) and c=41.0233(13)Å and a=5.4255(1), b=5.4440(1) and c=41.4023(13)Å respectively. The starting model for SrBi4Ti4O15 and PbBi4Ti4O15 was derived from abinitio methods using the package EXPO together with the information available in the ICDD database. The model was further refined to R_p=5.63%, R_{wp}=7.36% $R_{(I, hkl)}$=8.90% and R_p=7.25% R_{wp}=10.59% and $R_{(I, hkl)}$=10.25% respectively. It is seen that the A cations Ba and Sr are disordered over the Bi sites. However, the Pb analogue has a well-defined site at x=0.2816(7), y=0.2586(6) z =0.2185(1) for Pb which clearly indicates that Pb is the 2+ oxidation state. Also the B-O bonds in the perovskite layers are highly distorted forming the zigzag chains along the 'c' axis. There is a general displacement of the Bi atoms along the a axis which is responsible for the ferroelectricity in these compounds.

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A5-14

FORBIDDEN REFLECTIONS OF HEMATITE (Fe_2O_3) NEAR THE Fe K-ABSORPTION EDGE

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In order to investigate anisotropy of electronic and magnetic scattering from hematite, alpha-Fe_2O_3, we measured the forbidden reflections near the iron K-absorption edge using synchrotron radiation. At room temperature hematite has an antiferromagnetic structure. The spins, however, are slightly canted, and it has small magnetic moment perpendicular to [001]. We mounted a natural hematite crystal with a (001) surface on a four-circle diffractometer. Energy spectra and azimuthal angle dependence of the (003) and (009) reflections were measured.

The (003) and (009) reflections have similar energy spectra, which show only one resonant peak in the pre-edge region and a continuous non-resonant tail below the edge. Finkelstein et al. [1] attributed the peak to the electronic quadrupole transitions. We measured the azimuthal dependence of the integrated intensities at the peak position and the non-resonant tail. The azimuthal dependence of the (003) reflection measured for non-resonant tail shows twofold pattern. The site symmetry of iron atoms in hematite is 3, therefore this profile should be caused by non-resonant magnetic scattering. The azimuthal dependence of the (003) reflection measured at the peak position showed threefold pattern. On the other hand, the profile of the (009) reflection at the peak position showed threefold like pattern, but not a complete threefold pattern. We suppose that the resonant peak consists of two components, electric and magnetic scattering, and they intricately interplay.

[1] K. D. Finkelstein , Qun Shen and S. Shastri: Phys. Rev. Lett. 69 (1992) 1612.

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A5-15

X-RAY STUDY ON THE EFFECT OF HEAT TREATMENT ON THE GROWTH MODE IN ZnSe HETEROEPITAXY ON Te-TERMINATED GaAs (001) SURFACES

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The II-VI/III-V heteroepitaxial layers have been applied to the fabrication of wide-band-gap optoelectronic devices. For heteroepitaxy of ZnSe on GaAs, the epitaxial growth is relatively easy, since the lattice space mismatch between the two crystals is small, 0.27% at RT. However, a ZnSe epitaxial layer grown on a GaAs substrate contains many lattice defects which affect performance and reliability of a device. The formation of defects in epitaxial layers strongly depends on the initial pre-growth treatments of substrate surfaces prior to epitaxy, which consequently influences the growth mode. Therefore, there have been a great number of studies on the effects of pre-growth treatments on the growth mode and defect generation.

The effect of thermal annealing of the Te-terminated GaAs (001) surface on the interfacial structure of ZnSe/GaAs was studied by combining X-ray reflectivity and diffraction measurements. Comparing the results obtained by the two methods, we conclude that the growth of ZnSe epitaxial layers has changed from a 3-D island growth mode to a 2-D layer-by-layer mode, through thermal annealing. The transition layer between the substrate and epitaxial layers had electron density equal to that of Ga_2Te_3 and the thickness became thinner after the annealing. However, diffusion of Te into GaAs layers was also induced through the treatment.

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CRYSTAL STRUCTURE OF $Ba_nLa_4Ti_{3+n}O_{12+3n}$ HOMOLOGOUS COMPOUNDS

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The homologous $Ba_nLa_4Ti_{3+n}O_{12+3n}$ compounds are one of the microwave dielectric ceramics which are key devices holding the information technology. They have excellent microwave dielectric properties such as high dielectric constant ε_r =45, high quality factor $Q{\cdot}f$ =45000GHz and low temperature coefficient of resonant frequency τ_f =-10ppm/C. The $Ba_nLa_4Ti_{3+n}O_{12+3n}$ compounds exist on the tie line $BaTiO_3$-$La_4Ti_3O_{12}$ in the BaO-La_2O_3-TiO_2 system beside tungstenbronze-type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R=rare earth) solid solutions. There are three kinds of compounds : n=1, $BaLa_4Ti_4O_{15}$; n=2, $Ba_2La_4Ti_5O_{18}$; n=4, $Ba_4La_4Ti_7O_{24}$.

We got single crystals of n=1, $BaLa_4Ti_4O_{15}$ grown by self-flux method. The crystallographic data are space group: $P31c$ or $P\bar{3}1c$, Crystal system: trigonal, Lattice parameters: a=5.57Å, c=22.45Å. We will present crystal structure models of the homologous compound: n=1, $BaLa_4Ti_4O_{15}$. These compounds have the layered hexagonal perovskite-like structure, which has a common sub-structure in the crystal structure. There are hexagonal layer included octahedra contacted with face of polyhedron, and cubic layer included octahedra contacted with apexes.

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SYNTHESIS AND CRYSTAL STRUCTURE OF $Ga_2(PO_4)_2$(4,4'-bipy), A NOVEL GALLIUM PHOSPHATE CONTAINING EXCLUSIVELY FIVE-COORDINATED GALLIUM

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A new gallium phosphate, $Ga_2(PO_4)_2$(4,4'-bipy), has been synthesized by heating a reaction mixture of $Ga(NO_3)_3 \cdot 4H_2O$, 4,4'-bipyridine, H_3PO_4, tetraethylammonium bromide and water under hydrothermal conditions. The resulting product consists of colorless plate-shaped crystals of the title compound in 73% yield. Its structure has been determined by single crystal X-ray diffraction. Crystal data: triclinic, space group *P-1*, a = 4.9723(9), b = 5.770(1), c = 11.812(2) Å, α = 78.268(3), β = 89.159(3), γ = 88.344(3)°, V = 331.7(2) Å^3, Z = 1, and $R1$ = 0.0377. The structure consists of neutral sheets of gallium phosphate which are pillared through 4,4'-bipyridine ligands. A unique structural feature is that each gallium is coordinated by one 4,4'-bipyridine and four phosphate ligands to form a GaO_4N trigonal bipyramid. It is one of the few examples in which the gallium atoms are exclusively five-coordinate. The synthesis and crystal structure of the title compound will be presented.

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A5-18

THE NONLINEARITY, BICRYSTAL FORMATION AND STRUCTURE IN $KTiOPO_4$ AND ITS ANALOGUE CRYSTALS

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$KTiOPO_4$ (KTP) is an excellent nonlinear optical crystal for second-harmonic generation of lasers. We have successfully grown large size and optical quality KTP crystal by using flux method. During the growth process, the formation of bicrystal structure in KTP crystal was observed and then confirmed by etching method.

Many attempts have been undertaken to grow KTP analogue crystals by doping and varying the chemical compositions of KTP crystal. We have grown $RbTiOPO_4$ (RTP), $KTiOAsO_4$ (KTA), $RbTiOAsO_4$ (RTA) single crystals and KTP crystals with different dopants such as Nb, Na, Ga, Cr, Fe, Mn, Zn and rare-earth metals.

In this paper, we report the observation of a bicrystal structure. A simple model is proposed to explain the formation of the bicrystal structure in KTP crystals. The relationships between bicrystal structure and crystal properties are discussed. Growth morphology, defects and nonlinearities of KTP analogue crystals are also reported in the paper. The relationship between structure and physical properties is discussed.

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CRYSTAL STRUCTURE OF TWO POTENTIAL BATTERY CATHODES

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Nitro compounds are well known for their explosive and electrochemical properties. They are excellent precursors for aromatic amines (dyes) and medicinally important compounds. The new synthetic methodologies for polynitro compounds are of much importance in chemical industries and defence research today. α-Nitrostilbenes are excellent precursors for β - phenylethylamines which possess important biological activities. The studies on the crystal structure of compound (1) and (2) will help in understanding the detailed conformation of the molecules. Crystal data are as follows: compound (1) C_{14} H_8 N_4 O_8, Monoclinic, $P2_1/c$, a= 8.289(1), b= 11.353(2), c=16.716(2) Å, β =100.74(1)°, V=1545.5(4) Å^3 and Z= 4. Compound (2) C_{15} H_{10} N_4 O_{10} Monoclinic, $P2_1/c$ a= 7.0964(1), b= 8.550(3), c=28.101(5) Å, β =90.87(3)°, V=1704.7(1) Å^3 and Z= 4. The structures were solved by direct methods procedure using SHELXS97 program and refined using the full matrix least squares technique using SHELXL97. The final R- factor for compound (1) is 0.079 for 3836 symmetry independent [I > 2σ(I)] reflections and for compound (2) is 0.052 for 3105 symmetry independent [I > 2σ(I)] reflections. The details of the structural aspects will be presented.

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CRYSTAL GROWTH AND X-RAY STRUCTURAL REFINEMENT OF POTASSIUM ACID PHTHALATE SINGLE CRYSTALS

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Potassium Acid Phthalate, is also known as KAP, is a good electro-optic and non-linear optical material and also used as an analyzer material in X-ray spectroscopy. It is a semi-organic compound, crystallizes from its aqueous solution. Habitual morphology of the KAP crystal has 14 natural growth faces with dominating (010) plane. In the present investigation, KAP single crystals of good optical quality were grown by solution growth methods. Solubility of KAP in a range of temperature was determined and Solubility coefficients at different temperatures were calculated. The stability of the solutions in their supersaturated region was judged by measuring their metastable zone width by nucleation method. A novel method to enhance the metastable zone width by incorporating chelating agents was first time introduced into the world literature. The grown crystals were subjected to X-ray single crystal structural refinement analysis. X-ray data were collected at room temperature on a Siemens AED single crystal diffractometer using CuKa radiation (l=1.54178Å) in the q range 3-70°. In total, 861 reflections were collected and a check was monitored for every 100 reflections. The data were corrected for Lorentz and Polarization effects. The basic structure was refined using SHELX93 and the geometry of the molecules was determined using Crysruler package and the drawing was obtained through ORTEP3 program. The refined KAP structure belongs to orthorhombic system with space group Pca21. The cell constants are: a=9.622Å, b= 13.329Å and c=6.468Å and the cell volume is 829 $Å^3$. The "R" factor for the entire refinement was 0.076. Results will be presented in detail.

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STUDIES ON NIOBIUM SUBSTITUTED HEXAGONAL CESIUM TUNGSTEN BRONZES

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Tungsten bronzes are well-studied non-stoichiometric compounds having interesting chemical and physical properties[1]. Bronzoids are fully or partly oxidised analogues of bronzes, which are subjects of recent investigations[2]. Niobium substituted hexagonal tungsten bronzoids, $M_xNb_yW_{1-y}O_3$, where M= K and Rb have been reported recently[3,4].

Samples of $Cs_xNb_yW_{1-y}O_3$ with x= 0.25, 0.3 and y ≤0.20 have been prepared from appropriate amounts of Cs_2WO_4, WO_3 ,WO_2 and Nb_2O_5 at 800°C by solid state method. The samples were examined by optical microscope and also characterized by X-ray powder diffraction and spectroscopic methods.

The x-ray powder pattern of the samples reveal that Hexagonal Tungsten Bronze (HTB) type compounds could be synthesized with x = 0.25 and 0.30 and y ≤ 0.1 . The cell parameters increase with increasing niobium content, however, the a value shows some scattering. The optical reflectivity of the powder samples of $Cs_xNb_yW_{1-y}O_3$ can be explained by Drude- free carrier model. The IR spectra of the pure Cs-HTB with x ≥ 0.25 show metallic behavior with very low absorption. But the peak intensity of the spectra of niobium substituted Cs-HTB increases with increasing niobium content due to the decrease in carrier concentration.

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THERMALLY INDUCED RESIDUAL CHANGES IN THE CRYSTAL STRUCTURAL CHARACTERISTICS OF SOME POLYMERS

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Polymeric materials have an extensive range of applications, which may include repetitive use at elevated temperatures. Do repeated thermal exposures affect the initial structural characteristics? From a detailed study of five polymers exposed to temperatures in the range 150 to 700°C for durations ranging from 10s to ~7000h, it has been established that the parameters intensity, 2θ, halfwidth and azimuthal spread of X-ray reflections manifest significant residual effects. The shifts in the above mentioned parameters indicate introduction of changes in the physical characteristics viz., crystallinity, unit cell dimensions, crystallite size and/or microstrain and degree of molecular alignment respectively. As a typical example, it may be mentioned that after 1700 h of cumulative ageing at the constant temperature of 250°C, the high strength, high modulus aramid fibre Kevlar 49 loses ~50% of its X-ray crystallinity. Such a reduction implies deterioration in the exceptionally good initial tensile characteristics of the fibre, which has also been confirmed experimentally. Details of the residual effects of thermal ageing on the crystallographic characteristics of the polymers Kevlar, Nomex, Twaron, Nylon6,6 and Teflon have been studied in detail and this paper summarizes the results. The residual effects are indeed distinct from changes associated with phase transformations.

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A5-23

X-RAY FIBER DIFFRACTION STUDY ON CHITOSAN/HYDROIODIC ACID COMPLEX

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Crystal structures of two polymorphs of chitosan/hydroiodic acid(HI) complex were investigated by X-ray diffraction. One of the polymorphs (form I, fiber repeat=10.26Å) was obtained by immersing tendon chitosan in a colorless 6M HI aqueous solution for 20 minutes at room temperature. The other (form II, fiber repeat=39.85Å) was prepared by immersing in a brownish HI aqueous solution for 24 hours at 4°C. All the 39 observed reflections of the form I could be indexed in terms of a monoclinic unit cell with dimensions of a=9.43(3), b=9.86(2), c(fiber axis)=10.26(3)Å, and β=105.1(2)°. The intensity distribution in the fiber pattern together with the cylindrical Patterson map of the form I indicated that I^- ions were aligned along the c-axis at about 5Å interval and make a columnar structure. After locating I^- ions, the positions of chitosan were examined by the difference Fourier map. The sites of the I^- ions in the unit cell were very close to those of the water molecules in the hydrated form of chitosan. In addition, crystal structure of chitosan/HI form I was quite similar to that of chitosan/nitric acid complex. It was suggested that the columnar structure of water in the hydrated form plays an important role for the complex formation.

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STRUCTURAL STUDIES OF ATOMIC ARRANGEMENTS AND MAGNETIC CORRELATIONS IN PT-RICH PT-MN ALLOYS BY DIFFRACTION TECHNIQUES

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A Pt-rich Pt-Mn alloy system has been known for a long time to have a Cu_3Au ordered structure ($L1_2$) below the order-disorder transition temperature, T_c, whose regions extend from 10 to 35 at. % Mn. Several structural characteristics in Pt-rich Pt-Mn alloy system have been newly found with the use of electron, X-ray and neutron diffraction techniques. A cubic ABC_6-type ordered structure exists in a composition range between 12 and 14 at.% Mn below 900 K, where A, B and C correspond to Mn_xPt_{1-x}, Pt_xMn_{1-x} and Pt ($x>1/2$), respectively. A two-step phase transition from ABC_6-type structure to $L1_2$ and from $L1_2$ to A1 appears in this narrow composition range. The shape of magnetic diffuse scattering below room temperature strongly depends on both the heat treatment and the composition. For Pt-12 at. % Mn, diffuse maximum is observed at (1/2,0,0), which is due to short-ranged spin-density wave correlation originated by nesting a Fermi surface in the disordered state. In the ordered state, split diffuse maxima are also observed at (1/2,1/2,0) and (1/2,0,0). A Fermi surface nesting effect is enhanced due to the development of the atomic long-range ordering. For Pt-14 at.% Mn alloy, magnetic superlattice reflections appear at (1/2,1/4,0) and its equivalent positions in addition to the weak magnetic diffuse scattering ; the antiferromagnetic ordering appears below 20 K. For Pt-16 at.%. Mn alloy, there was no magnetic diffuse scattering. It is realized that there are strong relations between the atomic arrangement and magnetic correlations in Pt-rich Pt-Mn alloys.

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A5-25

THE INFLUENCE OF DIVALENT ELEMENTS (A'=Sr, Ca) ON CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF $La_{1-x}A'_xMnO_3$ (0<x<0.5).

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In $La_{1-x}A'_xMnO_3$ (A'=Sr, Ca), when the La^{3+} is progressively substituted by divalent cations, the proportion of Mn^{4+} increases and this leads to a change in magnetic properties, crystal structure and other properties. In this paper we study the influence of Sr^{2+} and Ca^{2+} with various contents on crystal structure and magnetic properties of $La_{1-x}A'_xMnO_3$. The Mn^{4+} content and some lattice parameters were calculated from results of Rietveld refinement of crystal structure with x-ray powder diffraction data. The obtained results were also used to explain magnetic properties of these materials.

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A5-26

IMPROVEMENT OF MECHANICAL PROPERTIES OF FERRO CAST DUCTILE 60 IRON TO ADI WITHOUT HEAT TREATMENT

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The nodular ductile iron is increasingly being used due to the benefits it offers over other alternatives, especially in vibrational absorbtion. Here we report a study of Ferrocast ductile FCD 60 (whose main elements are 3.5 % C, 2.5 % Si, 0.02 % P, 0.5 % Mn, 0.02 %S, and 0.3 % Cu), a material used in the Front Hub of Mercedez cars. The tensile strength of FCD was 60 600 N/mm^2 and its elongation was 6%. The common methods to change the mechanical behaviour of a material are to use the heat treatment process or to add an alloy. Here we aim to obtain core nodular Austemper Ductile Iron (JIS G 5503, atleast 900 N/mm^2 tensile strength and an elongation of 4%) without either the heat treatment or adding an alloy. The method used here is to increase the proportion of Mn to 0.9% and Cu to 0.5%. Various analyses carried out through X-ray flouresence, X-ray diffraction, scanning electron microscopy and Gas chromatography (RADIOGRAPHY TEST) reveal an average tensile strength of 898.10 N/mm^2, an elongation of 5.87% and a hardness of 263 HB for the nodular ductile iron, thus obtained, comparison with the JIS standards suggest that the mechanical behaviour of the material has approached that of the lowest level of Austemper Ductile Iron.

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RELATIONSHIP BETWEEN ISOMERIZATION OF HOST FRAMEWORKS AND PACKING COEFFICIENTS OF HOST CAVITIES IN ORGANIC POROUS CRYSTALS

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Polymolecular hosts are built with noncovalent bonds. It is difficult to design and construct host frameworks on purpose, because the frameworks change significantly according to molecular structures of host and guest molecules. Here we report a systematic & quantitative study of molecular recognition of steroidal bile acids by using a parameter called Packing Coefficients of host cavities (PC_{cavity}). PC_{cavity} is the ratio of the volume of host cavity to the volume of guest molecules. We found the correlation between the framework isomerizations and PC_{Cavity} in a series of inclusion compounds of cholic acid with monosubstituted benzenes. We have previously reported that the PC_{Cavity} are in the small range of 55 ~ 70%. Here, we report correlations between host framework isomerizations and PC_{Cavity} in various inclusion crystals of organic porous compounds with various guests. Organic porous compounds change the host frameworks and/or the host-guest ratios to fit the shape and volume of guest molecules. It is assumed that PC_{Cavity} of all the organic porous compounds are in the small range. Stability of organic porous inclusion crystals depends on the PC_{Cavity}. However hosts with hydrogen bonds between hosts and guests have relative larger range of PC_{Cavity} than hosts without hydrogen bonds between hosts and guests. This is because the hydrogen bonds between hosts and guests expand the PC_{Cavity}.

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EFFECT OF Pb ON CRYSTALLOGRAPHIC STRUCTURE AND ELECTRON DENSITY OF $Ba_{1-x}Pb_xTiO_3$ CERAMIC WITH x (NOMINAL) = 0.5

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The effect of Pb on crystallographic structure and electron density of $Ba_{1-x}Pb_xTiO_3$ ceramic, where x (nominal) = 0.5, has been investigated. The samples were synthesized using powder metallurgy method from $BaCO_3$, $PbCO_3$ and TiO_2, with purity better than 99%, available commercially from E-Merck. The X-ray diffractograms obtained at room temperature were refined using the crystallographic software package GSAS. Structural analysis shows that the crystal is $Ba_{0.7}Pb_{0.3}TiO_3$ with the perovskite-type $BaTiO_3$ structure, the space group tetragonal P4mm, a = 3.943(1) Å, c = 4.055, V = 63.035 Å^3 with 19 refined variables, the goodness of fit χ^2 is of 2.115 and the residual parameters Rp and Rwp are of 18.630% and 23.640% respectively. These results imply that Pb has no effect on the non-centrosymmetric structural change of barium titanate, except to contract a and b parameters and to extend c parameter with c/a ratio to 1.03. Studies on electron density show that the electron density measurements are consistent with the calculated structural parameters with maximum $\Delta\rho$ = 7.965 eÅ^{-3} and minimum $\Delta\rho$ = –2.555 eÅ^{-3}. The final results show that there is an increase in electron density at the substitute ion positions with maximum ρ = 180.069 eÅ^{-3} and 172.105 eÅ^{-3} for the observed and the calculated value respectively. These values are greater than the one from barium titanate. There is approximately 56% (53%) increase in observed (calculated) maximum electron density as compared to an approximate 33% when Pb substitutes Ba.

Keyword: barium titanate, lead titanate, X-ray diffraction, electron density

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A5-29

GROWTH OF HIGH DENSITY GRAPHITIC NANOTUBES (GNT) AND THEIR STRUCTURAL/ MICROSTRUCTURAL CHARACTERIZATION

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In the present investigation, the controlled high density multi walled aligned carbon nanotubes bundles have been synthesized by pyrolyzing a spray solution of Ferrocene [Fe(C5H5]2 and Benzene [C6H6] in an Ar atmosphere at ~900oC. A Carbonious hollow cylinder containing high density aligned GNT of length ~5cm and thickness 0.1 mm with outer and inner diameters are 1 cm and 9cm has produced. The GNT grows in redial direction of the cylinder. Scanning electron microscope (SEM) images show that the optimum length of tube bundles is very long and approaches ~0.1 mm. The bright field (BF) and dark field (DF) images of transmission electron microscope (TEM) show that Iron (Fe) has encapsulated inside the tubes during synthesis process Selected Area Diffraction Pattern (SAD) confirms that Fe exist in side the tube in crystalline form (bcc) having lattice parameter 2.8664A.

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A5-30

FLUXED MELT TECHNIQUE OF CRYSTAL GROWTH AS APPLIED TO OXIDE CRYSTALS – A BRIEF REVIEW

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Fluxed melt technique of crystal growth has established versatility in obtaining single crystal growth of a wide range of materials. The salient features of this technique with special reference to oxide crystals bearing perovskite and hexagonal structures are described. The main objective of growing crystals in the laboratory is to achieve high quality materials for device applications and for scientific investigations. Assessment of their physical and chemical perfection through various probes is essential. Flux growth has the advantage of producing facetted crystal, thus making it possible to use optical and scanning electron microscopy supplemented by energy dispersive X-ray analysis (EDAX) as an integrated method of investigating the defect structures in the crystals. Rare earth perovskite structured crystals of $RAlO_3$, $RCrO_3$ & $RFeO_3$ are interesting materials on account of their optical and magnetic properties. Ferrites, in general, are technical materials which find applications as permanent magnets, magnetic recording, computer, microwave communication devices, radios and televisions, telecommunication and other uses as in copying devices, magnetostrictive vibrators, electromagnet cores etc. Application of hexaferrites in devices operating at higher microwave and mm- wave frequencies is interesting. The renewal of interest in hexaferrites as "classical high frequency ferrites" has been realized. The devices of these types require high quality crystals. The development of growth technology of perfect single crystals either in the form of bulk or of thin epitaxial films is of immense importance. The LPE growth of hexaferrites requires a suitable and perfect substrate. The defect characterization of rare earth perovskite structured crystals ($RAlO_3$, $RFeO_3$ & $RCrO_3$) and substituted/ unsubstituted hexaferrites using surface methods like optical and scanning electron microscopy supplemented by EDAX techniques and etching as well as bulk methods such as X- ray topography is described and discussed. The defects and sources that generated them are traced. The major challenges in the fluxed melt growth of very perfect crystals are identified.

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A5-31

DISLOCATION ETCHING STUDIES ON NATURAL NATROLITE CRYSTALS.

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Natrolite bearing chemical composition as $Na_2Al_2Si_3O_{10}$. $2H_2O$ belongs to natrolite group having an orthorhombic structure. It exhibits cleavage along m (110) and b (010), the former being much more perfect than the latter. Etching experiments on (110) cleavages of natural natrolite crystals have been performed, taking different concentrations of H_3PO_4 in the range of 5-40% at different temperatures ranging from 20 to 80^0C. Effect of concentration and temperature on the depth and lateral extension of etch pits is critically studied. Velocities of etching along and perpendicular to (110) surfaces at different temperatures and concentrations are calculated. The results of etching kinetics are presented and discussed. It is reported that the etching behaviour follows Arrhenius equation. The Arrhenius factor and activation energies are calculated. It is reported that 10% H_3PO_4 at 40^0C yields best results so far as etching is concerned. The dislocation densities are measured. Comparison of etching of indented and unindented cleaved (110) planes of natrolite is presented. It is reported that though the dissolution rate of area around indentation is greatly enhanced, it does not increase the density of dislocations. The implications are discussed.

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A5-32

AN OVERVIEW OF SOME SUBSTITUTED BIPHENYLS IN RESPECT OF THEIR SINGLE CRYSTAL GROWTH AND X-RAY CRYSTAL STRUCTURE ANALYSIS

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There is scant availability of literature on the single crystal growth and three-dimensional structural aspects of substituted biphenyls. The work reported in this paper is an overview of three separate studies carried out on two kinds of substituted biphenyls i.e. 2,3,4-monosubstituted and 4,4'-linearly chained biphenyls (Liquid Crystals), with an aim to prepare X-ray diffraction quality single crystals of a series of chemically-similar-looking substances using slow evaporation and vapor precipitation techniques, and determining the three-dimensional structures of the grown materials using X-ray Crystallographic and Computational techniques. The study being reported is first of its kind on a series of biphenyl systems where an attempt has been made to:

i) investigate the role of solvent system in achieving quality crystallization.
ii) Study the phenomenon of polymorphism and multiple molecules in biphenyls.
iii) obtain the three-dimensional molecular and crystal structures.
iv) Study molecular packing, and
v) establish a correlation between the solvent system, crystal quality and crystal structure

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A5-33

DIELECTRIC AND MECHANICAL CHARACTERIZATION OF SAMARIUM DOPED LEAD TITANATE CERAMICS.

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Modified lead titanate ceramics have emerged as promising materials for piezoelectric applications owing to large electro-mechanical anisotropy in the coupling factors along transverse direction of polarization. These modified materials have potential for high frequency applications. Samarium doped lead titanate ceramic compositions (containing 2-20% samarium) have been prepared using solid state reaction method. Dielectric studies show peaks at transition temperature in all compositions: the magnitude of peak width being dependent on the frequency of measurement. The transition temperature decreases at the rate of ~12^0 C/mol % of samarium substitution. Mechanical characteristics of these ceramic samples were investigated using Vicker's Microhardness testing device. The value of microhardness (H_v) is observed to be dependent on load applied. H_v decreases rapidly in the load range of 0.1 to 0.5 N and thereafter achieves saturation. The behaviour of the dependence of H_v on load (0.1 to 1N) is similar in all concentrations of the dopant (Sm) compositions, although the maximum value of hardness increases with the increase in the concentration of samarium. The behaviour of H_v Vs load is not in accordance with the Kick's law, but the calculations indicate applicability of Hays and Kendall's law. The load independent values are calculated using the latter. The micro hardness analysis and the laws applicable are described and discussed.

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BULK CRYSTALS TO FILMS : X-RAY DIFFRACTION TO PROBE THE STRUCTURE OF PSUEDOBINARY ANTIMONY TELLURIDE

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The V_2VI_3 compounds like Bi_2Te_3, Sb_2Te_3 and Bi_2Se_3 are narrow band gap semiconductors having rhombohedral layer type crystal and display interesting thermoelectric properties. Amongst these Sb_2Te_3 has been found to exhibit p-type conduction, which no dopant has been found to change to n-type. In an attempt to improve its thermoelectric properties, the purpose of the present study was to explore a new aspect of this problem- namely, the interchange of atoms with the same nominal valence state between structures of different atomic symmetry. In particular, we have been concerned with the possible interchange of Bi or In with Sb between Bi_2Te_3 or In_2Te_3 and Sb_2Te_3.

X-ray diffraction is a tool which has been used for investigation of the physical perfection of the pseudobinary solid solution. The X-ray pattern for bulk and thin films of the crystals were obtained for 2θ angles between 20° and 60° for structural determination and to differentiate between phases having the same chemical composition but different crystal structure. The peaks in the powder pattern of Sb_2Te_3 were compared with those in the JCPDS data card and were found to match readily. The other powder patterns were indexed and the lattice parameters were evaluated. The patterns show no new peaks introduced by Bi and In indicating that Bi and In have assumed substitutional positions in the Sb_2Te_3 lattice. The crystallite size was evaluated for films of different thicknesses from the Full Width Half Maximum (FWHM) of the highest peak of the X-ray pattern of as-deposited and annealed films. While no reflections corresponding to the free elements were detected in the case of powder pattern and as deposited films, the annealed films show the characteristic peaks of free tellurium. The results are discussed in the paper.

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A5-35

SPHERULITIC GROWTH OF SINGLE AND MIXED RARE EARTH HEPTAMOLYBYDATES

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Rare Earth Molybdates, in general, have the potential of wide application in science and technology on account of their fluorescent, laser, piezoelectric, ferroelastic and ferroelectric properties. The rare earth molybdates bearing a general formula $R_2(MoO_4)_3$ have been acknowledged as ferroelectric materials. The growth of single crystals of praseodymium heptamolybdate and mixed crystals of didymium heptamolybdates is accomplished by allowing controlled diffusion of rare earth ions through silica gel impregnated with the lower reactant providing molybdenum ions. The system used is RCl_3 - $(NH_4)_6Mo_7O_{24}$ - NH_4 NO_3 - HNO_3 - Na_2SiO_3 (where R = Pr and Di). The grown crystals were characterized by using various characterization techniques, which include EDAX, XRD, IR, XRF, Scanning and Optical microscopy and Thermal analysis. The crystals assume varied morphologies including platelets, cuboids and spherulites. Spherulitic growth of praseodymium and didymium is found to be different as that of gadolinium heptamolybdate. The results are presented and discussed.

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CRYSTALLOGRAPHIC CHARACTERIZATION OF $KNbO_3$ THIN FILMS GROWN ON $SrTiO_3$ SUBSTRATES BY LIQUID PHASE EPITAXY

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$KNbO_3$ is one of the materials being expected as high-performance lead-free piezoelectric materials in place of the PZT ceramics. Application of this material will make it possible to decrease the size and improve the performance of the present electronic machine in such cases as the SAW (Surface Acoustic Wave) filter and the SHG (Second-harmonic generation) element. Because it has such characteristics, we paid attention to a $KNbO_3$ single crystal thin film, and tried to grow by means of liquid phase epitaxy (LPE). The high purity materials were mixed according to composition -52.5mol% K_2CO_3(99.99% purity) and 47.5mol% Nb_2O_5(99.9% purity)- in the platinum crucible, then melted above the melting-point and homogenized by stirring. A substrate (about 10mm x 5mm triangle shapes, t=1mm) was dipped into the melt. It succeeded in growing a (001) $KNbO_3$ single crystal thin film on the (001) $SrTiO_3$ single crystal substrates as a result. It is reported about the growth process and evaluated epitaxial relationship by means of XRD.

Crystallographic data of $KNbO_3$ Perovskite-type structure, Space grope: *Bmm*2(38), Crystal system: Orthorhombic Lattice parameters: a=3.973Å, b=5.695Å, c=5.721Å Crystallographic data of $SrTiO_3$ Perovskite-type structure, Space grope: *Pm*3*m*(221), Crystal system: Cubic Lattice parameters: a=3.904Å

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A5-37

STUDY OF LATTICE DISTORTION IN UREA DOPED KDP SINGLE CRYSTALS BY X-RAY DIFFRACTION STUDIES

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In view of the higher non-linear responses, good thermal and mechanical stability, an attempt has been made to grow single crystals of potassium dihydrogen orthophosphate (KDP), doped with different mole concentrations of urea using slow evaporation technique. The effect of impurities on the growth, surface morphology, structural, and optical properties have been investigated. With the increase of dopant concentration (1M% to 10M%), it was found that the dopant promotes the growth rate. X-ray diffraction studies were carried out on the crystals using a Philips X-ray diffractometer with Cu K_α radiation. X-ray study revealed that the structures of the doped crystals are slightly distorted as compared to the pure KDP crystal. This may be attributed to lattice strains with the adsorption of urea. FTIR and other studies will be carried out to reveal the presence of dopants in KDP.

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MEASUREMENT OF LATTICE PARAMETERS IN SOME MIXED CRYSTALS OF AMMONIUM SULPHATE AND POTASSIUM SULPHATE

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Ammonium Sulphate (AS) is a well-known ferroelectric having electro optic properties. On the other hand, Potassium Sulphate (PS) is an antiferroelectric. Both of them belong to the same β-K_2SO_4 family. Hence attempts have been made to substitute ammonium ion (NH_4^+) by potassium ion (K^+) to grow substitutional mixed crystals of Ammonium-Potassium Sulphate. Mixed system of AS-PS, $[K1_{-x}(NH_4)_x]_2SO_4$ were grown by the method of solvent-evaporation at an ambient temperature of 25^0C for molar concentration of ammonium in the range $0 \leq x \leq 1.0$. X-ray powder diffraction patterns were recorded in a Philips micro-processor controlled x-ray diffractometer (APD 1710) using nickel-filtered CuK_α radiation (λ=1.54Å) with an output power of (30kV, 20mA). The cell parameters, namely 'a' (Å), 'b' (Å), 'c' (Å) and cell volume 'v' ($Å^3$) of the mixed system with several molar concentrations(x) were determined using POWD program. It has been found that all the three lattice parameters and the cell volume increase linearly with increase in x. The lattice parameters were also estimated theoretically using Vegard's law. Composition dependence of lattice parameters (a and b) following the above law shows good agreement with the experimental results. However, an appreciable deviations from the above law exists in the lattice parameter 'c' which is the polar axis of the crystal. From the packing consideration, this may be due to comparably more elongation of the cell in 'c' direction than other two directions.

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A5-39

CHARGE-ORBITAL ORDERING IN THE BILAYER CMR MANGANITE $LaSr_2Mn_2O_7$.

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We have investigated the charge/orbital ordering in 50% hole-doped bilayer manganite $LaSr_2Mn_2O_7$ by X-ray and neutron diffraction on single crystals. High energy X-ray and neutron diffraction revealed superlattice reflections at positions corresponding to the propagation vector **k** = (-1/4,1/4,0). Temperature variation of the superlattice reflection indicated the development of a coupled charge/orbital ordering below $\mathbf{T}_{co}$=225 **K** which starts melting at about the same temperature at which A-type antiferromangnetic ordering (T_N=170 K) sets in. The intensity of the superlattice reflections becomes very small below about 100 K. A reentrant behavior of the charge/orbital ordered phase has been observed below about 50 K. We have investigated the resonance X-ray scattering from $LaSr_2Mn_2O_7$ at the Mn K absorption edge. A strong enhancement of the intensity of the superlattice reflection at Q= (-1/4,1/4,10) has been observed at the k absorption edge of Mn. The polarization of the scattered reflection shows oscillatory behavior between the σ-σ and σ-π channels as a function of the azimuthal angle with a period of about 90 degrees. All these results will be discussed in terms of newly developed theories of bilayer maganite.

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A5-40

THE CREATION OF "ISLANDS" INSIDE $Sn(y)O_x$-THIN FILMS UNDER BOMBARDMENT OF THE ELECTRON BEAMS

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SnO_x-thin films are widely applied for use not only in many optoelectronic devices, window heaters, electrodes for displays, but also in the field of gas chemical sensors. They are either semicondutors or dielectric substances depending on the amount of the oxygen (value of x in the formula). In recent years the films were improved by additives ranging from usual metals such as Sb, Al, to noble metals such as Ag, Pd, Pt, which has given rise to the fomula of al is $Sn(y)O_x$,in which y is the doped-material . In this work we have been using the electron beams of the transmission electron microscope EM-125K to study inelastic collisions inside of the $Sn(y)O_x$ thin films. The TEM- pictures show that the islands were created under bombardment of electron beams. Size of the "islands" is less than 10 nanometres. The results also show that the islands consist of two differential areas, which were represented and contrasted clearly by black and white .The islands strongly influence the properties of the films.

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A5-41

EFFECT OF SUBSTITUTION ON THE GROWTH OF RARE EARTH MOLYBDATE CRYSTALS

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Rare earth molybdate crystals are technologically important crystals as these crystals possess interesting properties viz., ferroelectric, ferroelastic, piezoelectric, fluorescent and other important properties. In the present case, we have achieved the growth of pure Gd-molybdate and substituted Gd-Ba-molybdate and Gd-Sr-molybdate crystals, using the system RCl_3 - $(NH_4)_6Mo_7O_{24}$ - NH_4NO_3 - HNO_3 - Na_2SiO_3 (where R=Gd, Gd:Ba, Gd:Sr). The grown crystals were characterized by using various characterization techniques, which include EDAX, XRD, FTIR, Scanning and Optical microscopy and Thermal analysis. It is observed that on addition of Ba or Sr to pure Gd-molybdate crystals, the morphology gets drastically changed. The pure Gd-molybdate grow as spherulites while as the substituted Gd-Ba-molybdate grow as well-facetted crystals. On the other hand Gd-Sr-molybdate grows in the form of agglomerations of hexagonal crystallites giving rise to star like shape, are illustrated. Experiments to make an in-depth study of the changes that are brought about in the morphology of crystals on addition of Ba and Sr are in progress. The implications are discussed.

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CHARACTERIZATION OF POLYCRYSTALLINE IRON SURFACE UNDER HIGH TEMPERATURE BY SMALL GLANCING ANGLE X-RAYS SCATTERING

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Characterization of polycrystalline iron surfaces by small glancing angle X-ray scattering has performed with use of a compact ultrahigh vacuum (UHV) X-ray diffractometer. With use of this equipment we investigated mechanically polished pure iron polycrystalline surfaces (ferrite, 3nines purity) before and after the baking at 500 for 20 hr in a vacuum of 10^{-6} Pa. Angular distributions of the scattered x-ray intensity from them were measured at several glancing angle incidence of the X-ray. A broadening of the scattered X-ray intensity profiles at small glancing angle incidence of the X-ray appeared on the baked specimen. The result of this experiment when compared with that of the simulation of some surface structure models, gives some clues to estimate the surface roughness. Based on these results, we propose a method of surface characterization.

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ATS SCATTERING FROM CUPRITE, Cu_2O

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Using ATS scattering [1], we can obtain local information about anisotropic environment for a specific atom. Though the scattering is very weak compared with Thomson scattering, we can obtain only an anisotropic factor by measuring a "forbidden" reflection because the isotropic part is excluded from the reflection.

Energy spectra of the ATS reflections of cuprite were measured near the Cu K-absorption edge from 8.941 keV to 9.023 keV. The spectra are distributed in a very wide range, over 50 eV, but there is no peak below the edge contrary to the observation by Kirfel *et al*[2]. The shapes of the energy spectra for the 001 and 003 reflections are essentially the same. This result indicates that these ATS scattering are caused by dipole transition process. In fact, the observed azimuthal dependence at 8.982 keV and 8.998 keV agrees with the curves calculated from atomic scattering tensors of second rank. The magnitude of an off-diagonal element of the scattering tensor for one copper atom is 1.9 electrons for the main peak at 8.982 keV. This value is very large compared with that for one iron atom in iron pyrite and magnetite, 0.2 and 0.3 electrons, respectively.[3,4] We presume that this large anisotropic term is due to the anisotropic environment of the copper atom with a strong linear coupling between oxygen atoms.

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[3] J. Kokubun et al.: J. Phys. Soc. Jpn. 67 (1998) 3114.
[4] K. Hagiwara et al.: J. Phys. Soc. Jpn. 68 (1999) 1592.

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A6 : Crystallography in biology, medicine and pharmacology

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A NOVEL REVERSED WOBBLE PAIRING OF OXIDIZED THYMINE RESIDUE WITH GUANINE RESIDUE IN B-FORM DNA, AND ITS BIOLOGICAL SIGNIFICANCE

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Activated oxygen atoms such as those of hydroxyl radicals, hydrogen peroxide and hydrogen superoxide anion radicals are potent mutagens, which produce several damages in DNA. Thymine base is oxidized to form 5-formyluracil (f^5U). In DNA replication, f^5U induces mis-incorporation of non-complementary nucleotide into a newly synthesized DNA strand. To investigate the hydrogen-bonding property of f^5U residue, crystal structures of DNA dodecamers with the sequences of d(CGCGXATf^5UCGCG), where X is A or G, have been determined. The dodecamers are associated to form a B-form duplex so that f^5U interacts with either A and G. Electron density maps show that the f^5U:A pairs occur only in the Watson-Crick geometry, and that there are two types of f^5U:G pairs. In the latter cases, one is wobbled and the other is also wobbled, but in the opposite direction. Such a reversed wobbling is a new type of pairing mode. Structure modeling of DNA polymerase with DNA fragments containing f^5U suggests that the Watson-Crick-type f^5U:A pair is acceptable in the enzyme with no structural interference, and that the wobble f^5U:G pair is sterically hard to enter the binding site of the enzyme, but the reversed wobble f^5U:G pair is acceptable. This mis-incorporation may induce mutagenesis.

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OPENING AND CLOSING OF THE ACTIVE SITE OF *C. PERFRINGENS* ALPHA-TOXIN BY ITS LOOP MOVEMENT – IS IT TRIGGERED BY MEMBRANE BINDING OR BY CALCIUM?

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Clostridium perfringens is a gram-positive anaerobic ubiquitous bacterium and secretes a range of toxins of which the α-toxin is the key determinant in gas gangrene and also implicated to several other diseases in man and animals. Alpha-toxin is secreted by the bacterium, and lowers the oxygen pressure in tissues, allowing the proliferation of the bacterium. Tissue necrosis occurs at the rate of a few cm/hr and is accompanied by a foul smelling exudate, which is the product of anaerobic fermentation, toxemia, and finally death with in few days. The only treatment is high dose of antibiotics or amputation of the organs. The toxin is a 370-residue, zinc metalloenzyme, phospholipase C, and binds to membranes in the presence of calcium.

We have solved the 3D-structure of α-toxin, in two different conformations: a closed and an open form. Recently we have also determined the 3D-structure of this toxin in presence of Ca^{2+} at pH4.7 and 6.8 in order to address its mode of function. The structure is composed of two domains: an N-terminal domain made of a nine-helix bundle and a C-terminal domain, which is an anti parallel beta sandwich.

The opening and closing of its active site and its implication towards its mechanism of function with the cell membrane will be discussed.

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A6-3

CRYSTAL STRUCTURE OF A RIBOSOME INACTIVATING VISCUMIN FROM INDIAN VISCUMIN ALBUM AT 2.8Å RESOLUTION

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Many Plants produce Ribosome Inactivating Proteins(RIPs)-enzymes that act on ribosomes in a highly specific way, thereby inhibiting protein synthesis. Some RIPs can bind to and enter cells, making them among the most-toxic substances known so far. The lectins from mistletoe belong, like ricin, abrin and modeccin to the group of toxic lectins of A and B chains. The A chain is an enzyme whereas the B chain is a lectin. The heterodimeric toxic viscumin was isolated from a partial-parasite obtained from Indian western Himalayas. The purified viscumin was crystallised by hanging drop vapour diffusion method against the same buffer containing 55% ammonium sulphate. The crystals belong to hexagonal space group $P6_522$ with a = b = 109Å and c = 309.4Å. The structure has been determined by molecular replacement method and is currently being refined. The present R-factor is 23.2% for all data to 2.8 Å resolutions. The overall protein fold is similar to ricin. It shows considerable sequence and structural differences with the european viscumin. The root mean-square-deviations (r.m.s) calculated for C_α – carbon atoms of european ML-1 and Indian viscumin show higher deviation for the A chain and lower for the B chain. The highest deviations are found for the residues on the surface. The association of A and B sub units is predominantly hydrophobic in nature.

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A6-4

INSIGHT TO STRUCTURAL SUBSITE RECOGNITION IN PLANT THIOL PROTEASE–INHIBITOR COMPLEXES: UNDERSTANDING THE BASIS OF DIFFERENTIAL INHIBITION AND THE ROLE OF WATER

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This work represents an extensive MD simulation / water-dynamics studies on a series of complexes of inhibitors leupeptin, E-64, E-64-C, ZPACK and homologous plant cysteine proteases (actinidin, caricain, chymopapain, calotropin DI) of papain family with a view to understand the various interactions, nature of water binding, factors influencing it and the structural basis of differential inhibition. The tertiary structure of the enzyme-inhibitor complexes were built by visual interactive modeling and were subjected to energy minimization followed by dynamic simulation of 120 ps in water environment. DASA study with and without the inhibitor revealed the contribution of potential subsite residues involved in inhibition. Though the interaction involving main chain atoms are quite similar, critical inspection of the model complexes reveal some significant differences in the side chain interactions in S_2-P_2 and S_3-P_3 pairs due to alteration in residues arising from sequence differences in the equivalent positions of respective subsites leading to differential inhibition. The key finding of the present study is a conserved site of a water molecule near oxyanion hole of the enzyme active site, which is found in all the modeled complexes as well as in the several solved crystal structures of papain family either native or complexed. Conserved water molecules at the ligand binding sites of these homologous proteins suggest the structural importance of the water, which could effectively change the conventional definition on chemical geometry of inhibitor binding domain by changing its shape thus affecting the complimentarity. Again, the water mediated recognition of inhibitor to enzyme subsites ($P_n...H_2O....S_n$) of leupeptin acetyl oxygen in caricain and chymopapain may also be an additional information, which could offer valuable insight to potent inhibitor design.

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A6-5

RECEPTOR BASED DRUG DESIGN OF NSAIDS: A KNOWLEDGE BASED MOLECULAR MODELLING STUDY OF COX-1 WITH N-PHENYL DICHLOROACETANILIDE.

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Apart from their extensive chemical significance, the anti-inflammatory and anti pyretic activities of acetanilide group of compounds and their derivatives are well documented (Goodman, L.S., & Gilman, A. 8th edition, vol1, 1991). Non-steroidal anti-inflammatory drugs (NSAID) are potent inhibitors of the synthesis of prostaglandins. The pharmacological target of NSAIDs is Cyclooxygenase (COX, also known as PGH synthase), the enzyme responsible for forming prostaglandin from arachidonic acid. Prostaglandins are potent mediators for causing hyperanalgesia associated with inflammation and pyretic response. To select and screen out prospective candidates with appropriate stereochemical geometry as potent drug with low toxicity for the suppression of elevated level of inflammation and fever, synthesis and crystal structure determination of N-phenyl dichloroacetanilide ($C_8H_7NOCl_2$) was done previously (Pal *et al.*,1998). A close inspection of binding site and molecular recognition in a number of reported structures for complex of cyclooxygenase with different structural classes of NSAIDs (Picot *et al.*, 1994; Loll *et al.*, 1995; Loll *et al.*, 1996) has enabled us to identify the key residues of the enzyme and a possible binding mode of acetanilide with COX-1. Difficulties associated with membrane protein crystallization have prevented us from obtaining strongly diffracting crystals of COX-acetanilide complex till now and motivated us to build computer aided knowledge based model of the complex to understand structure function relationship of the recognition when crystallization trials are being performed simultaneously. The three dimensional model structure of cox-acetanilide complex may be useful as a probe for solving the crystal structure of the same protein-inhibitor complex and additionally it serves as a structural reference for protein engineering experiments aimed at redesigning the functional properties of bio-active acetanilide.

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REFINEMENT OF TWO STRUCTURES OF THE Y174F MUTANT OF MN-SUPEROXIDE DISMUTASE AT ATOMIC RESOLUTION (0.9 Å).

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Aerobic and many anaerobic organisms contain superoxide dismutases (SODs) that remove $O_2^{-\cdot}$ through a cycle that alternately reduces and oxidises a metal centre:

$$\text{SOD-Mn}^{3+} + O_2^{-\cdot} \Longrightarrow \text{SOD-Mn}^{2+} + O_2$$
$$\text{SOD-Mn}^{2+} + O_2^{-\cdot} + 2H^+ \Longrightarrow \text{SOD-Mn}^{3+} + H_2O_2$$

$$2O_2^{-\cdot} + 2H^+ \Longrightarrow O_2 + H_2O_2$$

We have refined the structures of the Y174F mutant of Mn-SOD from *Escherichia coli* at 0.9 Å resolution. The structures are isomorphous and each comprises a non-crystallographic dimer of ~3470 protein atoms, 2 Mn atoms and ~880 solvent molecules. All non-hydrogen atoms have been refined with anisotropic thermal parameters and the final cycles of refinement have included all protons attached to non-ionisable protein atoms positioned by calculation. Many of the remaining hydrogen atoms were evident in the resultant difference maps. For wild-type MnSOD-Y174F, R_1 (observed data) = 0.099.

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A6-7

CRYSTAL STRUCTURES OF HUMAN DEOXY AND OXY HAEMOGLOBIN AT DIFFERENT LEVELS OF HUMIDITY

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We have been exploring protein hydration and its consequences using an approach involving water-mediated transformations in which protein crystals undergo reversible transformations with change in solvent content when environmental humidity is systematically varied. Using this approach it has been possible to establish a relation among hydration, mobility and action in lysozyme and ribonuclease A. The more complex, but equally well studied, multimeric protein haemoglobin is now being examined. Exploratory studies involving the solvent content of met horse haemoglobin have indeed been conducted during the infancy of protein crystallography. Following a well-laid strategy, the structures of human oxy haemoglobin have been analyzed at relative humidities of 93, 90, 88 and 84%. Also analyzed is a crystal partially dehydrated in an environment of 25% methanol. The corresponding deoxy form was studied at 90% relative humidity. The native structures, assumed to correspond to close to 100% humidity, of both the forms are already available. The oxy form does not exhibit any transformation while the deoxy form does. The low humidity form of the latter has two crystallographically independent molecules instead of one in the native crystals. The two molecules exhibit subtle and interesting differences in their relation to the liganded molecule.

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HIGH RESOLUTION CRYSTAL STRUCTURE OF HUMAN CCG1/TAFII250-INTERACTING FACTOR B (CIB)

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Transcription factor TFIID is a multi-protein complex composed of the TATA box-binding protein (TBP) and its associated factors (TAFs), and is required for accurate and regulated initiation of transcription by RNA polymerase II. The largest subunit of TFIID, CCG1, which serves a central architectural role in the assembly of TFIID has the histone acetyltransferase (HAT) activity. To investigate the functional regulation of CCG1 HAT domain, we screened some interacting factors with this domain using a yeast two-hybrid system. In this search, we have obtained the cDNA of a novel factor CIB (CCG1-interacting factor B). As the role CIB protein in the cell is not clearly known, we have initiated crystallographic, biochemical and genetic studies on this protein.

The CIB protein crystals were grown in 1.4-1.5M ammonium sulfate, 15mm urea, 70mM Tris-Cl, pH7.5, using hanging drop vapor diffusion method. Thin plate-like crystals in the orthorhombic space group $P2_12_12$ with one molecule in the asymmetric unit, with cell dimensions of a= 110.70, b=44.45, c=43.60 Å, appeared in one week. A complete data set was collected to a maximum resolution of 1.7Å , using the beam-line BL18B at the synchrotron facility, Photon Factory, Tsukuba. The structure was solved by MIR method using SOLVE package and the refinement was carried out using CNS. The present R-factor and R-free is 17.5% & 22.0%, respectively at 1.7Å resolution. Surprisingly, the overall tertiary structure of CIB protein is similar to that of α/β-hydrolases. Details of the structure and function of the protein will be discussed.

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A6-9

CRYSTAL STRUCTURE OF *M. tuberculosis* CHAPERONIN-10

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Chaperonin-60 and chaperonin-10 are homologues of the well-characterized GroEL and GroES molecular chaperones of *Escherichia coli*. Chaperonin-10 or GroES acts as an allosteric modulator of chaperonin-60 (GroEL) by interactions through its flexible 17-residue mobile loop. The chaperonin-10 of *M. tuberculosis* (Mt-cpn10) also acts as an important T-cell antigen during infection. The crystal structure of Mt-cpn10 has now been solved. c-centered orthorhombic crystals were obtained with unit cell dimensions (Å) of a=77.5, b=62.5 and c=125.6. The structure was solved by molecular replacement using the main chain coordinates of *M. leprae* heptamer using the Amore package of CCP4. The overall structure is a 4-stranded β-barrel with two long stretches of highly flexible segments, the dome loop and the mobile loop. The seven subunits in a heptamer have very little conformational differences and exhibit nearly perfect 7-fold geometry. Due to the flexibility of the mobile loop, its visualization has not been possible in the stand-alone structures of chaperonin-10 homologues solved thus far. Our structure identifies a partially-stable conformation of the mobile loop. Binding sites for metal ions in the dome loop have also been identified that have recently been shown to modulate the plastic states of Mt-cpn10.

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A6-10

X-RAY STUDIES OF TETHERED HIV-1 PROTEASE MUTANT AND INHIBITOR COMPLEXES

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HIV (Human immunodeficiency virus), which is the causative agent for the condition known as AIDS (Acquired immunodeficiency syndrome), encodes its own protease enzyme, HIV- PR which is absolutely essential for formation of infectious virions. The residue at position 95 has been conserved across many different strains of the virus, evnthough this residue is not part of the active site. Inhibitors of HIV-PR have been critical components of the HAART therapy for AIDS. The emergence of drug-resistant virus necessitates design of very many chemically different types of protease inhibitors through the process of structure-based drug-design.

We report here the 1.9Å structure of the tethered HIV PR carrying a mutation C95M in one of the subunits. Single crystals of size 0.3x0.1x0.1mm3 were grown by the hanging drop vapour diffusion method. X-ray diffraction data to was collected on a RAXIS IIC imaging plate detector system. The crystals belonged to the hexagonal space group $P6_1$ with cell dimensions a=b=63.15Å & c=83.6Å and gamma =120°. The structure was solved using the molecular replacement method. The major structure highlight is the closed conformation of the flaps as compared to the open conformation of flaps seen in all the earlier studies on the unliganded enzyme. Interestingly the overall conformation of the ligand free tethered enzyme reported here is unexpectedly similar to the ligand bound enzyme rather than to the ligand free wild type enzyme. The environment around M95 and C1095 are identical showing no drastic structural effect of this mutation at position 95.

X-ray crystallography has contributed immensely to drug development using the approach of structure based drug design. In an attempt at rational drug design, X-ray diffraction data was collected on crystals of HIV-1 PR soaked in solution of a lead compound, designed using computer docking. The structure of the complex was solved by the molecular replacement method. The inhibitor was located in the difference electron density maps contoured at 2 sigma. Possible modifications in the lead compound which could improve the potency of this compound will be discussed.

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STRUCTURAL CHARACTERIZATION OF INTERACTIONS FORMED BY IMPORTIN-α DURING NUCLEAR IMPORT

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Nuclear proteins are synthesized in the cytoplasm and need to be imported into the nucleus through the nuclear pore complexes. Such import is directed by special signals; the most common is the classical nuclear localization sequence (NLS), consisting of one (monopartite NLS) or two (bipartite NLS) clusters of basic residues. The receptor that recognizes NLSs is the importin heterodimer; importin-α contains the NLS binding site, and importin-β is responsible for the actual translocation through the pore.

To determine the structural basis of interactions formed by importin-α during nuclear import, we crystallized importin-α and its complexes with peptides corresponding to monopartite, bipartite and phosphorylation-regulated NLSs, and complemented the structures using a variety of biophysical techniques (biosensor, ELISA, analytical centrifugation). Jointly, our results yield the following account of recognition events during nuclear import.

Importin-α exists in an autoinhibited state and has a low affinity for NLS-containing proteins. The affinity for NLSs is increased through the association of its autoinhibitory domain with importin-β. Importin-α elegantly uses its superhelical structure (armadillo repeats) to bind both the NLSs and the autoinhibitory region; the spacing of the armadillo structural units is commensurate with the spacing of amino acids in the peptide.

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A6-12

STRUCTURAL STUDIES OF FOUR INACTIVE MUTANTS OF PENICILLIN V ACYLASE FROM *Bacillus sphaericus*

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Two types of Penicillin acylases, one specific for penicillin V and the other for penicillin G, account for all the enzymatic production of 6-aminopenicillanic acid (6-APA), the key intermediate in the preparation of semi-synthetic penicillins. We have been studying the structure activity relationship of penicillin V acylase (PVA) from *Bacillus sphaericus*. The structure of PVA was solveded in hexagonal and triclinic crystal forms. The structural comparison of PVA with penicillin G acylase (PGA) has shown that PVA like PGA belonged to the Ntn (N-terminal nucleophile) hydrolase family, and helped in the identification of the active site of the enzyme.

Based on information from structure comparison, selective mutants of PVA devoid of acylase activity could be prepared through site-directed mutagenesis. In order to understand the catalytic mechanism and specificity of the enzyme, the formation of crystal complex of the mutants with penicillin V has been tried. Specific mutants were prepared for probing into the mechanism of auto-catalytic processing that results in the active enzyme. Crystal structures of four mutants (1CysAla, 1CysGly, 175AsnAla and 228ArgSer) have been studied at various resolutions. The first two mutants lacked the precursor peptide at the N-terminus, whereas the second two had the precursor tri-peptide included in the clone. The crystal structures of the latter two mutants showed that they underwent post-translational processing, slower compared to native precursor, to change to the active form. Details of the mutant structures in comparison with the structure of the active form of PVA will be discussed.

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A6-13

CRYSTAL STRUCTURE OF MACROMOLECULAR ANTIBIOTIC Apo-C1027 AND COMPUTER MODELING ANALYSIS OF C1027 CHROMOPHORE PROTEIN COMPLEX

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C1027 isolated from the culture filtrates of *streptomyces globispourus* C-1027 (Wuhan, China), is a member of the macromolecular enediynes antitumor antibiotic, which also include s actinoxanthin (AXN), neocarzinostatin (NCS), auromomycin (AUR) and kedarcidin.

The three-dimensional structure of C1027 is required in order to deduce the factors that determine the stabilization of the chromophore by the apoprotein and to design stable analogues of the chromophore. By far, only one chromophore-apoprotein complex of NCS has been solved, while there is no information about the chromophore-apoprotein complex of C1027 being reported. Herein, we reported the 1.8 Anstrgom resolution apo-C1027 crystal structure. The protein crystallized in space group p31, with two molecules in the asymmetric unit and a solvent content of ~54%. The two structures in the asymmetric unit are very similar, significant differences being limited to the orientation of some of the surface side chains involved in crystallographic contact. The final R_{work} and R_{free} were reduced to 18.5% and 23.7% respectively. The final model statistics for our C1027 structure were 0.014 Å for bond length and 1.726 for bond angles. The overall apo-C1027 molecule consists primarily of β-sheets organized into two domains, separated by a deep cleft which is the putative chromophore binding site. The large domain forms a seven-stranded antiparallel β-barrel that contains two sheets: an external sheet consisting of strands 1,2 and 5(residues4 to8, 19 to24, and 62 to 66 respectively) and an internal sheet formed by strands 4, 3, 6, and 7 (residues 53 to 57, 30 to 35, 94 to 98, and 108 to 110, respectively). The smaller domain consists of two twisted, two-stranded, antiparallel β-sheets formed by strand 3a and 3b(residues 36 to 40, and 44 to 48, respectively) and strand 5a and 5b (residues 72 to 75, and 84 to 87, respectively).

Although the chromophore was included during crystallization, there is no strong electron density in the final model, suggesting that the chromophore is released from the apoprotein or is highly flexible and disorder. Based on the apoprotein structure, a modeling study of the C1027-Chr and Apo-C1027 complex by calculating van der Waals and electrostatic potential energies to explore the binding site of the chromophore and how the apoprotein stabilized the chromophore by the specific interaction that are unique to this complex.
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A6-14

CRYSTALLIZATION AND PRELIMINARY X-RAY STUDY OF FERREDOXIN ISOFORM II FROM EQUISETUM ARVENSE

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Ferredoxin (Fd) is an iron-sulfur protein with a molecular weight of 11 kDa. Fds containing the [2Fe-2S] cluster are distributed in photosynthetic organisms and called 'plant-type Fd'. It takes part in the photosynthetic electron transport chain and plays an important role of assimilatory reduction. In higher plants, there are several Fd isoforms, which are genetically and structurally distinct from each other. Leaves of field horsetail (*Equisetum arvense*) have two isoforms (Fd I and FdII). Fd I was characterized and crystallized as a representative of plant-type Fd. Its 3D structure was already solved (S.Ikemizu *et al.*, 1994) and structures around the [2Fe-2S] cluster were highly conserved. According to comparison of amino acid sequences of these two isforms, Fd II has appeared to have no arginine residue around the [2Fe-2S] cluster conserved among the other Fds. This Arg residue was thought to be crucial to form the microenvironment of the cluster. In order to elucidate how the active site of Fd II is stabilized without this Arg residue, we started the crystallographic study of Fd II from *E.arvense*. Crystallization was performed by the hanging drop vapor diffusion method at 4°C. Crystals of Fd II appeared in one week, diffracted at least to 1.8 Å resolution and belonged to the space group of *C*2. Here we report the preliminary crystallographic study aimed at higher resolution structure analysis.

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A6-15

STRUCTURE OF THE INDUCED ANTIBACTERIAL PROTEIN FROM TASAR SILKWORM, *Antheraea mylitta*: IMPLICATIONS TO MOLECULAR EVOLUTION

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The repertoire of proteins and peptides over-expressed on bacterial infection in insects provides the first line of defense and acts cumulatively against a wide spectrum of pathogens defining the humoral immune response. The crystal structure of one such antibacterial protein of immune origin, which was purified from tasar silkworm (*Antheraea mylitta*) larvae after induction by *E. coli* infection, has been determined. The core structure of this protein is similar to c-type lysozymes and α-lactalbumins. The catalytic residues are conserved with respect to the chicken lysozyme. While the *A. mylitta* protein is functionally similar to chicken lysozyme unlike human α-lactalbumin, it is significantly different in certain structural features with respect to the other two proteins. Although physiological origins of the tasar silkworm protein and chicken lysozyme are different, the catalytic mechanism employed by them would probably be similar with subtle differences in the specificity and level of activity. On the basis of the structural comparisons between tasar silkworm protein, chicken lysozyme and human α-lactalbumin it can be suggested that the conformational changes in a protein are minimal during rapid evolution as compared to those in the normal course of evolution.

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X-RAY CRYSTALLOGRAPHIC STUDIES OF CEPHALOSPORIN ACYLASE

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Cephalosporin acylases are a group of enzymes that hydrolyze cephalosporin C (CPC) and/or glutaryl 7-aminocephalosporanic acid (GL-7-ACA) to produce 7-aminocephalosporanic acid (7-ACA). The acylase from *Pseudomonas* sp. strain 130 (CA-130) is highly active on GL-7-ACA and glutaryl 7-aminodesacetoxycephalosporanic acid (GL-7-ADCA), but showed low activity for CPC. The detailed determination of the three-dimensional structure of this enzyme, the research of the relationship between the structure and functions and the site-directed mutagenesis for definite purpose will provide a new approach and a theoretical basis for improving the activity of this enzyme, so that an improved strain of cephalosporin acylase which is more stable and high-expressed is able to be obtained, the industrialization of producing cephem antibiotics with the enzyme can be realized.

CA-130 was crystallized in three different forms, two of which are suitable for structural studies. A tetragonal crystal form diffracted to 2.4 Å and belongs to the space group $P4_12_12$, with unit-cell parameters a=b=73.5Å, c=382.0Å. It is given that there is one αβ heterodimer per asymmetric unit. A second crystal form diffracted to 2.1 Å and belongs to the space group $P2_1$, with unit-cell parameters a=130.6 Å, b=108.6 Å, c=135.5 Å, β=116.0°. It is given that there are four αβ heterodimers per asymmetric unit. The tetragonal crystal structure of CA-130 was determined by MAD method, and the $P2_1$ crystal structure was then determined by Molecular Replacement method. The structure determination of the protein complex with some different substrates is being carried on, which may demonstrate the activation mechanism of this enzyme more deeply. Besides native protein, we have done a lot of work on cloning, expression, purification and crystallization of inactive mutant protein. Furthermore, we will try to soak the crystals in the substrates and also co-crystallize the inactive protein with the substrates.

A6-17

ENHANCED BINDING OF A RATIONALLY DESIGNED PEPTIDE LIGAND OF CONCANAVALIN A ARISES FROM IMPROVED GEOMETRICAL COMPLEMENTARITY

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The structural basis of affinity enhancement was addressed by analyzing the interactions between concanavalin A and the carbohydrate-mimicking peptide ligands. Based on the crystal structures of concanavalin A in complex with these peptides [Jain *et al.* (2000) J. Biol. Chem. 275,16098-16102; Jain, *et al.* (2001) Biophys. J. 80:2912-2921], a high affinity analog was designed. This analog (Acetyl-MYWYPY-amide) binds to the lectin with 32-fold enhanced affinity compared to the corresponding precursor peptides. Crystal structure of concanavalin A bound to the designed peptide has been determined. A peptide molecule binds to each of the crystallographically independent monomers of the tetrameric lectin. The four bound peptide molecules exhibit two major conformations both of which are extended. Unlike in the case of other concanavalin A binding peptides, the structural variations within different conformers of this analog are marginal. It is apparent that the deletion of the structurally variable region of the larger peptides has led to an improved complementarity and increased buried surface area in case of the designed peptide. The crystal structure also showed formation of two backbone hydrogen bonds between the ligand and the ligate which were not present in the complexes of the precursor peptides. The observed structural features adequately explain the enhanced binding of the designed analog.

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CRYSTAL STRUCTURE OF AMINOGLYCOSIDE (3') PHOSPHOTRANSFERASE-II, AN ENZYME IMPLICATED IN ANTIBIOTIC RESISTANCE

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The largest class of clinically relevant antibiotics, apart from the β-lactams, function by inhibiting protein synthesis. Amongst these are aminoglycoside antibiotics, such as kanamycin and tobramycin, which kill bacteria by binding to the 30S ribosomal subunit. Resistance to such antibiotics is mediated by enzymes that chemically modify the antibiotics by transferring nucleotide, acetyl or phosphoryl groups onto specific positions on the drug. As part of a program to investigate the molecular basis of aminoglycoside resistance, we have determined the structure of aminoglycoside 3'-phosphotransferase-II [APH(3')-II]. We have crystallized APH (3')-II in the presence of kanamycin, and solved and refined the structure at 2.1-Å resolution. APH (3')-II has a two-domain fold very similar to the protein kinases, with a deep cleft where the kanamycin molecule is bound. Kanamycin binds through a large number of hydrogen bonds to conserved residues in the protein. The ATP-binding site is occupied by a sulfate ion. The structure shows evidence of some flexibility around the active site cleft that may be related to its different substrate specificity. This involves a small loop and an α-helical bundle subdomain. The structural differences between this family of enzymes and the protein kinases will be presented.

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STRUCTURE OF A NOVEL ALCOHOL DEHYDROGENASE SOLVED BY MAD PHASING FROM A SINGLE COBALT ATOM

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Alcohol dehydrogenases (ADHs) are ubiquitous throughout all living species, because of the common use of alcohols as substrates in metabolic pathways. Structures are well known for several families of ADHs but other, apparently unrelated, ADHs exist. We have determined the 3D structure of an iron-dependent ADH from the bacterium *Zymomonas mobilis* (zADH), which has no sequence identity with any protein in the Protein Data Bank, but which is related to a much wider family of dehydrogenases. The structure of this 40 kDa enzyme has been solved by MAD phasing from a single Co^{2+} ion, substituted for Fe^{2+}. Remarkably, despite no sequence identity, the protein proves to be structurally homologous with the Zn-dependent enzyme dehydroquinate synthase (DHQS), which catalyses the second step of the shikimate pathway for aromatic amino acid biosynthesis. Both perform an alcohol oxidation, and both have similar metal and NAD(H) binding sites, albeit with different metal specificity. The zADH enzyme has also been used in random mutagenesis studies that allow us to pinpoint sites in the structure that alter metal, cofactor and substrate specificity.

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A6-20

CRYSTAL STRUCTURE OF PEA TOC34: A GTP-ASE TRANSLOCON AT THE OUTER MEMBRANE OF CHLOROPLAST

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Toc34, a 34-kDa integral membrane protein, is a member of the Toc (translocon at the outer envelope membrane of chloroplast) complex that associates with precursor proteins during protein transport across the chloroplast outer membrane. Toc34 is composed of an N-terminal cytosolic 29-kDa GTP-binding domain, a single transmembrane domain and a 3-kDa C-tail exposed to the intermembrane space. Toc34 is postulated to be involved in modulating the gating property of the main channel of the Toc complex, Toc75, or in recognition and presentation of the precursors. Here, we report the crystal structure of the cytosolic part of pea Toc34 in complex with GDP and Mg^{2+} at 2.0 Å resolution. The crystal structure of Toc34 reveals unique features that have not been observed in other GTPases reported to date.

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SOFTDOCK UNDERSTANDING OF MOLECULAR RECOGNITION THROUGH SYSTEMATICALLY DOCKING STUDY

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Keywords: Interface packing/Molecular complex/Molecular recognition/Soft dock/Systematic docking.

Molecular recognition and docking is essential to the biological functions of proteins. SOFTDOCK was one of the first molecular docking methods developed for protein-protein docking. Its ability to represent the molecular surface with different shapes and properties and to dock a variety of molecular complexes with certain conformational changes has been demonstrated in the previous study. In the present work, we study the effects of the docking parameters through statistical analysis. Seventy one typical binary complexes of different categories in PDB were also systematically docked for a test. 57 of them produced correct solutions with one set of docking parameters while the other 14 complexes required adjusting the docking parameters, by decreasing the softness of the recognition and hence the background noise. We found that these 14 complexes had special structural features. Our results suggest that a variety of mechanisms may be involved in molecular recognition rather than the shape complementarity only, which is very helpful in developing more powerful methods in predicting molecular recognition.

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ANALYSIS OF CATALYTIC MECHANISM OF β-AMYLASE FROM B.*cereus var. mycoides* BY X-RAY CRYSTAL STRUCTURE OF CATALYTIC RESIDUE MUTANTS

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The X-ray crystal structures of catalytic-site mutants E172A [Glu172 Ala] and E367A [Glu367 Ala] of β-amylase from *Bacillus cereus* var. *mycoides* in complex with maltopentaose (G5) has been determined at 2.1Å and 1.95Å resolution, respectively. Restrained crystallographic refinement has resulted in R-factors of 18.0% and 19.2 % in the 40.0 to 2.1Å and 40.0 to 1.95Å resolution ranges, respectively. Clear and continuous density corresponding to a pentasaccharide was observed in the E172A crystal in complex with G5, consisting of Glc1 to Glc5 (Glc1 is the non-reducing end glucose residue of the substrate). The conformation of the glucose residues of Glc2 and Glc3 shows a sharp turn without distortion of the puckering of Glc2. On other hand, each one molecule of glucose and maltotetraose was observed in the active site cleft of the E367A crystal in complex with G5. A carboxyl oxygen of Glu172 forms a hydrogen bond with the glucosidic oxygen in the scissile bond between Glc2 and Glc3. This hydrogen-bond indicates the protonated state of Glu172 in the initial kinetic complex between wild-type enzyme and substrate. A water molecule located near the carboxyl oxygen of the other catalytic residues Glu367 may be activated by Glu367. These results indicate that Glu172 acts as a general acid and Glu367 as a general base.

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CLONING, EXPRESSION, PURIFICATION AND CRYSTALLIZATION OF M31 CHROMO SHADOW DOMAIN

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The heterochromatin protein 1 (HP1) family of proteins represents the best-characterized heterochromatin-associated nonhistone chromosomal protein family in the eukaryotic kingdom. Its remarkable evolutionary conservation suggests a fundamental role of HP1 proteins in nuclear organization and a highly conserved set of macromolecular interactions. They are composed of two related domains: an N-terminal chromo domain and a C-terminal shadow chromo domain. In order to investigate the role of the shadow chromo domain of murine HP1-like protein, M31, in heterochromatin formation using the structural biology method, we have subcloned the CSD domain by PCR and ligated into the BamHI and XhoLI sites of the pGEX-4T-1 vector. Plasmid was transformed into host strain BL21 (DE3). After expression, protein was purified by GST chromatography and gel-filtration chromatography. Hanging drop vapor diffusion method was used to research the crystallization conditions. Crystals were obtained in about 7 days at 18°C under certain conditions and a set of data has been collected at 115K.

CRYSTAL STRUCTURES OF TWO ISOFORMS OF KRAIT PLA2S AS DIMERS AND TRIMERS AT 2.1 AND 2.5 Å RESOLUTIONS.

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Phospholipase A2 (PLA2s) enzymes hydrolyze phospholipids at sn-2 position of the glycerol backbone, releasing lysophospholipids and fatty acids. The venoms of many poisonous animals contain a diverse cocktail of toxins, often neurotoxins, conferring potency against a spectrum of targets and prey. The venom of krait contains α-bungarotoxins, which block acetylcholine receptors on the presynaptic membrane of neuromuscular junctions, and β-bungarotoxins a completely unrelated set of proteins, which inhibit neurotransmitter release from presynaptic membrane. In addition to bungarotoxins, the venom of Indian common krait (*Bungarus caeruleus*), also contains a number of isoforms of free PLA2 enzymes. Two new forms of krait PLA2s (KPLA2s) were isolated, crystallized and their three-dimensional structures were determined. One isoform was crystallized as a dimer while the other as a trimer. The crystals of dimer KPLA2 belong to rhombohedral space group R3 with a=b=80.4 Å, c= 57.9 Å and the crystals of trimer were monoclinic with space group C2 with a= 80.9 Å b=80.6 Å , c=57.1 Å, β= 90.3°. The crystals of dimer diffracted to 2.1 Å while those of trimer diffracted to 2.5 Å. The structure of dimeric and trimeric forms were refined to R-factors of 0.192 and 0.198 respectively. The structures of PLA2s in both forms are essentially similar. However, the interactions at the interfaces of dimers and trimers are strikingly different as altogether different amino acids participate in the interfacial interactions. It may also be mentioned that the previously reported isoform crystallized as a monomer. It appears that the different isoforms in KPLA2 aggregate differently to diversify its strategy to attain a higher of lethality against its prey.

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MECHANISTIC IMPLICATIONS FROM THE STRUCTURES OF THE Y174F MUTANT OF MN-SUPEROXIDE DISMUTASE AT 0.9 Å RESOLUTION.

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The superoxide ion, $O_2^{-\cdot}$, is a toxic byproduct of aerobic lifestyles. All aerobes and many anaerobes contain superoxide dismutases that convert $O_2^{-\cdot}$ to dioxygen and hydrogen peroxide (for removal by catalase and peroxidases):

$$SOD\text{-}Mn^{3+} + O_2^{-\cdot} \quad ==> \quad SOD\text{-}Mn^{2+} + O_2$$
$$SOD\text{-}Mn^{2+} + O_2^{-\cdot} + 2H^+ \quad ==> \quad SOD\text{-}Mn^{3+} + H_2O_2$$

$$2O_2^{-\cdot} + 2H^+ \quad ==> \quad O_2 + H_2O_2$$

The structures of wild-type and reduced forms of the Y174F mutant of Mn-SOD from *Escherichia coli* at 0.9 Å resolution provide unprecedented insight into the active site, in particular into the location of hydrogen atoms in the vicinity of the metal centre. To our surprise, the solvent species coordinated to the Mn(II) centre appears to be an hydroxide ion (not water), giving insight into the redox tuning and metal specificity exhibited by members of the closely homologous family of Fe- and MnSODs..

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A6-26

RE-REFINED STRUCTURE OF GARLIC LECTIN. EFFECT OF BETTER DATA PROCESSING AND REFINEMENT

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Garlic lectin is a dimeric protein, specific to mannose, belonging to the bulb family. Its structure, reported earlier (Chandra, N.R., Ramachandraiah, G., Bachhawat, K., Dam, T.K., Surolia, A. and Vijayan, M. *J Mol Biol.* 285, 1157-1168 (1999)), among other things, indicated the possibility of oligomerisation as a strategy for generating carbohydrate specificity. However, there were ambiguities in details such as the identification of the correct isolectin, presumably on account of the poor quality of the data. Better quality crystals could not be grown in spite of repeated efforts. Therefore, the same data were reprocessed using DENZO. The structure was refined using newly processed data employing X-PLOR and CNS. For comparison, the old data set in conjunction with CNS was used to produce another coordinate set in addition to the original data set obtained using X-PLOR. Thus the effort resulted in four sets of refined coordinates which enabled a comparative study of the two processing and refinement programs. The combination of DENZO and CNS produced the best results. The quality and the resolution of the map and the definition of the structure improved substantially. In particular, the amino acid residues at the variable locations in the sequence, and hence the isolectin, could be identified with a high degree of confidence. It could be established that the crystal asymmetric unit contains two identical hetero-dimers.

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A6-27

X-RAY CRYSTAL STRUCTURE OF A METHYLTRANSFERASE (Rv2118c) FROM *Mycobacterium tuberculosis* H37Rv IN COMPLEX WITH S-ADENOSYL L-METHIONINE.

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The Rv2118c is a 30kDa protein, belonging to the class of conserved hypotheticals from *M.tuberculosis* H37Rv. High resolution structure of Rv2118c, determined by MIR method, revealed that it is a S-Adenosyl L-methionine (Ado-Met) dependent methyltransferase. The crystallographic asymmetric unit consists of a monomer. The quaternary organization of the protein is a tetramer. Due to extensive dimeric interactions, it could be described as a dimer of tight dimers. This quaternary arrangement is consistent with the gel filtration experiments where the protein elutes at a tetrameric position.

The monomer can be functionally divided into two domains. The larger catalytic C-terminal domain is primarily a mixed α/β structure with modified Rossman fold. It is very similar to other Ado-Met dependent methyltransferases. The smaller N-terminal domain consists of β-hairpin motifs and has a unique fold not found in other methyltransferases of known structure. The N-terminal domain packs against the C-terminal domain contributing significantly to subunit interactions. The cleft between the two domains is probably significant in substrate recognition and binding.

Structure comparison and multiple sequence alignment studies indicate that three of the motifs reported to be highly conserved in diverse Ado-Met MTases are also present in Rv2118c. Database searches reveal significant sequence homology to several conserved hypothetical proteins particularly from Archae and Eubacteria. Some of these sequences have been classified as homologues of Protein Isoaspartyl Methyltransferase (PIMT). However sequence and structural studies indicate that they have a different functional role or at least represent a different class of PIMT. Comparison of catalytic domain of Rv2118c based on structural alignment with the corresponding domains from well-characterized Ado-Met Mtases indicated that Rv2118c might be closer in structure to RNA and small molecule MTases. Also structural analysis, homology to yeast Gcd14p and limited docking studies using tRNA substrate suggest that Rv2118c could be an RNA methyltransferase but further studies are required to conclusively prove its functional role.

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ALTERNATE CONFORMATIONS FOUND IN CATALYTIC SERINE OF *Bacillus subtilis* LIPASE DETERMINED AT 1.3Å RESOLUTION

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Bacillus subtilis extracellular lipase (BsL) has exceptionally small molecular weight (19.4kDa) in lipase family. BsL should be a potential enzyme for industrial purposes because of its enzymatic property. We started crystallographic study on BsL in order to design mutant BsL suitable for an industrial enzyme based on the three-dimensional structure. Recently, crystal structure of BsL was determined at 1.5Å resolution (Van Pouderoyen *et al. J. Mol. Biol.* (2001) **309**, 215-226). In the present study, we originally crystallized new crystal form of BsL, which gives diffraction with higher resolution, and determined structure at 1.3Å by MAD method.

It was found that the active site Ser77 has alternate conformers in its side chain. Oγ atom of the first conformer makes hydrogen bond to Nε atom of His155, a member of catalytic triad. In contrast, the second conformer is stabilized by hydrogen bonds to a water molecule and side chain of adjacent His76. These two conformers seem to be an active and an inactive state, respectively. Moreover, a glycerol molecule, which was used as a cryoprotectant, is located in the active site. From these observations, we constructed a substrate-binding model of BsL. In the presentation, we will discuss about a mechanism of catalytic reaction.

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CRYSTALLOGRAPHIC STUDY OF A PLATELET-AGGREGATION INHIBITOR, TRIMESTATIN FROM SNAKE VENOM

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Disintegrins from snake venom are generally defined as low molecular weight (49-84 amino acids), cysteine-rich, also containing Arg-Gly-Asp/Lys-Gly-Asp (RGD/KGD) tri-peptides that inhibit the binding of fibrinogen to integrin αIIbβ3 on platelet membranes, as well as the binding of other ligands, such as fibronectin, vitronectin, collagen and von Willebrand factor, to integrins on the surface of cells. Disintegrins have been described as being unique and potentially useful tools not only for investigating cell-matrix and cell-cell interactions but also for developing various agents, such as antithrombotic, antimetastatic in terms of their anti-adhesive property, anti-migration against certain tumor cells, and antiangiogenesis.

We have revealed the crystal structure of trimestatin at 1.7 Å resolution using the molecular replacement methods from NMR structures. The final R-factor and R_{free} are 18.7 and 21.7%, respectively. This is the first crystal structure of disintegrin, and flexible region of RGD tri-peptides in the NMR structures are now clearly seen. This stationary information of RGD sequence may help the radical design of anti-thrombosis drug such as (1) peptidyl competetor (like eptifibatide) and (2) non-peptidyl competetor (lamifiban, tirofiban).

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A6-30

STRUCTURE AND CARBOHYDRATE SPECIFICITY OF ARTOCARPIN

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Lectins are multivalent carbohydrate binding proteins that specifically recognize diverse sugar structures and mediate a variety of biological processes. The seeds of jack fruit (*Artocarpus integrifolia*) contain two lectins - jacalin and artocarpin. Both lectins are tetrameric with similar molecular weight, but differ in their carbohdyrate specificity. Jacalin is specific to galactose while artocarpin is specific to mannose. The crystal structure of jacalin complexed with methyl-α-galactose was solved earlier in this laboratory. Two crystal forms of artocarpin in the saccharide-free state were obtained and diffraction data from them (up to 2.4 Å) were collected. Partial sequence information available at that time indicated that this protein is similar to jacalin. The structure was solved using the molecular replacement method employing AMoRe, with the jacalin tetramer as the search model. The structures were refined using the available partial sequence information, the electron density map and the sequence of jacalin. The sequence of KM+, a lectin from South American jack fruit seeds and similar to artocarpin in its biochemical properties, became available during the later stages and was also used. The carbohydrate binding site can accommodate both galactose as well as mannose. Energy minimisations were performed on artocarpin-mannose and artocarpin-galactose complexes. A similar study was undertaken on jacalin as well. Interaction energy and buried surface area calculations of the minimised systems favour the correct ligand in both the proteins. The major difference in the carbohydrate binding region of the two proteins is the presence of aromatic residues in jacalin and their absence in artocarpin. This absence of stacking interaction could contribute to determining the sugar specificity of artocarpin.

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A6-31

ROLE OF COUNTER – ION OF THE SURFACTANT MOLECULE ON THE MICELLAR STRUCTURE

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Surfactant molecules (e.g. SDS), having dual affinity for water and oil, self aggregate into supermolecular structures when dissolved in water or oil. The simplest aggregate of these surfactant molecules is called a micelle. In general, micelles could be spherical, cylindrical, ellipsoidal or disk like in shape.

In case of ionic surfactants, such as Sodium Dodecyl Sulphate (SDS), $[CH_3(CH_2)\ldots SO4]^- Na^+$, The surfactant molecule ionizes in water and the micelle largely consists of Dodecyl Sulphate (DS^-) ions. The Na^+ ions referred to as counter ions, tend to stay near the surface of the micelle. To examine the effect of the size and the charge of the counter ion on the micellar structure, we have carried out Small Angle Neutron Scattering (SANS) experiments on LiDS, NaDS, KDS, RbDS, Cu $(DS)_2$, $Mg(DS)_2$, $Co(DS)_2$, $Ni(DS)_2$, using the SANS diffractometer at Dhruva reactor. The data analysis was done using Hayter and Penfold model. These studies show that micelles are ellipsoidal in above solution and a/b ratio of the ellipsoid depends both on sizes and valencies of the counter ions. Details of the experiments, data analysis and the results will be presented.

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A6-32

MECHANISM OF IRON-BINDING IN LACTOFERRINS: CRYSTAL STRUCTURE OF AN IRON-SATURATED INTERMEDIATE IN THE Fe^{3+} BINDING PATHWAY OF CAMEL LACTOFERRIN AT 2.7 Å RESOLUTION.

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This is the first ever protein intermediate obtained in the crystalline state by the simultaneous process of Fe^{3+} binding and crystal nucleation and is also the first structure of an intermediate of lactoferrin in the Fe^{3+} binding pathway. Lactoferrin is an iron binding 80 kDa glycoprotein. It binds Fe^{3+} very tightly in a closed inter-domain cleft in both lobes. The iron-free structure of lactoferrin, on the other hand, adopts an open conformation with domains moving widely apart. It implies that initial Fe^{3+} binding must be in the open form. The protein intermediate was crystallized by microdialysis method. The protein solution with a concentration of 100 mg/ml in 10 mM Tris-HCl pH 8.0 was loaded in a capillary and dialyzed against the same buffer containing 26 % (v/v) ethanol placed in a reservoir. $FeCl_3$ and CO_3^{2-} in excess molar ratios to that of protein in its solution were added to the reservoir buffer. The crystals appeared after some hours and grew to the optimum size within 36 hours. The structure was determined by molecular replacement method and refined to final R and free-R factors of 0.187 and 0.255 respectively. The present structure showed that the protein molecule adopts an open conformation similar to that of camel apolactoferrin. The electron density map clearly indicated the presence of two iron atoms, one in each lobe with four-fold coordinations: two by the protein ligands of Tyr 92(433) OH and Tyr 192(526) OH, and two other coordination sites are occupied by oxygen atoms of bidentate CO_3^{2-} ions leading to a tetrahedral intermediate. The CO_3^{2-} anion is stabilized through hydrogen bonds with the synergistic anion-binding site Arg 121(463) and with Ser 122 Oγ in N-lobe and Thr 464 Oγ in C-lobe. The third oxygen atom of CO_3^{2-} is interacting with a water molecule in both lobes.

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A6-33

STUDIES ON A RECOMBINANT CHYMOTRYPSIN INHIBITOR PROTEIN AND TWO OF ITS MUTANTS

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Based on an in depth analysis of the structural results available so far in the Kunitz (Sti) family of Serine protease inhibitors, Protein Engineering was initiated in our laboratory with an ultimate aim to alter the inhibitor specificity of wci, a 20 Kd Chymotrypsin inhibitor from Winged Bean Seeds, belonging to this family. The protein was cloned for structural and biochemical studies and was subjected to point mutations at a conserved position, Asn14. This residue, known to have a pivotal role in stabilizing the first reactive-site of the inhibitor, is highly conserved in the sequences of the other members of Kunitz (Sti) family. Crystallographic studies with 1.9 Å Synchrotron Cryo Datasets for a recombinant wci(Rwci), and two of its mutants (N14k and N14d) have been made. These studies on the recombinant and the mutant proteins are primarily aimed at understanding the importance of the protein Scaffolding towards the conformational rigidity of the reactive-site loop. Results will be presented.

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CRYSTAL STRUCTURE OF A HUMAN RHINOVIRUS TYPE 14 (HRV14):HUMAN IMMUNODEFICIENCY VIRUS TYPE 1 (HIV-1) V3 LOOP CHIMERIC VIRUS THAT ELICITS A NEUTRALIZING ANTIBODY RESPONSE AGAINST HIV-1

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The structure of a chimeric human rhinovirus type 14 (HRV14) that displays on its surface an immunogenic insert from the gp120 V3 loop of the human immunodeficiency virus type 1 (HIV-1) has been solved at 2.7 Å resolution. The virus, designated MN-III-2, was isolated from a combinatorial library by immunoselecting with a variety of anti-HIV-1 V3 loop monoclonal antibodies. The HIV-1_{MN} V3 loop segment, IGPGRAFYTTKN, was flanked by 0-3 randomized residues on each side and inserted between HRV14 viral protein 2 residues Ala159 and Asn160, allowing for diverse presentation of the V3 loop segment (Smith *et al.*, 1998, J. Virol. 72, 651-659). The V3 loop insert of MN-III-2 was flanked at its N-terminus by a three-residue linker, ADT. This chimeric virus was able to elicit the production of antisera in guinea pigs capable of neutralizing HIV-1 (MN and ALA isolates). Structure refinement of the current model has converged to an R-factor of 21.6%. The overall structure of MN-III-2 is similar to that of wild-type HRV14. The structure of the V3 loop insert is dominated by two type-I β turns. The first type-I β turn consists of residues GRAF and the second, residues TTKN. Comparisons with the previously reported structures of V3 loop peptides in complexes with Fab fragments of three neutralizing antibodies reveal that the V3 loop insert in the MN-III-2 chimeric virus adopts a conformation that is somewhat different from those seen in the Fab/peptide complexes. The major conformational difference is localized to the GR residues of the second β turn. However, the GPG and the RAF residues in the chimeric virus can be superimposed upon the corresponding segments in the Fab/peptide complexes. The results suggest that the V3 loop has an inherent conformational flexibility and can adopt multiple conformations. Thus, the relatively conserved GPGRAF motif of the V3 loop appears to consist of two well defined structural modules that can alter their relative conformations and orientations, resulting in distinct V3 loop conformations and, possibly, functions.

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A6-35

STRUCTURE OF THE RTP/DNA COMPLEX AND ITS ROLE IN POLAR FORK ARREST

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The arrest of replication forks and the coordinated termination of DNA replication in *Bacillus subtilis* is dependent upon the binding of the replication terminator protein (RTP) to its cognate DNA binding site (*Ter site*). The cooperative binding of two RTP dimers to the *Ter* site is able to arrest the helicase catalysed unwinding of duplex DNA in a polar manner. A complex between a ^{15}N-labelled mutant form of RTP and a symmetrical form of a DNA binding site was formed using NMR spectroscopy. By titrating the DNA, NMR was used to assess the stoichiometry of complex formation, with the sample containing the most homogenous solution of complex used in crystallization trials.

The 2.5Å resolution structure reveals a novel DNA interaction by a dimeric "winged-helix" domain protein, which differs from the predicted models. As expected the recognition helices of RTP are in contact with the major grooves of the DNA. However, the "wings" and N-termini of RTP do not significantly contact the DNA as forecast. This structure provides insight into the molecular basis of polar replication fork arrest and has been used to model the cooperative binding in the functional terminator.

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A6-36

STRUCTURES OF A SITE SPECIFIC MUTANT OF *Plasmodium falciparum* TRIOSEPHOSPHATE ISOMERASE AND ITS COMPLEXES.

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Triosephosphate isomerase (TIM) is an extensively investigated glycolytic enzyme that catalysis the isomerization between dihydroxyacetone phosphate (DHAP)and D-glyceraldehyde-3-phosphate(D-GAP). The mobility of loop 6 of the β-barrel domain of TIM is believed to be crucial for the efficient catalysis of the enzyme and for preventing the release of the toxic intermediate, methylglyoxal. One of the residues in that loop, W168, was mutated to Phe to monitor the resulting changes at the active site. The mutant protein could be crystallized at pH 8.5 from Tris-HCl using PEG 1450 as the precipitant in the presence of 100mM Li_2SO_4. These crystals diffracted to 2.3Å resolution. Crystals of this mutant complexed to the natural substrate DHAP and a substrate analogue β-glycero phosphate (β-GP) were also obtained under similar conditions. These crystals belong to the orthorhombic space group $P2_12_12_1$ and are comparable to the mutant crystals in terms of diffraction quality. However, the mutant and its β-GP complex contain one dimeric molecule in the asymmetric unit in contrast to the DHAP complex, which has two dimeric molecules in the asymmetric unit. These structures could be determined by molecular replacement using the native TIM as the starting model. In these complexes, the flexible loop 6 is in the open conformation in all the monomers. Hence, mechanism of catalysis is likely to be distinct in the plasmodium enzyme.

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COMPARATIVE ANALYSIS OF THE STRUCTURES OF A XYLANASE FROM THERMOASCUS AURANTIACUS DETERMINED AT ROOM AND CRYO TEMPERATURES TO ATOMIC (1.11 Å) AND ULTRA HIGH (0.89 Å) RESOLUTIONS.

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We have determined the crystal structure of a thermostable xylanase isolated from Thermoascus Aurantiacus at atomic resolution of 1.11 Å, at room temperature and at ultrahigh resolution of 0.89 Å, at cryo temperature with synchrotron X-ray diffraction data. The structures have been refined to R/R-free of 9.16, 11.67% respectively for room temperature data and R/R-free of 8.85, 10.41% respectively for cryo data. We have carried out a comparative analysis of the structures determined at the two temperatures. The F-family xylanase assumes the $(\alpha/\beta)_8$ triose phosphate isomerase fold with 303 amino acid residues in the single chain. Upon least squares superposition of the corresponding C^{α} atoms of the structures, it is found that the interior β-strands superpose with lower average RMS deviation of 0.08 Å, the deviations for the α-helices and loop regions being 0.21 Å and 0.22 Å respectively. The helix α8 at the C-terminus has larger deviation of 0.35 Å. Structural plasticity of a few salt bridges at the two temperature is noticed. From the analysis of the B-factor ratios, it is found that on the average β-strands have lower ratios than α-helices. As expected from the least square superposition analysis, α8 has more ratio compared to that of other secondary structural elements. Hydrogen bonding patterns, water structure and anisotropic temperature factor distribution are also compared between the two structures. Disorder of some of the amino acid residues is seen in the cryo temperature structure, which might explain the earlier observaion of the xylanase to cleave xylan specifically without any contaminating cellulase activity.

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IONIZATION STATE, STOICHIOMETRY AND AMINO ACID AGGREGATION IN THE COMPLEXES OF TARTARIC ACID WITH L-ALANINE AND L-HISTIDINE HYDROCHLORIDE

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As a continuation of crystal structure investigations on amino acid – carboxylic acid complexes, we have recently elucidated the crystal structures of complexes of L-alanine and L-histidine hydrochloride with tartaric acid. Some useful and important information on the ionization states and stoichiometry of the individual molecules have been obtained. L-alaninium tartrate [$P2_1$, a = 5.145(1)Å, b = 13.721(3)Å, c = 7.475(1)Å, β = 98.09(1)°, Z = 2] has the usually expected ionization states and stoichiometry. The molecular aggregation pattern has striking similarities with those observed in sarcosinium tartrate and L-prolinium tartrate. In L-Histidinium hemihydrochloride ditartrate sesquihydrate, $(C_6H_{12}N_3O_2^{2+})$. ½ (H^+Cl^-). $2(C_4H_5O_6^-)$. $\frac{3}{2}H_2O$ [C2, a = 35.857(6)Å, b = 7.481(1)Å, c = 7.678(1)Å, β = 93.19(2)°, Z = 4], the L-histidinium moiety exists in the crystal as a dication. Both the crystallographically independent tartaric acid molecules exist as semi-tartrate anions. *Cl* and a proton are found lying in the two-fold axis leading to the formation of a hemihydrochloride in the crystal. This proton, in turn, is also shared between *Cl* and a water oxygen which lies very close to a two fold axis. A detailed comparison of the conformation, stoichiometry and aggregation patterns with other similar structures will be presented.

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OBSERVATION OF ADDITIONAL CALCIUM ION IN THE CRYSTAL STRUCTURE OF THE BOVINE PANCREATIC PHOSPHOLIPASE A_2 :

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Phospholipase A_2 catalyses hydrolysis of the ester bond at the C2 position of 3 – *sn* - phosphoglycerides. Here we report the 1.9Å resolution crystal structure of the triple mutant K56, 120, 121M of bovine pancreatic phospholipase A_2. The structure was solved by molecular replacement method using the orthorhombic form of the recombinant phospholipase A_2. The refined protein model contains all the 123 amino acid residues, two calcium ions, 125 water molecules and one 2-methyl-2-4-pentanediol (MPD) molecule. The final model has an R- factor of 19.6% [R_{free} of 25.9%] with good stereochemistry. The conformation of the residues, 60 to 70, varies substantially compared to that of the trigonal and the orthorhombic forms of the recombinant enzyme. The notable observation in the present study is, in addition to the functionally important calcium ion in the active site, one more calcium ion is found near the N-terminus. This is the first time such a second calcium ion is found in the bovine phospholipase A_2 structure. The organic solvent MPD has also appeared in the active site of the structure and its hydroxyl groups are involved in hydrogen bonding with the polar atoms of the protein molecule as well as with two other water molecules, out of which one water molecule is a natural ligand for the functionally important calcium ion. The details will be presented

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A6-40

PLANT LECTINS: DIVERSITY IN STRUCTURE AND SPECIFICITY.

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Crystal structures of six different plant lectins belonging to three distinct structural families, namely, peanut lectin and basic and acidic winged bean agglutinins of the legume, jacalin and artocarpin of the *Moracea* and garlic lectin of the bulb families have been determined in our laboratory. The structures revealed how carbohydrate specificity can be generated in different lectins by specific residues at the carbohydrate binding sites, using water bridges, posttranslational modification and oligomerization. Structures of the three legume lectins, peanut lectin with its unusual tetrameric association and the two dimeric winged bean lectins indicated that large variations in the mode of oligomerization of legume lectins result from small variations in the amino acid sequence. A phylogenetic analysis of legume lectins has also revealed that the primary structures of legume lectins contain signatures of quaternary structure and carbohydrate specificity. Tetrameric jacalin and artocarpin exhibit a novel lectin fold, the β prism I fold, whereas the dimeric garlic lectin has a β prism II fold. Both peanut lectin and jacalin have a high affinity for T-antigen though the architectures of the two binding sites are entirely different.

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CRYSTAL AND MOLECULAR STRUCTURE OF DIETHYL TETRAHYDRO-1, 1-DIOXO-3, 5-DIPHENYL-1, 4-THIAZINE-2, 6-DICARBOXYLATE.

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The title compound C22H25NO6S is an intermediate derivative of tetrehydro-1, 4-thiazine-1, 1-dioxide and is used in the synthesis of many pharmacologically important compounds. Tetrahydro-1, 4-thiazine-3,5-dicarboxylic acid, a metabolite has been detected in the bovine brain as well as in human urine.

The compound was crystallized from chloroform by slow evaporation method at room temperature. The crystals were colourless blocks, in the space group P_1 with lattice parameters a=10.217(1)Å, b=10.713(2) Å, c=11.397(1)Å, α=98.14(1)^0, β=109.38(1)^0, γ=107.25(1)^0 with number of atoms Z=2, density 1.323 mg/m3 volume=1083.2(3) Å^3.

The structure was determined by direct methods and refined to a final R-value 0.054. There is disorder in one of the ethoxy group of the molecule, which could not be detected by any other method. The interesting results of the structure and conformation will be discussed in the presentation.

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APPLICATION OF RAPID SOAKED HALIDES IN PHASING PROTEIN STRUCTURES

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A quick, less than a minute, soak of protein crystals in a cryo-solution containing bromide or iodide anions leads to incorporation of these anomalous scatterers into the ordered solvent region around protein molecules. The anomalous signal from these halides can be used to solve the phase problem in protein crystallography. This approach has been successfully used to solve several protein structures. Details on soaking method, concentration of halides, soaking time, phasing successes and failures will be discussed at the meeting.

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A6-43

ANALYSIS OF PROTEIN INTERFACES BY GRAPH SPECTRAL METHODS

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The quaternary structures impart structural and functional credibility to proteins. In a multi-subunit protein, it is important to understand the factors that drive the association or dissociation of the subunits. It is a well-known fact that both hydrophobic and charged interactions contribute to the stability of the protein interface. The interface residues are also known to be highly conserved. Though they are buried in the oligomer, these residues are either exposed or partially exposed in the monomer. It is believed that a systematic and objective method of identifying interface clusters and their analysis can significantly contribute to the identification of a residue or a collection of residues important for oligomerization. Recently, we have applied the techniques of graph-spectral method to a variety of problems related to protein structure and folding. A major advantage of this methodology is that the problem is viewed from a global protein topology point of view rather than localized regions of the protein structure. In the present investigation, we have applied the methods of graph-spectral analysis to identify side chain clusters and their cluster centres at the dimer interface of a set of homodimeric proteins. These clusters are analyzed in terms of properties such as amino acid composition, accessibility to solvent and conservation of residues. Interesting results such as participation of charged and aromatic residues like Arginine, Glutamic acid, Histidine, Phenylalanine and Tyrosine, consistent with earlier investigations, have emerged from these analyses. Important additional information is that the residues involved are a part of a cluster(s) and that they are sequentially distant residues which have come closer to each other in the three dimensional structure of the protein. These residues can easily be detected using our graph spectral algorithm. This method has also been used to detect dimerization sites on the monomer. The dimerization sites on the monomer have been identified as exposed and conserved clusters on the monomer, which also have residues that are preferred at the interface. The dimerization sites thus detected on the monomer are found to correlate very well with the actual dimerization sites.

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A6-44

PRELIMINARY X-RAY ANALYSIS OF CHLOROPLASTIC ASCORBATE PEROXIDASE FROM TOBACCO PLANTS

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Higher plants contain ascorbate peroxidase (APX) isoenzymes as H_2O_2-scavengers. APX isoenzymes are distributed in at least five distinct cellular compartments: stroma and thylakoid membrane in chloroplast, microbody, mitochondria and cytosol. All of these APX isoenzymes require ascorbate (AsA) as a specific electron donor. In particular, the chloroplastic isoenzymes are rapidly inactivated in the absence of AsA, in contrast with other isoenzymes. We have initiated an analysis for the crystal structure of s omal APX from tobacco plants to obtain some stereochemical information abou the mechanisms of the rapid inactivation and of the recognition of AsA as an electron donor.

The recombinant APX was overexpressed in *Escherichia coli* and purified by chromatography. The enzyme was crystallized by using PEG 4000 as a precipitant. Data to a resolution of 1.6 Å were collected using synchrotron radiation at the Photon Factory, Japan. The crystals belonged to the orthorhombic space group $P2_12_12_1$ with unit-cell parameters a = 37.2, b = 76.8 and c = 98.8 Å. A molecular-replacement solution was obtained using the structure of cytosolic APX from pea as a search model. Refinement of the model was performed, resulting in an R-factor of 0.40 and an R_{free} of 0.44. Manual modifications of the model structure are currently in progress.

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A6-45

STRUCTURE AND ASSEMBLY OF TOBACCO NECROSIS VIRUS

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Tobacco necrosis virus is a spherical plant virus that is composed of ssRNA and 180 chemically identical coat proteins. Its structure was determined by X-ray crystallography at 2.25Å □ resolution. Three Stereochemically non-identical (A, B and C) subunits are arranged according to icosahedral symmetry to form *T*=3 capsid, in which the N-terminal segments of the C subunits cluster around the 3-fold (quasi 6-fold) axis. Five calcium ions per icosahedral asymmetric unit are located at the interfaces between subunits. Of these three are on the outer surface of the capsid. Virus particles were dissociated in 2M NaCl to protein and RNA, and they could be assembled by desalting to particles that are identical to the native ones in EM. RNA appears to stabilize the particles. When the N-terminal segment was cleaved off by limited proteolysis, the protein was assembled to smaller spherical particles, probably *T*=1 icosahedral particles. These assemblies require calcium ion.

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A6-46

TRIPLE-HELICAL STRUCTURE OF (PRO-PRO-GLY)9 IN THE *c*=80Å CELL

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Recently, single crystal structures of collagen-model peptides have been reported from several groups. Among these, peptides with simple repeating unit like (Pro-Pro-Gly)10 and (Pro-Hyp-Gly)10 gave us only average structures in the *c*=20Å pseudo-cell since their diffraction patterns have remarkable features that there are strong reflections on the layer lines corresponding to the helical repeating period of 20Å and very weak reflections on the rest of the layers. On the other hand, single crystals of (Pro-Pro-Gly) 9 ($P2_1$, a=26.30, b=26.85 c=81.07Å and β=90°) showed a clear axial repeat of 80Å together with the strong 20Å repeat along the *c*-axis (BL40B2, SPring-8). The triple-helical structure found in this crystal showed a very good agreement with the 7/2-helical model for collagen proposed by one of the authors (K. O.). More than 150 water molecules were found in an asymmetric unit. Many of them are involved in the hydrogen-bond schemes same as those observed in the other related model peptides.

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A6-47

REFINED MOLECULAR AND CRYSTAL STRUCTURE OF SILK I BASED ON Ala-Gly and (Ala-Gly)$_2$-Ser-Gly PEPTIDE SEQUENCE

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It is known that there are three silk modifications: Silk I of fibroin, Silk II of spun silk and Silk III of fibroin in a solvent. Of these, Silk II crystal structure is very well established. We report here the refined molecular and crystal structure of one of the crystalline modifications of *Bombyx mori*, Silk I by X-ray diffraction method. Cell dimensions are found to be essentially the same as in the synthetic poly (L-Ala-Gly) peptide model. The (ϕ,ψ) values of L-Ala and Gly in the repeating unit are observed to be in the *Bridge* and the fourth quadrant regions of Ramachandran map and are given by (-112°,-6°) and (71° , -99°) respectively. The molecular conformation in the present study has a Crank-Shaft or an S-shaped zigzag arrangement leading to a remarkable agreement of observed and calculated structure amplitudes for both dipeptide and hexapeptide sequences and also has a reasonable hydrogen bond networks. Even though overall arrangement of the molecular chains appear to be similar (ϕ,ψ) values are found to be quite different from those reported by Lotz and Keith. In spite of intra- and inter-molecular hydrogen bond networks, silk I structure changes easily to the silk II by a mechanical deformation. This fragility may be due to the above peculiar "Crank-Shaft" conformation deduced from the alternating structure of alanine and glycine.

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CRYSTAL STRUCTURE OF *Nicotiana alata* S_{F11}-RNase ASSOCIATED WITH GAMETOPHYTIC SELF-INCOMPATIBILITY

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Nicotiana alata (ornamental tobacco) S_{F11}-RNase is an *S*-glycoprotein associated with gametophytic self-incompatibility. Crystals of the S_{F11}-RNase had been grown at room temperature using polyethylene glycol as a precipitant. The crystal structure was determined by MAD method with synchrotron radiation at RIKEN Beamline I (BL45XU) of SPring-8. The native crystal diffracted beyond 1.55 Å resolution. The protein consists of eight α-helices and seven β-strands. The tertiary structure is the typical motif of the RNase T2 family, which composed of a variant of the (α + β) fold. Asn28 was linked with Hybrid-type oligosaccharides. The residues that serve as the catalytic acid and base are assigned to His32 and His91, respectively. Two 'hypervariable' regions, known as HVa and HVb, are the proposed sites of *S*-allele discrimination during the self-incompatibility recognition, and in the S_{F11}-RNase, these are separated from the active site. HVa and HVb are composed of the positively charged long loop followed by the part of an α -helix (Lys47-Leu63) and the negatively charged short α -helix (Phe72-Pro82), respectively. The S_{F11}-RNase structure shows both hypervariable regions are accessible to the solvent and could participate in the process of self-nonself discrimination between *S*-RNase and unknown pollen *S*-gene product(s) upon pollination.

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A6-49

AB-INITIO PHASING OF A PROTEIN CYTOCHROME C_6 BY DIRECT METHOD.

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Cytochrome C_6, obtained from the green alga monoraphidium brauni, is a 89 amino acid heme-containing redox protein with 151 solvent water molecules have been redetermined, ab-initio, from a single native Synchrotron X-ray data set without using any known fragment or MIR phases. Several thousand phase sets at 1.1Å resolution were generated with 1200, 1500 and 2000 largest $|E|$ values using MULTAN. The E-map corresponding to the phase set having lowest mean phase error (MPE) 45.4° showed an octahedral coordination around the Fe atom. Successive difference Fourier maps followed by least squares refinement using SHELXL97 converged to R=0.30. The protein model building was, however, difficult owing to discontinuity in the polypeptide chains. To improve the quality of the electron density map, the density-modification procedure was tried. Initial phases calculated from Fe, (Fe+S), (Fe+S+3N) coordinates obtained directly from the E-map of MULTAN with 40 cycles of refinement by density modification changed MPE from ~70° to ~40° (the map correlation coefficient from ~0.33 to ~0.72) and resulted in an interpretable electron density map. The successful application of direct method in reciprocal space along with density modification in real space reveals the possibility of substantial automation in the structure determination of metalloproteins with high resolution data.

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A6-50

CRYSTAL STRUCTURE ANALYSIS OF A CYCLOPHANE

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Cyclophanes represent the central class of synthetic receptors in molecular recognition. The aromatic structural units present in them ensure the necessary rigidity of the molecular structures and also provide orientation sites for the cooperative binding of the guests. We have synthesised for the first time a cyclophane molecule with unusual amino acid (α-aminoiso butyic acid) unit as a side-chain. We report here the crystal structure of this novel molecule. Cyclophane crystallises in the triclinic system with unit cell parameters a = 11.332(4)Å, b = 12.984(4)Å, c = 15.787(2)Å, α = 78.00(2)°, β= 76.45(2)°, γ = 88.39(3)°, V= 2213(1)Å^3, Z=2. Density = 1.143(Mg / m ^{3}), λ = 0.71069 Å, μ = 0.78 cm^{-1}. F(000) = 806 and space group P1. The structure was solved by direct methods and refined by blocked full matrix method. Final R-factor is 0.12. Hydrogens were fixed and riding atom corrections were applied to them during refinement. The crystal asymmetric unit contains two molecules. Hydroquinone, acetonitrile, ethanol and water have also been located in the crystal structure. The two cyclophane molecules are oriented almost perpendicular to each other. Each cyclophane molecule has two N-H...O intra-molecular hydrogen bonds. The hydroquinone links the two symmetry related molecules through a C-H...O hydrogen bond. The NH-CO groups are oriented on opposite directions with respect to the macrocycle.

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X-RAY CRYSTAL STRUCTURE DETERMINATION OF 3-[(4-HYDROXY-8-METHYL-2-OXO-2H-CHROMEN-3-YL)-CHLOROPHENYLMETHYL]-8-ETHYL-2-OXO-2H-CHROMEN-4-OLATE

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The title compound otherwise known as dicoumarol has received importance recently for its pronounced antiHIV study by various researchers. They were tested for inhibition of related retroviral integrase form HIV-2 and Simian immunodeficiency virus(SIV). They are found to be inhibited with 3'-processing and strand transfer activities against HIV-1 and HIV-2 and SIV integrases, with no remarkable selectivity noted. It was found that the role of substitution on benzenoid part would have some specific effect on these structures as integrase inhibitors. In the present investigation, the structure determination was carried out to study the hydrogen bond characteristics and to find out the possible structure activity relationship.

A derivative of dicoumarol, $C_{27}H_{19}O_6$ Cl, Mr =474.9, monoclinic, $P2_1/c$, a =11.307 (3) ; b = 10.488 (4), c = 19.004.(6) Å ; β = 92.89(3) °; V = 2250.8 (13) Å^3 , Z = 4, D_x = 1.401 Mgm^{-3}, λ = 0.71073 Å , μ = 0.21mm^{-1} , $F_{(000)}$ = 984 , T = 293 K , wR = 0.180 and final R = 0.068 for 2277 observations. In the title compound, two 4-hydroxy coumarin moieties are linked through a methylene bridge on which one of the two hydrogens has been replaced with a phenyl group.

The coumarin rings are individually planar with the two planes inclined at 57.4 (1) ° to each other. The phenyl mean plane is inclined at 63.5 (1)° to one and 63.8(1)° to the other 4-hydroxycoumarin. All principal bond angles about methylene carbon are widened over normal tetrahedral values. Steric crowding about the methylene carbon may be responsible for this feature. The orientations of the coumarins about the methylene bridge may be described by torsion angles C4-C3-C21-C13- 84.0 (6)° and C3-C21-C13-C12 83.5(5)°. The C21-C22 distance of 1.545(6)Å is longer than an unstrained C(sp3)-C(Ar) bond , but in the range characteristic of related sterically crowded structures. The 4-hydroxycoumarins are intramolecularly hydrogen bonded between hydroxyl and cabonyls, with O...O separations 2.598 and 2.688 Å respectively.

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CRYSTAL AND MOLECULAR STRUCTURE OF 2 [N-(2,6-DICHLOROPHENYL) -2-OXOINDOLIN-3-YLIDENE] METHYL PHENYL ACETATE

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Indole derivatives, widely distributed in living cells as tryptophan metabolites, have important biological functions. They are found to possess CNS depressant, antidepressant, antihypertensive, psychotropic muscle relaxant, anti-microbial and anti-inflammatory activities. The interaction of indole with DNA has been widely reported. The structure determination of the title compound was taken up to study the effect of the substituents and also the conformation of the oxoindoline ring. This compound $C_{23\ H15}\ NO_3Cl_2$ crystallizes in the monoclinic space group C2/c with Z = 8. Cell parameters: a =16.724 (2) ; b = 8.739(2), c = 28.287(11) Å ; β = 98.8(1) °; V = 4085.8 (8) Å^3 , D_x = 1.380 Mgm^{-3}, λ = 1.5418 Å , μ = 3.063mm^{-1} , Mr =4 24.26 , $F_{(000)}$ = 1744 , T = 293 K , wR = 0.138 and final R = 0.053 for 3873 observations.

The phenyl and the oxoindoline rings are planar. The substitution of methyl group in one of the phenyl rings prevents coplanarity between oxoindolin and this phenyl ring. The dihedral angle between them is 52.1(1) °. The methyl acetate group makes an angle of 74.0(8) ° with oxoindolin ring and 81.9(11) ° with this phenyl ring. The magnitude of the dihedral angle [81.9(11) °] appears to be a common feature among the acetic acid or carboxylate as substituent group. This dihedral angle is observed to be either close to 0 or 90° in all plant growth hormones. In the present structure, the methyl acetate moiety adopts nearly perpendicular orientation with respect to this phenyl ring. The bond length C2-O3 and C11-O3 show partial double bond character. C--H..O type intermolecular hydrogen bonds are formed in the title compound.

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A6-53

CRYSTALLOGRAPHIC STUDIES OF CAD DOMAIN OF DFF45

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Apoptotic DNA fragmentation and chromatin condensation are mediated by DFF, a heterodimeric protein composed of a 40kD caspase-activated DNA fragmentation factor (DFF40) and its 45kD inhibitor (DFF45). In non-apoptotic cells, DFF40 is kept as an inactive complex with its inhibitor DFF45. When various apoptotic stimuli activate the caspase cascade, caspase 3 cleaves DFF45 and the released DFF40 degrades chromosomal DNA in nuclei. The CAD domain of DFF45 executes the function of inhibiting the DNase activity of DFF40 and helping in its correct folding as a chaperone.

We cloned the human DFF45 CAD domain into pQE-30 vector and expressed it as a His-tag protein. The purified DFF45 was obtained by Ni-NTA affinity chromatography followed with resource-Q ion exchange column. We now have crystals by vapor diffusion in hanging drops. Preliminary X-ray crystallography study is in progress.

This research will give useful information for learning the mechanism of DNA fragmentation process in apoptosis.

A6-54

PURIFICATION, CRYSTALLIZATION AND X-RAY ANALYSIS OF SWINE VESICULAR DISEASE VIRUS.

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Swine vesicular disease virus (SVDV) is the etiological agent of swine vesicular disease, a highly contagious disease in pigs, and is related to Coxsackie B virus. Crystalline arrays of SVDV can be observed in the cytoplasm of cells 4.5 hours after inoculation to porcine kidney cells (IBRS-2 cells). We obtained crystals from virus isolated from two cell lines of the JX/78 strain of SVDV and present the crystallization conditions together with preliminary X-ray data to 3.6 Å resolution.

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CRYSTALLOGRAPHIC STUDIES OF CYTOCHROME P450CAM MUTANT (F87L/Y96F/L244A/V247A)

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Cytochrome P450 enzymes are heme-containing monooxygenases, which are involved in many vital processes in the biosythesis and degradation of steroids and other hormones, as well as in the metabolism of xenobiotics. Cytochrome P450cam from *Pseudomonas putida* is by far the most characterized member of the P450super-family. The structure of the enzyme complexed with the natural substrates and many other substrates and inhibitors has been studied crystallographically.

We got several constructors of P450com mutants from the lab of Dr.L.L.Wong, Oxford University.We studied four site mutants (F87L/Y96F/L244A/V247A). The mutants were expressed in *E.coli* BL-21, induced with 1mM camphor,purified through DEAE Sepharose F.F.at pH6.5,FPLC at pH7.4(ResourceQ 1ml) at pH7.4 Superdex75 at pH7.0. Crystals of the protein were obtained at 298K by the vapor-diffusion method using PEG8000 as a precipitant. 1ul of protein solution was mixed with 1ul of 30%PEG8000 in buffer [100mM cacodylate, 200mM sodium Acetate pH6.5]. Crytals appear within 1 day. After data was collected by X-ray diffraction, the structure was determined by Isomorphous Difference Fourier method. Its space group is $P2_1$ and unit-cell parameters are a=67.011, b=62.187, c=95.561Å, β=90.571°.Now we are also studying the complex of the mutant with its substrate, phenanthrene.

Key words : Cytochrome P450 mutant Crystallization

A6-56

UNUSUAL IONIZATION STATE, STOICHIOMETRY AND AGGREGATION IN BIS(DL-SERINIUM) OXALATE DIHYDRATE

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X-ray studies on crystalline complexes of amino acids with simple carboxylic acids, which are believed to have existed in the prebiotic earth, are expected to provide useful and important information on the nature of intermolecular interactions and biomolecular aggregation patterns, at atomic resolution. The crystal structure of bis(DL-Serinium) oxalate dihydrate, $2(C_3H_8NO_3^+).C_2O_2^{2-}.2H_2O$ [$P2_1/c$, a = 4.869(1)Å, b = 17.199(7)Å, c = 17.172(4)Å, β = 91.68(2)°] has been determined and refined to R = 0.037 for 2528 observed reflections. The asymmetric unit contains two crystallographically independent serinium cations, a double negatively charged oxalate anion (uncommon in similar crystal structures) and two water molecules. The oxalate anion lies across the inversion center. There are no direct interactions between the amino acid molecules. The oxalate anions and water molecules mediate interactions between amino acid molecules in forming a layer parallel to the ab plane. The aggregation pattern of the individual molecules is distinctly different from those observed in other amino acid – oxalic acid complexes. A detailed comparison of the ionization state, characteristic aggregation and interaction patterns with other similar complexes will be presented.

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CRYSTAL AND MOLECULAR STRUCTURE OF A NOVEL THIENOPYRIDINE: 2-CARBETHOXY-3-AMINO-4-(4-METHYLPHENYL)-6-PHENYLTHIENO[2,3-B] PYRIDINE

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Thieno[2,3-b]pyridines are isosteres of isoquinoline.Some of the thienopyridine show an important biological properties such as antimicrobial, antihypertensive, antidiabetic etc. and interesting biological activities of these compounds are also observed in nature. Therefore to correlate the structure-function relationship, crystal and molecular structure of 2-carbethoxy-3-amino-4-(4-methylphenyl)-6-phenyl thieno[2,3-b]pyridine is determined. The compound crystallizes in a monoclinic system having a space group $P2_1/c$. The crystal parameters are: a = 9.200(3), b = 22.465(5), c = 9.708(3)Å, β = 94.06(3)°, Z= 4, V = 2001.4(1) Å^3, ρ_c = 1.289 Mg m^{-3}, μ = 0.183 mm^{-1}. Final residual index is 0.0586 for 3513 unique reflections. Thiophene ring is coplanar with pyridine ring plane. One of the phenyl ring is almost coplanar with pyridine ring having dihedral angle 5.18(22)° whereas other one is inclined at 69.64(12)° to the pyridine ring plane. As usual in heterocyclic compounds, the structure is mainly stabilized due to weak van der Waal Interactions.

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CRYSTAL STRUCTURE OF AN "EXTERNAL" FUNTIONAL UNIT FROM *Rapana thomasiana* HEMOCYANIN

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Rapana thomasiana hemocyanin is a representative of giant molluscan (gastropodan) dioxygen-transporting proteins. The cylindrical hemocyanin aggregates are composed of two structural subunits, RHSS1 and RHSS2. The 420 kDa subunit RHSS2 contains eight 50-55 kDa functional units. Each unit has a single dioxygen-binding dinuclear copper-containing active site. Molluscan hemocyanin functional units can be subdivided into "internal units", forming the so called "arch" inside the hemocyanin cylinders, and "external" units, building the cylinder wall of the aggregates. The "external" oxygenated functional unit RtH2-e of the *Rapana* hemocyanin subunit RHSS2 was isolated and crystallized. Intensity data were collected to 3.3 Å at 120 K using synchrotron radiation. Molecular replacement calculation with the "internal" subunit Odg from *Octopus dofleini* as the search model led to satisfactory structure solution with three molecules per asymmetric unit.

Refinement and model building, currently at an R-factor of 0.25 (R_{free} of 0.33) are still in progress. Interestingly some kind of molecular self-assembly can be observed by the crystal structure. The monomers interact in a "head to tail" manner and are stabilised by intermolecular interactions revealing a non-crystallographic trimer. Furthermore two trimers are related by a crystallographic two-fold axis. As a result regular hexameric cylinders are the repeating component in the crystal structure.

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STRUCTURE OF THE BINDING DOMAIN OF TETANUS NEUROTOXIN IN COMPLEX WITH DOXORUBICIN

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Clostridial neurotoxins comprising the seven serotypes of botulinum neurotoxin and the tetanus toxin are so far the most potent neurotoxins known to affect humans. They cause spastic and flaccid paralysis in humans. Biochemical, electrospray ionization mass spectroscopy (ESI-MS) and computation docking studies have shown that doxorubicin, a well- known DNA intercalater, binds to these neurotoxins. Here we present the crystal structure of the C-fragment of tetanus toxin complexed with doxorubicin to identify the binding site for the drug and its interaction with the protein molecule. The crystals of the complex were prepared by soaking native crystals in the mother liquor containing doxorubicin. X-ray diffraction data were collected at the liquid nitrogen temperature at the National Synchrotron Light Source, Brookhaven National Laboratory. The drug molecule was identified from the difference Fourier map and the structure was refined using CNS until convergence. Doxorubicin binds in a site that has been identified as the binding site for gangliosides. Doxorubicin stacks against the conserved residue Trp 1289 and interacts with another conserved residue, His 1271. Results from this study and their implications in drug design will be discussed.

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A6-60

INTER ATOMIC CONTACTS IN CRYSTALS OF VIRAL CAPSIDS

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Spherical viral capsids possess icosahedral symmetry and are made of a large number of protein subunits, each subunit consisting of thousands of atoms. When crystallized, the capsids pack densely resulting in a large number of close interactions between atoms of neighboring virus particles. The contacts between atoms of protein subunits within a virus particle are important for understanding the forces responsible for the integrity of virus particles. Similarly, interactions between virus particles are also of much interest. However, evaluation of the distance between several hundred thousand atoms of one virus particle and those of another is a non-trivial computational task. A method based on representing the three dimensional shape of the virus particle as a binary map allows this computation to be accomplished with minimal computational requirements. This representation could be of some general interest in the examination of the spatial relation of three-dimensional objects.

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A6-61

STRUCURE OF A TERNARY COMPLEX OF TRYPSIN WITH BENZAMIDINE AND A NATURAL INHIBITOR AT ATOMIC RESOLUTION

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Proteases are a group of abundant enzymes serving a variety of different functions in the living organisms. Mechanistically, they can be subdivided into four different groups: serine, aspartic, thiol and metalloproteases. Trypsin is a serine protease involved in digestion. The catalytic triad in trypsin comprises Asp102, His57 and Ser195, which are interconnected via hydrogen bonds. In order to understand the functional mechanism precisely, the structures of macromolecules at atomic resolution are required. Refinement of such structures routinely incorporates the refinement of anisotropic temperature factors which aid in the delineation of loop motions and far ranging disorder. The recognition of hydrogen atoms and the identification of the protonation states and the disposition of hydrogen atoms is critical to further our understanding of structure and function of enzymes. The trypsin was cocrystallized with benzamidine and a designed synthetic inhibitor. The crystals belong to trigonal space group $P3_221$ with a=b=68.55, c=73.33Å and diffract to 0.97Å resolution. The asymmetric unit contains 1 trypsin molecule, 449 water molecules, 1 calcium ion, 1 benzamidine molecule, 1 ethane sulfonic acid, 1 glycerol molecule, two molecules of the inhibitor and 1603 H-atoms. The structure has been refined to an R-factor of 13.4% (R_{free}=17.9%). The two molecules of the inhibitor completely saturate the binding site and also interact directly with O^{γ} of Ser195 and $N^{\epsilon 2}$ of His57. The molecules of benzamidine are held on the surface and fill the interstitial sites. There are clear electron density peaks for the hydrogen atoms associated with the O^{γ} of Ser195 and $N^{\delta 1}$ of His57.

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A6-62

CRYSTAL STRUCTURE OF A MANNOSE-SPECIFIC LECTIN, CONCANAVALIN A BOUND TO A PORPHYRIN, *meso*-TETRASULPHONATOPHENYLPORPHYRIN.

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Concanavalin A (ConA) is an extensively studied plant lectin, known to bind to mannose rich complex carbohydrates. Recently ConA was reported to bind a variety of porphyrins. In the present study, the crystal structure of Concanavalin A complexed with *meso*-tetrasulphonatophenylporphyrin (H_2TPPS) was determined at 1.9 Å resolution. The crystals obtained belong to space group F222 with cell dimensions of 106.0, 117.3 and 126.0 Å. The sulphonatophenyl group of the H_2TPPS molecule occupies the same binding site on ConA as that of methyl α-D-mannopyranoside, a natural ligand. A pair of stacked porphyrin molecules stabilizes the crystal structure by end-to-end cross-linking with ConA. This crosslinking of lectin brought about by non-covalent interactions is similar to that observed in other lectins in complex with various biantennary carbohydrate or glycopeptide ligands. The porphyrin binds to ConA predominantly through hydrogen bonds and water-mediated interactions. Comparison of the crystal structure of ConA in complex with methyl α-D-mannopyranoside and H_2TPPS shows excellent equivalence of interactions. Seven of the eight hydrogen bonds observed between methyl α-D-mannopyranoside and ConA are mimicked by the sulphonatophenyl group of porphyrin after incorporating two water molecules.

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STRUCTURE OF THE 20S PROTEASOME FROM BOVINE LIVER AT 2.75 Å RESOLUTION

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Proteasome has a molecular weight of 750 kDa and sedimentation coefficient of approximately 20S. It is composed of two copies of hetero-heptamerα-type subunits and β-type subunits, $(\alpha 1\text{-}7\,\beta 1\text{-}7)^2$ in eukaryotic cells, and otherwise homo-heptamer of identical α - and β -type subunits, $(\alpha\ 7\,\beta\ 7)^2$ in prokaryotic cells. In mammalian cells, three additional non-essential subunits of the 20S proteasome, LMP2, LMP7 and MECL1 can replace constitutive components upon induction by the T-cell-derived antiviral cytokine interferon-γ. It is known that mammalian proteasome is involved in generating antigen peptide that is presented by class I MHC molecule.

We determined the structure of 20S proteasome from bovine liver at 2.75 Å resolution using the molecular replacement method with the structure of yeast 20S proteasome as a search model. The electron density map was interpretable without any collision in the orthorhombic crystal lattice. Model building and structure refinement have been completed. We found a putative new active site that was different from yeast proteasome.

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STRUCTURE AND DYNAMICS OF THE CENTRAL STALK IN ATP SYNTHASE: LARGE CONFORMATIONAL CHANGES IN THE ε-SUBUNIT REGULATE THIS ROTARY MOTOR ENZYME VIA A RATCHET MECHANISM

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F_0F_1 ATP synthases utilize energy from a transmembrane proton gradient to synthesise ATP in bacteria, mitochondria and chloroplasts. In bacteria, the enzyme can hydrolyse ATP to generate a proton gradient (Senior, 1990). Previous studies had established that the central stalk, made of the γ and ε subunits in the F_1 part and c subunit ring in the F_0 part, rotates relative to a stator composed of $\alpha_3\beta_3\delta ab_2$ during ATP hydrolysis and synthesis. How this rotation is regulated has been less clear. Here we show that the ε subunit plays a key role by acting as a switch of this motor enzyme.

Two different arrangements of the ε subunit have been visualized recently. The first has been observed in beef heart mitochondrial F_1-ATPase where the C-terminal portion is arranged as a two α–helix hairpin structure, which extends away from the $\alpha_3\beta_3$ region, and toward the position of the c subunit ring in the intact F_1F_0 (Gibbons *et al.*, 2000). The second arrangement was observed in the structure of a complex of the γ and ε subunits of the *E. coli* F_1-ATPase (Rodgers and Wilce, 2000). In this, the two C-terminal helices are apart and extend along the γ to interact with the α and β subunits in the intact complex.

We have been able to trap these two arrangements by cross-linking after introducing appropriate Cys residues in *E. coli* F_1F_0, confirming that both conformations of the ε subunit exist in the enzyme complex. With the C-terminal domain of ε toward the F_0, ATP hydrolysis is activated but the enzyme is fully coupled in both ATP hydrolysis and synthesis. With the C-terminal domain toward the F_1 part, ATP hydrolysis is inhibited and yet the enzyme is fully functional in ATP synthesis, i.e. it works in one direction only. These results help explain the inhibitory action of the ε subunit in the F_1F_0 complex and argue for a ratchet function of this subunit.

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A6-65

TWO ALTERNATE FACES OF METHOXYLATED CYTOSINE RESIDUES FOR PAIRING WITH G AND A IN THE WATSON-CRICK GEOMETRY, LEADING TO PURINE TRANSITION MUTAGENESIS,

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Methoxyamine is known to be a potent mutagen, which attacks cytosine moiety to produce N^4-methoxycytosine (mo^4C). This chemical modification induces purine transition (A<--->G) during DNA replication. The DNA polymerase accepts only the Watson-Crick base pairs in *B*-form DNA. To investigate the interaction property of mo^4C residues in *B*-form DNA, crystal structures of DNA dodecamers with the sequences d(CGCXAATTmo^4CGCG), (X=A and G) have been X-ray analyzed. In either dodecamer, the oligonucleotides are associated to form a B-form duplex. In the dodecamer with X=G, electron density maps show that one of the two mo^4C residues is in the *amino* tautomeric state with an *anti* methoxy group forms a canonical Watson-Crick base pair with the guanine residue of the opposite strand, and that the other mo^4C residue is in the *imino* tautomeric state with a *syn* methoxy group and forms a base pair with the guanine residue in the wobbled geometry. While in the case of X=A, the mo^4C residues are in the *imino* tautomeric state with an *anti* conformation form pairs with adenine residues at the two sites. The pairing geometry is very similar to the Watson-Crick type. Based on these interaction geometry, two routes for purine transition mechanism have been proposed.

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EXPRESSION, PURIFICATION, CRYSTALLIZATION AND X-RAY STRUCTURE OF HETERODIMER OF HIV-1 PROTEASE

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An alternative strategy to small molecule inhibitors that target the active site of HIV-1 protease, is to engineer a molecule that disrupts the dimerisation of the protease. Such a strategy is going to be more immune to the problem of drug resistance mutations. 3-D structure of hetrodimers are shown to be important for the design of such a molecule. Heterodimer of HIV-1 protease containing C95M mutation on first monomer and C95A mutaion on the second monomer was overexpressed in the E Coli strain BL21 DE(3) pLysS and the protein was extracted and purified for crystallization. Crystals were obtained by hanging drop vapor diffusion method with reservoir containing ammonium sulfate in phosphate citrate buffer. The crystals diffracted to 2.1 Å resolution on our Rigaku x-ray generator R-AXIS IIC image plate detector system. 44 oscillation frames were collected with 1° oscillation. The data was processed using DENZO and unit cell dimensions were found to be a=b=61.06 Å and c=83.42 Å. Scaling was done by SCALEPACK and the R_{merge} was 7.9% in the space grooup $P6_1$. Completeness of the data was 93.5%. The structure was refined to 2.1 Å resolution using XPLOR 3.8 and CNS 1.0 to a R-factor of 19.5% and R-free of 25.5%. Some of the interesting features of this structure: 1) two flaps in this unliganded structure are closed, 2) one water molecule hydrogen bonds to carboxyl groups of both Asp^{25} and Asp^{1025}, 3) the environment around the mutation site is not significantly altered and 4) the main chain segment containing active site aspartyl residues Asp^{25} and Asp^{1025} along with the bound water has moved by ~0.5 Å in a direction that would render this side chain and the catalytic water more accessible to the substrate. This may explain why this mutant is more active during refolding step.

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A6-67

SYNTHESIS OF N-NITRASO PIPERIDINE THIOSEMICARBAZONE DERIVATIVES

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N-substituted nitraso group in piperidine derivatives possesses high carcinogenic activity in the biological system. A number of N-nitraso piperidine thiosemicarbazone derivatives have been synthesized and the level of carcinogenicity depends on the substitution in various positions of the piperidine ring. The derivatives are synthesized by Mannich condensation reaction by different amines, aldehydes and ketones at 1: 2: 1 ratio. The second step of the reaction was carried out with 0.01 M of piperidine-4-one with equal mole of nitrous acid in suitable condition. The product N-nitraso piperidine-4-one was then reacts with 0.01M of thisemicarbazide in alcohol medium. The white colour solids obtained was crystallized in ethanol.

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PRELIMINARY CRYSTALLISATION STUDIES ON OUTER MEMBRANE PROTEIN C (OmpC) - LACTOFERRIN (Lf) COMPLEX.

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OmpC (Trimer, MW 120 kD) an immunologically important integral membrane protein implicated in virulence of *S.typhi* is being crystallized in our lab. Lactoferrin (Lf, MW 80 kD) an iron binding bacteriostatic protein is found to bind specifically to OmpC from *S.typhi* and *E.coli*. Structural analysis of this protein complex will help to understand the mechanism by which Lf damages cell membrane and exerts its antibacterial activity. Initial crystallisation trials (designed using CRYSTOOL program) on this protein complex were carried out using Microdialysis, Vapour diffusion-Sitting Drop methods. Detergent combination of Octyl PoE with C_8E_4/C_8HESO/$C_{12}E_9$ /OTG/OG /LDAO/ CYMAL5 at cmc gave small plates, needle cluster and rod shaped crystals with precipitant combinations of PEG 400/1000/1500/2000 and $(NH_4)_2SO_4$. Cationic additive ammoniums, potassium, sodium, guanidium in combination with anions like nitrate, chloride, iodide, thiocyanate, tartarate were found to be promising. The interaction between these two proteins is clearly demonstrated on SDS-PAGE and protein complex was recognised by anti-porin monoclonals in Western blot. SPRIA studies show low percentage binding between OmpC and iodinated-Lf. Further studies are being carried out to refine conditions for getting diffraction quality crystals.

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A6-69

CRYSTAL STRUCTURE OF RIBOSOME RECYCLING FACTOR WITH DIFFERENT DETERGENTS FROM ESCHERICHIA COLI

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Ribosome recycling factor (RRF) is required for ribosome disassembly after the termination of translation. RRF is an open L-shaped molecule composed of two domains. Domain I has three alpha helices and the domain II consists of one alpha helix and six beta strands. RRF is regarded as a good target for antibacterial drug development, because it is essential for bacterial growth. Inhibitors of RRF targeted to the contact region between RRF and its counterts can be candidates for designing a novel compound with antibacterial activity. A small molecule bound to the hydrophobic cleft may also inhibit RRF activity by preventing the domain movement that could be important for the role of RRF. Domain movements found in tRNA and EF-G have been suggested to be necessary for their binding to the ribosomal A-site. Therefore we took up the task of determining the crystal structure of RRF with different detergents. Five different detergents which are confirmed to interact with RRF were used for crystallization of complexes. Diffraction data from the complexes were collected at beamline PL6B (Wavelength = 1.00875 Å) using MacScience 2030b image plate detector at Pohang Accelerator Laboratory. The data were processed and integrated by DENZO and scaled by SCALEPACK in HKL program suite. The crystals belong to the space group P3(1)21. It is found that only one molecule is present in the asymmetric unit. The rigid body refinement followed by simulated annealing and temperature refinement was performed with the program CNS. The analysis of the interaction between detergents and residues in the cleft of RRF could be useful for designing a novel compound as a RRF inhibitor.

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A6-70

CRYSTAL STRUCTURES OF THE COMPLEXES OF L-ARGININE AND L-HISTIDINE WITH GLUTARIC ACID AND A COMPARATIVE STUDY OF AMINO ACID-GLUTARIC ACID COMPLEXES.

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X-ray analysis of crystalline complexes involving amino acids and peptides with carboxylic acids, which are believed to have existed in the prebiotic milieu, has served to understand a variety of biomolecular interactions and aggregation patterns. Complexes of glutaric acid with L-arginine and L-histidine (2 forms) have been prepared and analysed. These three complexes exhibit different stoichiometries and ionization states. Interestingly, and indeed surprisingly, the structure of L-arginine hemiglutarate monohydrate is nearly identical to that of DL-arginine acetate monohydrate and DL-arginine formate dihydrate. DL-arginine succinate shares some important features with all the three arginine complexes. The histidine ribbons in form I of the histidine complex are also found to occur in L-histidine semisuccinate, again emphasising the relative invariance of some elementary patterns of amino acid aggregation. While the structures of the L-arginine complex and form I of the L-histidine complex emphasize the relatively invariant feautures of amino acid aggregation, form II of the histidine complex illustrates their variability. The variability in the ionization state and stoichiometry observed in these and other amino acid-dicarboxylic acid complexes appears to represent subtle differences in the response of a molecule to the presence of another type of molecule in its neighbourhood. The change in the chirality of the component molecules in the complex could lead to drastic changes in the aggregation pattern; alternatively, the effects of the change are accommodated through small adjustments in essentially the same pattern.

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STRUCTURAL STUDIES ON *Mycobacterium tuberculosis* RECA COMPLEXED WITH ADP AND ATP-γ-S.

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RecA protein plays a crucial role in homologous recombination and repair of DNA. All activities of the RecA protein require Mg^{+2} –ATP and single stranded DNA. We have recently solved the crystal structures of RecA from *M.tuberculosis* in its apo form as well as a complex with ADP-AlF_4. Analysis of these structures revealed the expansion of the P-loop region in MtRecA compared to its homologue in *E.coli*, which explained the reduced affinity of MtRecA for ATP. The bundle formation was also found to be weaker in MtRecA, than in *E.coli* RecA, which may have implications for recombination in mycobacteria. Here we report crystal structures of MtRecA into which ADP was soaked and that of a co-crystallized complex with ATP-γ-S. Comparison of all the three ligand bound structures with the apo MtRecA structure reveals the rigidity of the nucleotide binding pocket as well as the interactions crucial for nucleotide binding. Unlike the consensus residues of the P-loop, Gln195, a residue of the DNA binding loop L2, shows significant variation in conformation. In the ATP-γ-S complex, the binding site of the thiophosphate moiety is very close to the AlF4 moiety in MtRecA-ADP-AlF_4 complex, confirming it to be the terminal phosphate binding site in the RecA protein. The orientation of the nucleotide in all three ligand bound structures is similar, implying that there is no major change in the mode of binding of ADP and ATP.

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LACTOFERRIN - MELANIN INTERACTION AND ITS POSSIBLE IMPLICATIONS IN MELANIN POLYMERIZATION: CRYSTAL STRUCTURE OF THE COMPLEX FORMED BETWEEN MARE LACTOFERRIN AND MELANIN MONOMERS AT 2.7Å RESOLUTION

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The concentration of melanin determines the intensity of colours of the skin and hair of animals. Melanin pigments are tyrosine-based polymers formed in melanocytes within specialized organelles called melanosomes. In order to understand the mechanism of melanin polymerization, lactoferrin, a basic protein with a pI value of 9.0 was used to produce melanin. Lactoferrin is a monomeric iron binding protein with a molecular weight of 80 kDa. The crystals of lactoferrin were soaked in a solution containing dihydroxy phenylalanine (DOPA) and tyrosinase enzyme. These crystals were used for X-ray intensity data collection. The intensity data were collected to 2.7Å resolution to an overall completeness of 91% with an R_{sym} of 0.071. The crystals belong to orthorhombic space group $P2_12_12_1$ with cell dimensions: a = 85.0Å, b = 99.8Å, c = 103.4Å. The structure was determined by molecular replacement method using the model of native mare lactoferrin and refined to an R factor 0.215 (R_{free} = 0.287) for all the data to 2.7Å resolution. The final model comprises 5281 protein atoms from 689 amino acids, $2Fe^{3+}$, $2CO_3^{2-}$ ions, 2 Indole -5,6-quinone molecules (IQ) and 73 water molecules. Two IQ molecules, one in each lobe bind to lactoferrin. In the C-lobe, the IQ binds in the iron binding cleft whereas in the N-lobe, it is located in the side pocket between two α-helices which is filled with solvent molecules in the native iron-saturated mare lactoferrin. The IQ molecules interact with protein molecule mainly through glutamic acid in both lobes without significant perturbation to the protein structure. The orientation of N- and C-lobes in the present structure is similar to that observed in the native iron saturated protein. However, as a result of the binding of IQ molecules, the orientations of the domains N1, N2 and C1, C2 in the two cases differ slightly as compared to those observed in the native diferric protein.

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PRELIMINARY X-RAY CRYSTALLOGRAPHY STUDIES OF A NOVEL PTKs BINDING PROTEIN

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We have identified a novel gene from screening the human cDNA library. Sequence analysis suggests the protein encoded by this novel gene may belong to a new adaptor protein family. Proteins of this family are known to interact with PTKs. The overexpression of this protein decreases the growth rate in k562 cell, thus suggesting that it is related to cancer regulation and may be a regulator of MAP kinase and cell proliferation.

Homology analysis showed PTKs binding domain of this protein is a key in understanding its function. It involves in the formation of a multimolecular signaling complex in signal transduction. We cloned the PTKs binding domain of this protein within GST vector. It was expressed as a GST fusion protein in *E. coli* strain BL21 and isolated by glutathion-agarose affinity chromatography. The PTKs binding domain protein was obtained by cleaving the eluted fusion protein with bovine thrombin and further purified by resource Q anion exchange and Gel filtration Superdex G75 chromatography. The crystal was obtained by vapor diffusion in hanging drops. Crystal grows to a typical size in about 1 day. The aim of our study is to elucidate the structure of the PTKs binding domain of this protein and to further understand its function by X-ray crystallography.

A6-74

NEW MECHANIC INSIGHTS REVEALED BY STRUCTURE ANALYSIS OF THE DIOL DEHYDRATASE COBALAMIN COMPLEXES

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We have carried out the structural studies of diol dehydratase-cobalamin complexes, and described the exact details of enzyme-coenzyme interaction of the adenine moiety. In the course of these studies, we also found that the electron density corresponding to the cyano group of the enzyme-bound cyanocobalamin is almost not observable at room temperature and very low even at cryogenic temperature, suggesting its disscociation from the cobalt atom upon X-ray irradiation. On the contrary, the adenine moiety of the enzyme-bound adeninylpentylcobalamin was clearly located in the map. When the enzyme-adeninylpentylcobalamin complex was illuminated with visible light, the electron density between the 5'-carbon and cobalt atoms disappeared, and the temperature factors of the atoms comprising the pentamethylene group became much larger than those in the dark. This indicates the cobalt-carbon bond cleavage and suggests that the adenine moiety remains held by hydrogen bonds with some residues in the enzyme. Thus, the formation of an adenine-anchored radical upon illumination was demonstrated crystallographically with this complex. These observations clearly indicate that homolysis of the cobalt-carbon of alkylcobalamin takes place upon illumination with visible light but not readily cleaved during X-ray irradiation.

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A6-75

HYDROGEN BONDING PATTERNS IN AMINOPYRIMIDINE - CARBOXYLATE COMPLEXES, AN OVERVIEW

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Hydrogen bonding patterns play vital roles in various biomolecular recognition processes and interactions. Aminopyrimidine-carboxylate interactions are involved in Protein-nucleic acid recognition, enzyme-drug binding, etc. As simple models for these interactions a number of aminopyrimidine-carboxylates have been investigated by X-rays in our laboratory (for examples Ref. 1-3). These results will be presented along with some examples retrieved from the literature.

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HYDROGEN BONDING PATTERNS IN TRIMETHOPRIM SULPHATE TRIHYDRATE [$(TMPH^+)_2 (SO_4)^{2-}$, $TMPH^+$ = TRIMETHOPRIM CATION]

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Trimethoprim [2,4-diamino-5-(3',4',5'-trimethoxybenzyl)pyrimidine] is an antibacterial agent. In its N1-protonated form, it inhibits the bacterial DHFR (dihydrofolate reductase). The present study has been undertaken to explore the conformation and the hydrogen bonding patterns of trimethoprim in a variety of molecular environments. Hydrogen bonding patterns involving sulphate ion in biological systems are of current interest[1]. In this structure, two crystallographically independent trimethoprim cations are paired through a pair of N2-H...N3 hydrogen bonds. These pairs are further bridged by hydrogen bonds involving water molecules and sulphate ions. The details of hydrogen bonding networks and the conformation of the drug will be presented.

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A6-77

DISSECTING PROTEIN-PROTEIN RECOGNITION SITES

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Protein-protein recognition sites in 70 complexes of known three-dimensional structure are dissected in a set of surface patches by clustering atoms at the protein-protein interface. In complexes where the interface buries less than 2000 $Å^2$ of protein surface, recognition sites usually form a single patch on the surface of each component protein, whereas larger interfaces are multi-patch. In multi-patch interfaces, there is at least one pair of patches that are equivalent in size to a single-patch interface. Each recognition site, or patch within it, contains a core made of buried interface atoms, surrounded by a rim of atoms that remain accessible to solvent in the complex. The rim is similar to the rest of the protein surface, but the core has a distinctive amino acid composition, which may help in identifying potential protein recognition sites on single proteins of known structures.

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A6-78

PURIFICATION AND CRYSTALLOGRAPHIC STUDIES ON A CHICKEN SERUM TRANSFERRIN

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Proteins of the transferrin family which include Serum transferrin, Ovotransferrin and lactoferrin play a key role in controlling the levels of iron in the vertebrate body fluids. Serum transferrin specifically acts as an iron transporter, delivering bound iron to target cells via receptor mediated endocytosis. Chicken Serum transferrin from the blood Serum of ovulating white leghorn has been isolated and purified in our laboratory and crystals of both the the apo- and holo- forms have been obtained. The former crystals belong to the tetragonal space group $P4_32_12$ with unit cell parameters a=b=96.2, c=180.2 Å. From maps calculated using a 3.85 Å cryo data set, the Cα chain could be traced. Crystals of the holo- form were found to belong to a primitive monoclinic space group with cell dimensions a=73.1, b=59.2, c=84.0 Å, γ=97.4°. Preliminary X-ray analyses will be reported.

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A6-79

STRUCTURAL STUDIES ON MODIFIED CYTOSINE RESTRICTION ENDONUCLEASE A FROM *E. coli* K-12.

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Modified cytosine restriction endonuclease A (McrA) (MW 31 kD) is encoded by the e14 prophage element found in *E.coli* K12 genome. The protein restricts entry of T-even (gt) phages by restricting hydroxymethylated, non-glucosylated DNA. It also cleaves DNA methylated by methylases like HpaII and SssI. The protein is reported to be localised on the membrane.

We used the recombinant over expressed full-length (McrA31) protein; an N-terminally modified construct (McrA29) and the N-terminal His tagged (McrA6H) protein. The protein was purified using different column chromatography techniques in each case. The protein was seen to form soluble oligomeric aggregates, which do not disassociate even in the presence of Urea and disassociate only in the presence of SDS. The C-terminal region contains a HNH motif identified as involved in DNA binding and contains 4 of the 7 cysteines in the protein. A C-terminal deletion construct was made. However, this also showed aggregation. There is a hydrophobic stretch in McrA in the N-terminal region. A recombinant protein with the hydrophobic region deleted was constructed. Initial studies on this protein suggest that this also tends to show similar oligomeric aggregation. Circular dichroism studies suggest that McrA is $\alpha + \beta$ protein. The structure shows high temperature stability. The β component of the structure is resistant to denaturation with 8M urea. Experiments with $\alpha^{32}P$ labeled ATP suggest that the protein bind ATP. Crystallization conditions were screened for McrA using a Sparse Matrix screen using the sitting drop vapour diffusion technique in crystal clear strips. The refined crystallisation conditions showed improved crystal habit in the presence of ATP. The crystals obtained have characteristics similar to protein crystals. However, high-resolution diffraction spots as from salt crystals dominate the diffraction pattern. The structural studies and crystallisation trials of McrA will be reported.

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STRUCTURAL INVESTIGATION OF 1α,3αDIHYDROXYAZADIRACHTOL ISOLATED FROM NEEM KERNELS

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Azadirachtins belong to a class of highly oxidised tetranortriterpenoids characteristic of the genera *Azadirachta* and *Melia*. Among the azadirachtins, Azadirachtin-A is the highly potent antifeedant even at low concentration against over 200 agricultural pests and is also ecofriendly. One such azadirachtin, 1α,3αdihydroxyazadirachtol was isolated from ethanolic extract of neem kernels. The chemical structure was assigned based on1D and 2D NMR data. The structure was unequivocally established by single crystal X-ray diffraction studies. The compound was crystallized by hanging drop vapour diffusion technique in $P2_12_12_1$ with cell parameters a=14.142(6) Å, b=17.287(3) Å, c=21.505(4) Å. The structure was solved by SHELXS 97 and refined by SHELXL 97. The solution revealed two molecules in the asymmetric unit. The two molecules were held together by hydrogen bonds and they differed predominantly in the orientation of the functional groups attached to them. The relative orientation of the two moieties namely decalin and dihyrofuranyl moiety, is similar to that observed for azadirachtins H & I. The antifeedant activity of this compound is 6 times that of Azadirachtin-A against 3rd instar larvae of *Spodoptera litura* (tobacco cut worm). A comparative study with other azadirachtins will be presented.

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A6-81

PURIFICATION, AND CHARACTERIZATION OF CATECHIN OXYGENASE FROM ACINETOBACTER CALCOACETICUS

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Acinetobactor calcoaceticus is a bacterium that grows on the surface of liquids of tannery pits and tannery waste and oxidize tannin. An enzyme found in *Acinetobacter calcoaceticus* cleaved catechin by oxygenation. The protein has been expressed in *Escherichia Coli* and purified to homogeneity. The preliminary characterization shows that the enzyme was active in a pH range 2 to 8 and at 50°C. Enzyme activity was maximum at pH 7.0. Further, the Km value of the enzyme was 4 x10-7 moles per liter with catechin as substrate and the molecular weight was 47KDa.

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CRYSTAL AND MOLECULAR STRUCTURE OF β-[(1-PHENYL)-1-YLOXY]-α-(1,1-DIMETHYLETHYL)-1H-1,2,4 TRIAZOLE –1 –ETHANOL.

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The Crystals of the title compound were grown from its solution in Toluene at room temperature. The compound is a systemic fungicide and we are trying to establish a relationship between the structure and its activity. The crystal data are : $C_{10}H_{16}NO_3$, a=7.8651(3)Å , b = 13.1227(4) Å, c = 15.1304(5) Å, β=101.7550(10)°, $P2_1/c$, V = 1528.88(9) $Å^3$, Z= 4, μ = 0.082, radiation used MoKα. The three- dimensional intensity data were collected on an Enraf-Nonius CAD –4 diffractometer. The structure was solved by direct methods using SHELXL-97 using full matrix least square refinement . Final R =5.7% and wR= 8.2% for 10655 observed reflections with I > 2.0σ)1). Molecules are held together by Hydrogen bonds. The complete structural details will be presented.

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CONFORMATIONAL CHARECTERISTICS OF PEPTIDES CONTAINING GLYCYL RESIDUES: X-RAY CRYSTALLOGRAPHIC STUDY AND CRYSTALLOGRAPHIC DATABASE ANALYSIS.

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Structural studies of short oligopeptides and analysis on conformation of the same oligopeptide sequences in protein structures leads to a better understanding of the relationship between amino acid sequences and polypeptide chain conformation. This is very crucial in the *de novo* design of peptide mimics for defined structural motifs. We present the crystal structure of the tripeptide Z-Gly-Gly-Val and analysis of the conformation of the tripeptide sequence in protein structures and Gly-Gly segment in peptide structures. The tripeptide crystallizes from CH_3OH/H_2O mixture in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit. The structure has been solved by direct methods and refined using least squares technique. The molecule takes an extended conformation with antiparallel β-sheet hydrogen bonding motif, in contrast to the type III β-turn conformation of unprotected Gly-Gly-Val, already reported. An analysis of the conformations taken by Gly-Gly-Val segment in proteins, using PDB, revealed that the glycines have a very high propensity for loops (72% and 67.7% respectively for Gly(1) and Gly(2)) whereas the valine residue has almost equal propensities for loops and β-sheets (34.4% and 36.6% respectively) with only a slightly less propensity for helices(25.8%). Only in 12.9% of the cases are all the three residues seen in helices. Our analysis of the peptide crystal structures containing the Gly-Gly doublets taken from the CSD revealed that conformation of the glycines are similar to those in proteins. Details of the structure of Z-Gly-Gly-Val and the results of database analyses will be presented.

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A6-84

CRYSTAL STRUCTURE OF FIRST ACIDIC PHOSPHOLIPASE A2 FROM COBRA (*Naja naja sagittifera*) VENOM AT 2.1 Å RESOLUTION

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Phospholipase A2 (PLA_2) hydrolyzes the sn-2 ester of phospholipids, preferably in lamellar or micellar aggregates. PLA_2 plays a part in a number of physiologically important cellular processes such as inflammation, blood platelet aggregation and acute hypersensitivity. These processes are all initiated by the release of arachidonic acid from cell membrane, which is catalyzed by intracellular PLA_2s and followed by conversion of arachidonic acid to prostaglandins, leukotrienes or thromboxanes. An imbalance in the production of these compounds can lead to chronic inflammatory diseases such as rheumatoid arthritis and asthma. Therefore structural information about PLA2s is necessary in the design of therapeutic drugs. Here, we report the crystal structure of an acidic PLA_2 from the venom of *Naja naja sagittifera* (nns). The purified PLA_2 was crystallized by vapour diffusion with a protein concentration of 2.5 mg/ml in 10 mM phosphate buffer containing 40% ethanol. The crystals belong to tetragonal space group $P4_1$ with a=b=42.8 Å, c=65.8Å. The structure has been refined to an R-factor of 0.192(R_{free} =0.220). The structural features of acidic PLA_2 corresponding to various functional loop regions including the C-terminal fragment are very different from those observed in other PLA_2 of group I. It implies considerable function differences between this and other group I PLA2s. Further datails will be discussed.

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A6-85

CONSEQUENCES OF CHANGE OF CHIRALITY, ON THE ASSOCIATION OF HELICES OF AN APOLAR HELICAL HAIRPIN MOTIF.

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Design of helical super secondary structural motifs is expected to provide important scaffolds to incorporate functional sites, thus allowing the engineering of novel miniproteins with function. We have recently studied the helical hairpin motif (PNAS, 98, 870-874, 2001), where we have observed that helices of opposite handedness are associated through an extensive network of side-chain backbone C-HΛO interactions. In order to study the consequences of change of chirality, on the association of helices, we have replaced the D-Ala residues to L-Ala in the sequence Acetyl-Gly-ΔPhe-(D-Ala-ΔPhe-ΔPhe)$_2$-D-Ala-(Gly)$_4$-ΔPhe-(L-Ala-L-Leu-ΔPhe)$_2$ -L-Ala-NHMe. The peptide of length 21 residues was synthesized and crystallized. The data collection was done at Brookhaven National Laboratory U.S.A, using synchrotron radiation. The crystal belongs to monoclinic system. Space group C2, with the unit cell parameters as a = 46.651Å, b= 20.987Å, c = 14.449Å and β = 94.662°. The structure solution was obtained by Direct Methods using SnB (Shake and Bake) program. The R-factor at present stage of refinement is 16.84%. All the residues including (Gly)$_4$ linker were clearly seen. The molecule still folds into helix turn helix motif wherein both the helices are right handed 3_{10} helices, but the nature of association is different from earlier. The two helices are associated through the wedge into groove type. The (Gly)$_4$ flexible linker appears to be optimal for the association. The structure will be compared with that of the earlier HTH motif.

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TOWARDS STRUCTURAL STUDIES ON COMPLEXES OF THE OUTER MEMBRANE PROTEIN OmpC WITH ANTIPORIN ANTIBODIES

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The homotrimeric (M.W. 120 kD) outer member protein OmpC from *S.typhi* is an immunologically important porin. Large amounts of antibodies to porin are found in the sera of patients with typhoid, caused by *S.typhi*. The structurally homologous 16 stranded beta barrel trimeric porins primarily differ in the size and nature of the loops. Structural studies and crystallisation of *S.typhi* OmpC have been carried out earlier by our group. However, the crystal diffracted to low resolution. Fab mediated co-crystallisation will help in increasing the polar surfaces, which helps in better ordering of the lattice. Moreover, the structure of the complex between Fab and porin will help the understanding the recognition process.

Three monoclonal antibodies viz. MPN5 (IgG2b), MP1 (IgG2a) which are salmonella porin specific and P7D8 (IgG2a) Enterobacterial porin specific were available for this study. The antibodies are purified using affinity chromatography and ammonium sulfate precipitation followed by ion exchange chromatography. The purified antibodies were subjected to papain digestion and the Fab fragment was obtained. The Fab fragments were used for the crystallisation screens. Binding studies were also done by our group with the same antibodies to *S.typhi* OmpC and found that P7D8 binding was stronger than MPN5. It was found that MPN5 binds at a pH around 5.0 and P7D8 around 9.0. The purification, crystallisation of Fab and the binding studies of the two antibodies (MPN5 & P7D8) will be reported.

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POLYPEPTIDE CHAIN REVERSAL MEDIATED BY C-H···O HYDROGEN BONDS AT HELIX TERMINI.

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The site-specific insertion of D-amino acids into all L-peptide sequences provides a convenient means for controlling polypeptide chain folding. The crystal structures of two decapeptides containing two contiguous D-amino acids are compared. Peptide 1, Boc-Leu-Aib-Val-Ala-Leu-Aib-Val-^{D}Ala-^{D}Leu-Aib-OMe [S. Aravinda, N. Shamala, Animesh Pramanik, Chittaranjan Das, P. Balaram (2000) Biochem.Biophys.Res.Commun. 273, 933-936], and peptide 2, Boc-Leu-Aib-Val-Gly-Leu-Aib-Val-^{D}Ala-^{D}Leu-Aib-OMe (this study). Residues Leu(1) to Val(7) adopt completely helical conformations. ^{D}Ala(8) is the site of chiral reversal resulting in helix termination by formation of a Schellman motif. Residues 9-10 adopt nonhelical conformations. The extended conformation at ^{D}Leu(9) [ϕ = +130°, ψ = -160° for peptide 1, and ϕ = +126° , ψ = -156° for peptide 2] results in a compact folded structure, stabilized by a potentially strong C-H···O hydrogen bond between Ala(4) $C^{\alpha}H$ and ^{D}Leu(9) CO in peptide 1, and Gly(4) C^{α} H(2) and ^{D}Leu(9) CO in peptide 2. The distance and angle parameters for C-H···O interaction are $C^{\alpha}\cdots O$ = 3.27Å, $\angle C^{\alpha}$-H···O =176°, and O···H^{α} = 2.29Å in peptide 1, and $C^{\alpha}\cdots O$ = 3.59Å, $\angle C^{\alpha}$-H···O = 133°, and O···H^{α} = 2.86Å in peptide 2. Inspection of the molecular conformation of peptides 1 and 2 reveals that chain reversal has been effectively achieved by the conformation adopted at the residues 8 and 9, resulting in a compact fold.

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A6-88

STRUCTURE AND HYDRATION OF TETRAGONAL LYSOZYME GROWN IN THE PRESENCE OF SUCROSE, SORBITOL AND TREHALOSE.

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Sugars and polyols are often used to enhance the stability of proteins. Thermodynamic and physico-chemical studies indicate that the stabilising effect of these compounds is achieved by the modulation of the solvent structure around the protein molecule. In order to elucidate the effect of the stabilising additives on the structure of proteins and the associated ordered water molecules in the hydration shell, the crystal structures of tetragonal lysozyme grown in the presence of sucrose, sorbitol and trehalose have been refined. Also refined are the structures of orthorhombic and monoclinic lysozyme grown under conditions in which tetragonal lysozyme is normally grown. A comparison of the two sets of structures with the structure of native tetragonal lysozyme reveals that the effect of the additives on the structure of the protein molecule is less than that of the normal minor changes associated with differences in molecular packing. The additives do not even affect the level of hydration as indicated by the numbers of ordered water molecules associated with the protein. Still more surprisingly, they do not cause any significant reorganisation of water molecules in the hydration shell. Thus it appears that the cause of the stabilising effect of the additives need to be sought outside the immediate neighbourhood of the protein molecule. Among the three additives, only one interacts with the protein in a coherent manner. A sucrose molecule binds at the active site groove of the enzyme molecule.

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A6-89

CRYSTAL STRUCTURE OF MIMOSINE REDUCED CYTOCHROME C FROM HORSE HEART

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Eukaryotic cytochrome *c* is an electron carrier protein found between the outer and inner membranes of mitochondria. The electron transfer occurs from cytochrome reductase to cytochrome oxidase through cytochrome *c*. Cytochrome *c* from horse heart, reduced by mimosine, a plant allelochemical has been crystallized at 293K using hanging drop vapour diffusion technique. The crystal diffracted up to 2.9Å in $P4_122$ space group with cell parameters a= 73.74, b= 73.74, c= 39.56Å; Z=8. The structure was solved by molecular replacement using oxidized cytochrome c without heme as search model. The $2F_o$-F_c map calculated without heme coordinates initially showed only one heme position. Refinement of the structure showed the existence of a second heme position, which was parallel to the first one and the position of the mimosine molecule. With occupancies of 0.5 for both the heme positions and mimosine, the Rfactor and R_{free} were reduced to 0.30 and 0.43 respectively. The analysis of the structure reveals changes in conformation near the heme crevice where the heme has rotated approximately 90° from its original position and has occupied two alternate positions. The invariant residue Phe82 which is implicated in the reduction process of cytochrome *c* is exposed to the external medium and has moved outwards against the heme allowing the mimosine molecule to place itself in between the two heme positions. Mimosine molecule interacts with the propionate sidechains of one of the heme groups and Cys 14. The structure also explains the molecular mechanism of mimosine action and the electron transport mechanism.

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ATOMIC RESOLUTION (1.1Å) STRUCTURE OF *Plasmodium falciparum* TRIOSEPHOSPHATE ISOMERASE – 2 - PHOSPHOGLYCERATE COMPLEX

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We have determined structures of various *P. falciparum* Triosephosphate isomerase (PfTIM) complexes in view of the importance of the enzyme as a potential chemotherapeutic target. The structural features at the active site and the catalytic mechanism of the parasitic enzyme appear to be different from those of its homologues. Important substitutions found near the active site of PfTIM are Ser96Phe adjacent to catalytic electrophile His95, and Ala73-Phe74 by Ser73-Tyr74 at the dimeric interface. The catalytic loop (residues 166-176) adopts the "open" conformation in the structures of PfTIM 3-phosphoglycerate and glycerol-3-phosphate complexes. Crystals of PfTIM-2-phosphoglycerate (2PG) complex diffracted to 1.1Å resolution. Data were collected using X11 beam at DESY, Hamburg. The structure was refined to an R factor of 13.7% using CNS_0.4 and SHELX-97 programs. This represents the highest resolution structure for TIM and reveals the active site geometry in great detail. As in other PfTIM - substrate analogue complexes, the catalytic loop adopts the "open" conformation in this case also. The crystal belongs to $P2_1$ space group and contains a molecular dimer in the asymmetric unit. Interestingly, 2PG had well defined density only in the B subunit. The density in the A subunit was broken and the pieces were interpreted as 2-oxoglycerate (2OG) and meta phosphate ions (PO_3^-). This is the first time a monomeric meta phosphate ion has been found in an enzyme active site. Cleavage of 2PG could have occurred due to radiation or could be an inherent property of PfTIM.

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STRUCTURES OF _*Plasmodium falciparum* TRIOSEPHOSPHATE ISOMERASE SUBSTRATE ANALOGUE COMPLEXES: IMPLICATIONS FOR THE DESIGN OF ANTI-MALARIAL DRUGS

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Protozoan parasites like *Plasmodium falciparum* (Pf) lack functional tricarboxylic cycle and depend on glycolysis for energy requirement. Therefore, glycolytic enzymes of these organisms are attractive targets for the design of chemotheraphatic agents. The emergence and global spread of Pf resistant to anti-malarial drugs necessitate the identification of new targets. The structure of Pf Triosephosphate isomerase (PfTIM) suggested that the replacement of a highly conserved Ser at position 96 by Phe could be exploited for the) design of anti-malarial drugs. We have determined the structures of two PfTIM-Substrate analogue complexes, (3-Phosphoglycerate (3PG) and Glycerol-3-phosphate (G3P)) with the view of obtaining further insights into the interactions involving Phe96. The complexes belong to monoclinic $P2_1$ and contain a dimeric molecule in the asymmetric unit. The structures have been determined and refined at 2.4Å resolution. The most intriguing observation is that the catalytic (flexible) loop exists in the "open" conformation. This loop is known to move by about 7 Å towards the active site during catalyssis and as been observed in the "closed" conformation in structures of TIM-ligand complexes from other sources. Superposition of PfTIM complexes with the corresponding complexes of *Trypanasoma cruzei* TIM showed that the extensive steric clash that would occur between the loop and Phe96, Ile174 in the "closed" conformation of the catalytic loop in PfTIM prevents loop closure. Proximity between the C2-hydroxyl group of the ligands and Phe96 indicates possible strategies that might be exploited for the design of anti-malarials.

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STRUCTURE OF *Plasmodium falciparum* TRIOSEPHOSPHATE ISOMERASE - PHOSPHOGLYCOLATE COMPLEX IN TWO DIFFERENT CRYSTAL FORMS: IMPLICATIONS FOR THE CATALYTIC MECHANISM

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Triosephosphate isomerase (TIM) catalyses the isomerization of dihyroxyacetone phosphate (DHAP) and D-glyceraldehyde-3-phosphate (D-GAP) and is thought to be an evolutionarily perfect enzyme. The structural aspects of its catalytic mechanism are well characterized using a variety of techniques. The reaction intermediate, *cis*-enediol (diolate), is highly reactive and can undergo rapid phosphate elimination to form cytotoxic methlyglyoxal. This is prevented by a 7Å movement of the catalytic (flexible) loop, comprising of residues 166-176, towards the active site sequestering and binding the intermediate in a conformation that is not suitable for phosphate elimination. The catalytic loop has usually been observed in the "closed" conformation in TIM-ligand structures. In the *Plasmodium falciparum* (Pf) TIM-Substrate analogue complexes, the catalytic loop adopts the "open" conformation, suggesting that the replacement of conserved Ser96 by Phe in Pf could profoundly influence the catalytic mechanism. The structure of Phosphoglcycolate (PG, a transition state analogue) was determined to gain insights into the contrasting features of catalysis by PfTIM and its homologues. PfTIM-PG complex crystallized in both orthorhombic ($P2_12_12_1$) and monoclinic (C2) forms and diffracted to 2.8 and 1.9Å resolution, respectively. The $P2_12_12_1$ form contains two dimers in the asymmetric unit while the C2 form has only a monomer in the asymmetric unit. In contrast to other PfTIM substrate analogue complexes and $P2_12_12_1$ form of PG complex, the catalytic loop adopts the "closed" conformation in the C2 form. The closed conformation is achieved by forcing the residues Phe96 and Leu167 into alternative conformations. Implications of these structural results to TIM catalysis are discussed.

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A6-93

CRYSTAL STRUCTURE OF TGCGCA AT 1.6Å RESOLUTION

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It is known that the alternating copolymer d(CG)n, when exposed to high salt or ethanol concentration, adopts a left handed helical structure, namely Z-DNA. In our program to study the effect of AT base pairs in such structures, we have earlier studied and reported the micro heterogeneity in the structure of canonical Z-DNA sequence d(CGCGCG) that occurs when AT base pairs are introduced into the sequence at different positions viz., d(CACGCG).d(CGCGTG) and d(CGCACG).d(CGTGCG). To study the effect of AT base pairs at the terminals of the sequence, we are working on the crystal structures of d(CGCGCA).d(TGCGCG) and $d(TGCGCA)_2$. Here we report the room temperature X-ray crystal structure of $d(TGCGCA)_2$ refined at 1.6Å resolution. The crystal belongs to the space group $P2_12_12_1$ with unit cell parameters a=21.18Å, b=28.36Å and c=44.44Å. The overall structure of the sequence falls in the category of Z DNA. The refinement converged to an R value of 21.3% (R_{free} = 27.9%) for 3445 reflections between 19.0Å and 1.6Å. Comparison of the present structure with that of the same sequence at low temperature (120K) reported earlier (Harper et al, 1998 *Acta Cryst.* **D**54, 1273.) showed that the present structure is larger by 0.22Å along the axis of the Z-DNA than the low temperature structure, but the value of rise at the virtual step between the symmetry related duplexes is less in the present structure. The base step and base pair parameters at the terminals show significant variation from the low temperature structure due to the flexibility of the terminal AT base pairs at higher temperature. However, comparisons of the structures at the two different temperatures with others in the database show that the effect of sequence on the structural features is greater than the effect of temperature.

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STRUCTURES OF TWO COMPLEXES OF PROTEINASE K WITH DESIGNED PEPTIDES (I)Pro-Ala-Pro-Phe-ΔAla-Ser-Ala AND (II)Pro-Ala-Pro-Phe-ΔAla-Ala-Ala AT ATOMIC RESOLUTIONS.

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Serine proteases are found in all organisms, functioning in digestion , post translational processing, processing of secreted proteins, neurotransmitters and hormones, blood coagulation and complement fixation. These are therefore, attractive targets for specific drug design in pathological conditions. The approaches of structure-based drug design through evaluation of the interactions formed between the enzyme and designed peptides are logical steps. We report here the crystal structures of two complexes formed between proteinase K and the two designed peptides at 1.0 Å resolution. The intensity data on the complexes were collected with synchroton beamlines at DESY. The unique reflections for the first complex were 119,145 whereas in the second structure the unique reflections were 101,462. Both the structures have an overall completeness of more than 99%. Both the structures were refined to R-factors of 11.5% and 12.0% respectively. In both the structures, hydrogen atoms appear as significant peaks in the F_o-F_c difference electron density maps and carbon, nitrogen and oxygen atoms can be differentiated. The estimated standard deviations for all main chain non-hydrogen atoms are 0.011(0.013)Å in bond lengths and $0.6^0(0.7^0)$ in bond angles. Hydrogen bonds are resolved in the serine protease catalytic triad (Ser-His-Asp) and in the complex with the peptides. The density for the peptide atoms is clearly observed. More than 450 water molecules were identified from the difference Fourier maps.

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A6-95

STRUCTURAL COMPARISON OF A FEW THIOL PROTEASES

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Ervatamia Coronaria, a flowering plant indigenous to India, is known to have medicinal importance and other applications. Ervatamin B (26kd) which is a highly stable Cysteine protease has been isolated and purified from the latex of this plant. It exhibits some novel properties distinctly different from papain and other cysteine proteases, though it probably shares an ancestral gene with that of papain. The structure has been solved at high resolution (1.63 Å) and the stability of the protein has been studied from a structural point of view. A unique substrate specificity of the enzyme could also be explained from its three dimensional structure. Amino acid sequence of the protein has also been determined using Crystallography.

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STRUCTURE AND FUNCTION OF HUMAN HEMATOPOIETIC PROSTAGLANDIN D SYNTHASE ACTIVATED BY MAGNESIUM ION

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Prostaglandin D_2 (PGD_2) is responsible for the symptoms seen in mastocytosis patients, such as flushing, diarrhea, tachycardia, dyspnea, and deep sleep. Especially PGD_2 released from mast cells is an allergic and inflammatory mediator, as demonstrated an allergic asthma model with the PGD receptor gene-disrupted mice. The structure of the prostaglandin D synthase (PGDS) is a potent target for the anti-allergic drug design.

We have determined the 1.8 Å X-ray structure of human hematopoietic PGDS, which catalyzes the production of an allergic mediator, PGD_2, in the presence of glutathione. A metal binding site of Mg^{2+} or Ca^{2+} has been identified at the dimer interface clustered by six aspartates, Asp93, Asp96 and Asp97 and those corresponding residues in the counterpart of the dimer.

The Mg^{2+}-bound form displays the remarkable change of metal coordination structure from the Ca^{2+}-bound form. The rearrangement of the hydrogen bond network has also occurred. The interaction between Asp96 and the Mg^{2+} ion is expected to strengthen the structure and that with Arg14 leads to a certain degree of rotation. The rotated Arg14 could hydrogen bond to glutathione and Mg^{2+} extremely improves the Km value for glutathione.

In this work we're discussing the novel reaction mechanism with the Mg^{2+}-bound structure.

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CRYSTAL STRUCTURE OF TTR INSIGHTS INTO ITS MECHANISM AS AN ACETYLTRANSFERASE

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Tabtoxin Resistance protein (TTR) is an enzyme endowing Tabtoxin-producing pathogens, *Pseudomonas syringae* pv. Tabaci, resistance to their toxins. The crystal structure of TTR complexed with AcCoA was determined at 1.55 Å resolution by MAD method. The structure resembles a letter V, with an AcCoA inserting between the two arms. The natural binding of AcCoA to TTR *in vivo* as well as the structural homology of TTR to the proteins belonging to the GCN5-Related N-acetyltransferase (GNAT) superfamily confirm TTR as a member of the superfamily. The high resolution structural data supports a facile single-step acetyl-transfer catalytic mechanism and a reasonable self-protection mode of pathogen from its toxin. Furthermore, as a member of GNAT superfamily, the structure of TTR sheds light on the catalytic mechanism of some proteins with biologically significant role in the superfamily, especially in understanding the important role of the conserved residue Tyr equivalent to Tyr141of TTR.

CRYSTAL STRUCTURE OF *THERMUS THERMOPHILUS* LIPOAMIDE DEHYDROGENASE (L-PROTEIN) OF THE GLYCINE DECARBOXYLASE MULTIENZYME SYSTEM.

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The glycine decarboxylase complex (GDC) consists of four different component enzymes (P-, H-, T- and L-proteins). In order to determine the structure of GDC, all the component enzymes of *Thermus thermophilus* GDC were cloned and overexpressed in *Escherichia coli*. Crystallization conditions for the purified components were separately screened. To date, L- and H-proteins have been crystallized and the structure of L-protein has been solved. In this meeting, we report the crystal structure of L-protein and a new method of co-expressing two subunits of P-protein to fold into its native structure.

The structure of L-protein (lipoamide dehydrogenase; EC 1.8.1.4) was solved by molecular replacement method. The final value of crystallographic R-factor after refinement was 22.9% at 2.8 Å resolution with good geometry of the final model. The enzyme has two identical subunits related by a non-crystallographic twofold axis. The tertiary structure is similar to those of yeast, pea and other prokaryotic enzymes. The active site, consisting of FAD, Cys47, and Cys52 from one subunit and His446' from the other, is highly conserved. In order to understand the substrate recognition mechanism of this enzyme, the screening of crystallization conditions for the L-protein in complex with substrate is now in progress.

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THE CRYSTAL STRUCTURES OF CYTOCHROME C FROM HORSE, BOVINE AND TUNA: THE EFFECT OF NITRATE IONS IN THE PACKING

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Tuna ferricytochrome c was crystallized using two salts, ammonium sulfate (AS) and $NaNO_3$, as precipitants (1), while horse ferricytochrome c was crystallized using AS and NaCl (2). Ataka *et al.* have succeeded in growing crystals of cytochrome c from horse, bovine, tuna and yeast, using AS and $NaNO_3$ as precipitants, and suggested the importance of NO_3^- ion for the crystal growth (3). In order to examine the role of NO_3^- ion in the crystallization process, X-ray structure analyses of horse, bovine and tuna cytochrome c's were carried out at 2.1 Å, 2.35 Å and 1.8 Å resolution, respectively.

Crystallization conditions: for horse and bovine, hanging-drop method, 0.52 g AS and 0.18 g $NaNO_3$ were dissolved into 1 ml of 0.05M ammonium phosphate buffer (pH 6.0) for the reservoir solution; for tuna, batch method, 0.35 g AS and 0.10 g $NaNO_3$ were dissolved into 1 ml of the buffer.

The trigonal crystals of horse protein ($P3_1$, a=80.75, c=90.85 Å) and bovine protein ($P3_2$, a=85.1, c=88.5 Å) contain 6 molecules per asymmetric unit, respectively. In the horse crystal, there were 2.5 NO_3^- ions per cytochrome c molecule. The packing scheme in the horse crystal suggests that Asn103 played an important role in the formation of the lattice by interacting with one of the NO_3^- ions, in spite of the disappearance of the corresponding NO_3^- ion in the bovine crystal. The tetragonal crystals of tuna protein ($P4_3$, a=75.00, c=36.68 Å) were isomorphous to the type B crystals (1), and contain 1.5 NO_3^- ions per cytochrome c molecule.

1) R. Swanson et al. (1977) *J. Biol. Chem.* 252, 759-775 .
2) G. W. Bushnell et al. (1990) *J. Mol. Mol.* 214, 585-595.
3) T. Kubota et al. (2001) *J. Crystal Growth*, in press.

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A6-100

STRUCTURAL STUDIES ON COBRA VENOM FACTOR

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Cobra venom factor (CVF) is the complement-activating protein in cobra venom. It is a three-chain glycoprotein with a molecular weight of 149 kDa. In serum, CVF forms a bimolecular enzyme with the Bb subunit of factor B. The enzyme cleaves C3 and C5, causing complement consumption in human and mammalian serum. CVF is frequently used to decomplement serum to investigate the biological functions of complement and serves as a tool to investigate the multifunctionality of C3. Furthermore, CVF bears the potential for clinical applications to deplete complement in situations where complement activation is involved in the pathogenesis of disease. CVF was isolated from Indian cobra (Naja naja sagittifera) venom. The protein was crystallized at room temperature using the sitting drop vapour diffusion method. The crystals diffract to 2.7 Å resolution and belong to the tetragonal space group $P4_1$ with unit-cell dimensions a = b = 62.7 Å and c = 368.1 Å. As no similar structure is available in the database, several heavy atom derivatives have been prepared. The structure analysis is posing problems but further efforts are underway. The unique features of the structure and the problems encountered will be discussed.

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A6-101

CRYSTALLIZATION AND PRELIMINARY X-RAY ANALYSIS OF MAIZE GLUTAMINE SYNTHETASE

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Glutamine synthetase (GS) is a key enzyme in the assimilation pathway for ammonium. It catalyzes the formation of glutamine from ammonium and glutamate using adenosine triphosphate. Especially in higher plants, glutamine is an organic nitrogen donor in amino acid biosynthesis and GS plays an important role. Bacterial GS, which has been widely studied structurally, is usually composed of 12 subunits. Eukariotic GS comprises 8 subunits and its three dimensional structure remains still unknown. The crystal structure of this enzyme from maize (*Zea mays*) will be essential for understanding the mechanisms of fixation of ammonium in eukaryote, and we started the crystallographic work of maize GS. Recombinant maize GS was overexpressed in *E. coli* and purified. Crystallization was performed by the hanging-drop vapor diffusion method using PEG 8000 as a precipitant. Crystals of GS appears at 20 °C within two weeks and belong to the monoclinic space group *P*2 with unit-cell parameters a = 109.6, b = 186.6, c = 180.0 Å, β = 101.5°. A native data set was collected to 3.0 Å resolution on a Cu $K\alpha$ rotating-anode X-ray source. The Matthew's coefficient is 2.9 A^3 /Da, corresponding to two octamers with a total molecular mass of 640 kDa in the asymmetric unit.

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STRUCTURE DETERMINATION OF THE ORF7 NUCLEOCAPSID PROTEIN OF PORCINE REPRODUCTIVE AND RESPIRATORY SYNDROME VIRUS (PRRSV)

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Porcine reproductive and respiratory syndrome virus (PRRSV) is a widespread, highly infectious and economically important virus of pigs. It belongs to the *Arteriviridae* family and has a single-stranded positive-sense RNA genome. The virion contains an isometric nucleocapsid core comprised of the orf7 gene product, surrounded by a lipid envelope containing a number of membrane proteins which are the gene products of orf2–6. The orf7 nucleocapsid protein has 123 amino acids and contains a highly positively charged and flexible N terminus, which presumably binds the RNA genome.

We have cloned, expressed and crystallized, a 6×His-tagged, truncated form of the orf7 protein, referred to Orf7.2, which containing the C-terminal 63 amino acids of Orf7. Orf7.2 crystallizes in the $P3_121$ spacegroup with a=44.5Å, c=125.1Å, and contains a dimer in the asymmetric unit. We have solved the structure of Orf7.2 to 2.5Å resolution using MIR with two derivatives, $K_2Pt(CN)_4$ and $KAuCl_4$.

Preliminary analysis of the solvent-flattened map shows the protein dimers which appear to have a predominantly β-sheet structure.

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A6-103

PRELIMINARY CRYSTALLOGRAPHIC STUDY OF CALCIUM/CALMODULIN - DEPENDENT PROTEIN KINASES α FROM RAT CEREBRAL CORTEX

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Three multifunctional calcium/calmodulin-dependent protein kinases (CaM kinases), CaM kinase I, CaM kinase II and CaM kinase IV, are reported to play important roles in controlling a variety of neuronal functions in response to an increase in intracellular Ca^{2+} concentration. Among three kinases, CaM kinase I and IV are activated by CaM kinase kinases (CaMKKs).

One of CaMKKs, CaMKKα is known to phosphatize Thr196 of CaM kinase IV and activate it in nerve cell nucleus after binding Ca2+-calmodulin. In the present study, recombinant CaMKKα from a rat cerebral cortex cDNA clone was expressed in *Escherichia coli* and was purified by the procedures including Calmodulin Sepharose affinity chromatography [Kitani, T., Okuno, S. and Fujisawa, H. (1997) J. Biochem. 121, 804-810]. This purified enzyme gave one major protein band corresponding to a molecular weight of about 66k upon SDS-PAGE, although the enzyme was a molecular weight of about 56k calculated from its amino acid sequence. It is necessary to investigate the structure of CaMKKα in order to know the physiological functions, the molecular mechanisms, and the reactions with ligands. From this aspect, we start to screen the crystallization conditions in order to solve the structure by means of X-rays. We wish to report a preliminary crystallographic study of CaMKKα.

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CRYSTAL STRUCTURE OF POLYMETHOXYGALACTURONASE FROM *Trichosporon penicillatum*

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Pectic substances are acid polysaccharides of high molecular weight that are widespread in the plant kingdom. Polymethoxygalacturonases (PMGs) catalyze the hydrolysis of α-1,4-glycosidic linkages in the methoxylated polygalacturonate which is a component of pectic substances. We have initiated an analysis for the crystal structure of PMG from *Trichosporon penicillatum* to elucidate the recognition mechanism of the substrate. The enzyme, consisting of 334 residues, was crystallized using PEG 1000 as a precipitant. The crystal belongs to monoclinic, space group *C*2 with unit cell parameters of a = 165.6, b = 61.0, c = 48.7 Å, β = 93.1°. A native data set from a crystal was collected to 2.1 Å resolution at room temperature on a Rigaku R-AXIS IIc imaging-plate system using Cu *K*α radiation. A total of 106223 observed reflections were scaled and reduced to yield a data set containing 28168 unique reflections with an R_{merge} of 7.6%. Molecular replacement calculations were carried out with the program *AMoRe* using endopolygalacturonase II from *Aspergillus niger* as a starting model. The best solution had a correlation coefficient of 0.599 and an R-factor of 0.434. The refinements including solvent molecules are now in progress.

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A6-105

CRYSTAL STRUCTURE OF DECAMERIC E. *coli* KETOPANTOATE HYDROXYMETHYLTRANSFERASE BY MAD PHASING WITH 160 Se-Met SITES

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Ketopantoate hydroxymethyltransferase (KPHMT) catalyzes the first committed step in the biosynthesis of coenzyme A (CoA), namely conversion of α-ketoisovalerate (α-KIVA) to ketopantoate (3,3-dimethyl-2-oxobutanoate). Here, we report the crystal structure of decameric KPHMT from *E. coli* bound to product, ketopantoate and determined to 1.8 Å resolution, through the use of multiwavelength anomalous dispersion (MAD) with 160 selenomethionine (SeMet) sites. This number is the largest structure to date that has been solved by MAD. Ketopantoate is shown to bind to a magnesium ion through its keto and carboxyl groups. Similar binding for the substrate, α-KIVA, is believed to orient and activate the C3 position for deprotonation and subsequent nucleophilic attack. Additionally, we propose a mode of binding for the cofactor, N^5, N^{10}-methylenetetrahydrofolate (5,10-CH_2-H_4folate).

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A6-106

2-CARBETHOXY-3-AMINO-4-(4-METHYLPHENYL)-6-PHENYL FURO[2,3-B] PYRIDINE - A NOVEL FUROPYRIDINE

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Furopyridines consists of π-excessive furan ring and π-deficient pyridine ring which are of interest to study the annelation perturbing electronic structure which is manifested on reactivity of substances. These group of compounds also play an important role in many biologically active substances. We report, therefore, crystal and molecular structure of 2-carbethoxy-3-amino-4-(4-methylphenyl)-6-phenyl furo[2,3-b]pyridine. Crystals of title compound are orthorhombic having space group Pbca obtained from methanol solution by slow evaporation method. Crystal parameters are: a = 7.755(3), b = 21.231(6), c = 23.020(7) Å, Z = 8, V = 3790(2) Å^3, ρ_c = 1.303 Mg m^{-3}, μ = 0.183 mm^{-1}.Final residual index is 0.043 for 2466 unique reflections. Furan ring is non-coplanar and best plane of it is almost coplanar having dihedral angle of 2.42(12)° with pyridine ring plane. Steric interactions forces the phenyl rings away from the pyridine ring plane by 45.34(1)° and 18.57(1)° respectively. The structure is mainly stabilized due to weak van der Waal forces as no hydrogen bond is observed.

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BIMETAL COMPLEX OF A NUCLEOTIDE: STRUCTURE OF SODIUM-POTASSIUM SALT OF CYTOSINE-5'-MONOPHOSPHATE HEXAHYDRATE METHANOL SOLVATE

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Bimetallic Sodium-Potassium complex of Cytosine-5'-Monophosphate, [(C_9 H_{12} N_3 O_8 P^{2-}).(1.25 Na^+).(0.75 K^+).(5.75 H_2O).(0.5 CH_3OH)] crystallizes in the monoclinic space group $P2_1$ with cell dimensions a = 8.869(2), b = 20.580(6), c = 23.179(1) Å, β = 105.791(1)°, Z = 2, V = 4070.9(13) $Å^3$ with four molecules in the asymmetric unit. The MoK_α intensity data at 213 K consisted of 16,184 unique reflections. Final R = 8.09 %. All the four molecules in the asymmetric unit show anti conformation about the glycosidic bond, C2'-endo sugar puckering and gauche-gauche (g^+) conformation about the exocyclic C4' - C5' bond. There are some conformational differences between this structure and other 5'-CMP and 5'-dCMP structures reported earlier. The K^+ ions coordinate with base, ribose, phosphate and water oxygens besides the base nitrogen. The Na^+ ions, however, do not bind to the base oxygen. The cytosine bases show alternate base-base and base-ribose O4' stacking along the c-axis with Na^+ and K^+ ions forming channels between them parallel to the molecular columns.

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4- AMINO - N (2 -QUINOXALINYL) BENZENE - SULFONAMIDE, $C_{14}H_{12}N_4O_2S$

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Sulfaquinoxalinyl, 4 - amino - N - (2 - quinoxalinyl) benzene - sulfonamides, $C_{14}H_{12}N_4O_2S$ is a well-known member of antimicrobial sulfonamide family. It is a potent antitumor drug. Its chlorine substituted derivative shown in vitro antitumor activities against human lungs. Transparent tiny single crystals of the title compound are obtained from the mixture of acctonitrile and methanol in the presence of few drops of ethyl acetate. It crystallizes in monoclinic space group P21 /a with Z=8. Crystal data are a = 15.627(10), b = 6.183(17), c = 28.949(9) Å, β = 103.87 °, Dm = 1.469Mgm-3. SHELX-97 program is used to solve and refine the structure. There are two molecules in the asymmetric unit. Geometry around sulfur is as usual a distorted tetrahedron. Quinoxaline part of both the molecules are planar. Phenyl ring of sulfonyl moiety of mole A makes an angle of 78.99° to the quinoxaline system whereas the angle is 78.91° for mole. B. The conformation is 'CIS' for mole. A and mole. B with respect to S-N bond. Extensive hydrogen bonds both intra & inter stabilized the structure. Hydrogen bonding network will be discussed in detail.

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A6-109

THE STRUCTURE OF THE RIPPLE PHASE OF SOME PHOSPHOLIPID BILAYERS

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We have calculated the electron density maps of the ripple phase of some phospholipids multibilayers, namely, dimyristoylphosphatidylcholine (DMPC), palmitoyl-oleoyl hosphatidylcholine (POPC), dihexadecyl phosphatidylcholine (DHPC) and dilauroyl phosphatidylcholine (DLPC). In all these systems except in DLPC, the rippled bilayers have a saw-tooth shape, with one arm almost twice as long as the other. The bilayers lack a mirror plane normal to the ripple wave vector, thus making them asymmetric. We show that the maps of all the lipids studied are consistent with the presence of an average tilt of the hydrocarbon chains of the lipid molecules along the direction of the ripple wave vector. The asymmetry of the rippled bilayers is generally assumed to arise from a saw-tooth height profile. However, we find that in the case of DLPC, the asymmetry is due mainly to different bilayer thicknesses in the two arms and the height profile itself is almost symmetric. Our results provide important inputs for theoretical models of phase transitions in lipid bilayers.

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CRYSTAL STRUCTURE OF L22 RIBOSOMAL PROTEIN MUTANT RENDERING BACTERIAL RIBOSOME RESISTANT TO ERYTHROMYCIN

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The ribosomal protein L22 is a core protein of the large ribosomal subunit and interacts with all domains of the 23SrRNA. L22 is involved in binding of the ribosome with erythromycin, which is known as an inhibitor of protein synthesis. It was observed that the Met82-Lys83-Arg84 triplet deletion in *E.coli* L22 β-hairpin produced cells resistant to erythromycin.

A mutant form of L22 from *Thermus thermophilus* was overexpressed in *E.coli*. The crystal structure has been determined at 1.8Å resolution. The β-hairpin conformation with three amino-acids deletion is significantly different from that in the native L22. The β-hairpin is bent inside of the ribosome tunnel modifying the shape of the narrowest part of this tunnel and affecting the L22 and 23SrRNA interaction.

23SrRNA nucleotides of domains II and V participating in erythromycin binding are located on the opposite sides of the tunnel and appear to be brought to those positions by the interaction of the 23SrRNA with the L22 β-hairpin. Mutation in the L22 β-hairpin destabilizes the erythromycin binding "pocket". Erythromycin, while still be able to communicate with one of the tunnel sides, cannot reach both its preferable sites of binding simultaneously and therefore is unable to block the polypeptide growth.

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DESIGN OF A β TURN-II CONFORMATION WITH α, β– DEHYDRO-RESIDUES AT (i+1) POSITION: SYNTHESES, CRYSTAL STRUCTURES AND MOLECULAR CONFORMATIONS OF THREE PEPTIDES: (I) N-carbobenzoxy- ΔVal-Ala-Leu-OCH_3 (II) N-Carbobenzoxy- ΔIle-Ala-Leu-OCH_3 and (III) N-Carbobenzoxy- ΔLeu-Ala-Leu-OCH_3.

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Highly specific peptide structures can be designed by inserting dehydro-residues into peptide sequences. The conformational preferences of branched β-carbon residues are known to be different than other residues. It has been shown that the non-branched β-carbon dehydro-residues induce β-turn II conformation when placed at (i+2) position while branched β-carbon dehydro-residues induce β -turn III conformation. However, the effects of various dehydro-residues, when substituted at (i+1) position are not yet fully understood. In order to clearly define the role of dehydro-residues for peptide design through their substitutions at (i+1) position, three peptides: (I) Cbz-ΔVal-Ala-Leu-OCH_3 (II) Cbz-ΔIle-Ala-Leu-OCH_3 and (III) Cbz-ΔLeu-Ala-Leu-OCH_3 were synthesized, two with branched β-carbons and the third with a non-branched - β-carbon dehydro-residue. Because of the branching at the β -carbon, the bond angles C^{α}-C^{β}-C^{γ} in (I) and (II) are significantly different [123.3(5)° and 122.6(5)° respectively] than that observed in ΔLeu [127.9(4)°]. Despite this, the structures of the three peptides were found to be identical as all the three adopt β-turn II conformation with torsion angles : (I) ϕ_1 = 41.5(5)°, ψ_1 = -142.3(3) ° ; ϕ_2 = -91.2(4)° ; ψ_2 = 8.1(4)° (II) ϕ_1 = 37.0(6)°, ψ_1 = -123.6(4)° ; ϕ_2 = -93.4(4)° ; ψ_2 = 11.0(4)° and (III) ϕ_1 = 47.7 (5)° , ψ_1 = -137.4(3)° ; ϕ_2 = -87.3(4)°, ψ_2 = 9.8(4)°. All the peptide structures are stabilized by intramolecular 4→1 hydrogen bonds with distances of (I) N_3-----O_0' = 2.69(6)Å (II) N_3-----O_0' = 2.897(4)Å and (III) N_3-----O_0' = 3.186(4)Å. Though, the space groups are same, their molecular packings are different as in the former two, there are two intermolecular hydrogen bonds whereas, the latter has only one hydrogen bond indicating dissimilar intermolecular interactions. From these three structures, it can be concluded that a dehydro-residue at (i+1) position induces a type II β-turn conformation irrespective of the nature of branching of its side-chain.

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VITAMIN E INHIBITS PHOSPHOLIPASE A2 AND INDICATES A RELIEF IN ALZHEIMER'S AND PARKINSON DISEASES: STRUCTURE OF THE COMPLEX FORMED BETWEEN PHOSPHOLIPASE A2 AND VITAMIN E AT 1.8 Å RESOLUTION.

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Phospholipase A2 (PLA2) specifically catalyzes the hydrolysis of the acyl ester bond at the sn-2 position of membrane phospholipids to release arachidonic acid for the synthesis of biologically active prostaglandins and their related compounds, the prostacyclins, thromboxanes and leucotriens: known collectively eicosanoids. The vitamin E, also known as α-tocopherol is understood to regulate eicosanoid production by inhibiting PLA2. We present here the first structural evidence of vitamin E binding to PLA2 in the form of a detailed three-dimensional structure of the complex formed between PLA2 and vitamin E at 1.8 Å resolution. The structure reveals the details of the specific binding of vitamin E and specific conformational changes in PLA2, upon binding to vitamin E. The PLA2 from russells viper (DPLA2) crystallizes as a dimer with a long interface in a back to back fashion. As a result of it the binding site of one of the moleculeS is not accessible to non-aggregated phospholipidic inhibitors and substrates. Thus vitamin E binds to only one molecule and inhibits its function. When activity is measured with aggregated phospholipids it shows 50% activity, However with monodisperse substrates the enzyme shows no activity. It indicates that the activity of DPLA2 against ordered membranes can not be inhibited beyond 50%. It appears to be a self-defence mechanism to keep the physiological functions going. The structure of the complex has been refined to an R-factor of 0.197. The overall conformations of two molecules are essentially similar. The only difference occurs in the binding site particularly in the orientation of Trp31. The binding of vitamin E to one molecule of DPLA2 is strong with various hydrogen bonds and van der Waals interactions. The binding site in the other molecule is empty.

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A6-113

ARISTOLOCHIC ACID BLOCKS THE ARACHIDONATE ACID CASCADE TO DECREASE INFLAMMATORY EFFECTS: CRYSTAL STRUCTURE OF A SPECIFIC COMPLEX FORMED BETWEEN PHOSPHOLIPASE A2 AND ARISTOLOCHIC ACID AT 1.7 Å RESOLUTION.

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Phospholipase A2 (PLA2) mediated hydrolysis of fatty acids, especially arachidonate from the sn-2 position of membrane phospholipids is important because this rate limiting step liberates the requisite substrate for the biosynthesis of eicosanoids and it has been implicated in the pathogenesis of inflammatory diseases. Recently, it has been found that aristolochic acid inhibits phospholipase A2 in vitro and also decreases oedema induced by snake venom or human synovial fluid PLA2. Here we present the first structural evidence of the inhibition of PLA2 by aristolochic acid. The purified PLA2 from Daboia russelli pulchela (DPLA2) was co-crystallized with access of aristolochic acid after incubating the mixture for 6 hours. The crystals belong to orthorhombic space group $C222_1$ with a=76.1, b=89.5, c=76.9 Å. The structure was refined to an R-factor of 0.184 (R-free=0.201). The structure contained 1888 protein atoms from two molecules in the asymmetric unit, one sulfate ion, 2 glycerols, 2 dioxanes, 1 acetate, 1 complete molecule of aristolochic acid and 312 water molecules. The overall structure of the two molecules in the asymmetric unit is essentially similar but the hydrophobic channels including Trp31 are considerably different. The hydrophobic channel of one of the molecules has shrunk significantly due to the association of two molecules while in the second molecule, it is appropriately ordered. As a result of this change, the aristolochic acid is able to bind only to one molecule whereas the binding site of second molecule is empty. The enzyme assay with micellar substrate, still shows 50% activity indicating that the aggregated substrate can induce a suitable conformation in the second molecule to generate products but isolated inhibitors or substrate molecules do not succeed in entering to the active site of the conformationally constrained molecule.

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A6-114

PRELIMINARY CRYSTALLOGRAPHIC STUDIES OF NON-SPECIFIC ACID PHOSPHATASE OF *Salmonella typhimurium*.

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Non-specific acid phosphatases (NSAP) catalyze phosphomonoester hydrolysis. NSAP-A gene (*phoN*) of *Salmonella typhimurium* was expressed in *E coli* using pSK- plasmid as cloning vehicle. Protein purification was achieved by ion exchange, hydroxy-apatite and phenyl sepharose column chromatography matrices using Biologic LPLC system. DNA sequencing of the construct using automated Perkin-Elmer DNA sequencer confirmed amino acid sequence of the protein. Size of the signal peptide (20AA) was asertained using N-terminal sequencing of the mature protein. The protein has been crystallized using modified sparse matrix grid. The protein crystallizes in $C222_1$ space group with two molecules of 27kDa in the asymmetric unit and unit cell parameters of a=45, b=190, c=106Å. Crystals growing in a day were observed to be highly mosaic with mosaic spread estimated to be ~1°. The 3-dim intensity data to 3Å resolution has been acquired with R-AXIS IIC and MAR imaging plate systems using rotating anode x-ray generator. Molecular replacement calculations using homology derived model are in progress.

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RATIONAL PROTEOMICS: PREDICTING THE STRUCTURES, FUNCTIONS, COFACTORS, SUBSTRATES, INHIBITORS AND MULTIMERIC FORMS OF 1500 HYPOTHETICAL GENE PRODUCTS IN THE SCOR FAMILY.

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We have developed procedures for structure, sequence, and functional analysis of families of enzymes having 30% amino acid identity with a known crystal structure that can reliably predict the three-dimensional structure, cofactor preference, biological function, probable substrate, lead compound for inhibitor design, role of surface residues in multimer formation and tissue specificity, and probable relation of multimeric formation to function of thousands of hypothetical gene products. Our results have the potential for successful application to unknown gene products having as little as 20% homology with a known crystal structure. The short chain oxidoreductase (SCOR) family of enzymes includes over 1500 members identified in sequenced genomes. Over 200 of these enzymes have been functionally characterized and the crystal structures of twenty have been reported. Sequence analysis and homology modeling have been used to define the signatures of subgroups of the 1000 SCOR proteins of unknown function. The signatures of subgroups of the SCOR superfamily are composed of 40-50 residues conserved at 80% homology or better distributed throughout the seven β-strands and six α-helices of the Rossman fold. Many of the conserved residues are in direct contact with each other and/or with the NAD or NADP cofactor. The conservation of almost all residues in contact with the cofactor illustrate a jigsaw lock-and-key fit that suggests strict co-evolution of fold and cofactor. Asp or Arg residues associated with NAD and NADP binding respectively occur on the β2α3 turn in 75% of 900 member of the SCOR family and can be reliably used to predict cofactor presence of unknown proteins. Quasi-conserved aromatic and charged residues on the outer surface of the α5 helix stabilize dimerization and variations in the pattern of these quasi-conserved residues control the details of dimer association and generate subfamilies of multimeric forms. Co-variance at the 30% or lower level of residues in the active site or on the enzyme surface can be used to predict substrate preference and cell and membrane specificity. This research is supported by NIH Grant No. DK 26546.

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PRELIMINARY X-RAY ANALYSIS OF TWO DNA BINDING PROTEINS IN ARCHAEA

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A gene of a DNA binding protein in *Sulfolobus shibatae*, ssh10b, has been identified by bioinformatics methods, and homologous proteins to Ssh10b are found in each of all archaea species whose genomes have been completely sequenced but not in species of either bacteria or eukarya , which constitute Sac10b family. This ubiquity and specificity to archaea implies an important physiological role for these proteins. Here we report expression, purification and crystallization of two DNA binding proteins in Sac10b family, Ssh10b from *Sulfolobus shibatae* & Mja10b from *Methanococcus jannaschii*

After heating and precipitating with 80% ammonium sulfate, followed by further purification with three columns chromatography, homogeneous Ssh10b protein was obtained from which crystals suitable for X-ray analysis were obtained by vapour diffusion. Crystals belonging to space group P6122/P6522 with unit cell a=83.74 Å, b=83.74 Å, c=164.08 Å, $\alpha=\beta=90°$,$\gamma=120$, and maximum resolution of 6.5Å. The crystals in monoclinic space group(C2), diffracting to 3.0 Å, had unit cell dimensions a=177.63 Å, b =60.75 Å, c=162.32Å.

At the same time, Mja10b was prepared after heat denaturation and saturation with 80% ammonium sulfate, followed by dialysis in 0.2M sulfuric acid and cation exchange column chromatography. Crystals obtained by vapour diffusion, diffract to 2.4 Å and belong to space group C2221 with cell unit parameter a=44.10 Å, b=118.53 Å, c=69.09Å, $\alpha=\beta=\gamma=90°$.

Preparations of selenionmethionione derivative of these two DNA binding proteins are under way in order to develop suitable crystals for structure determination by multiple-wavelength anomalous diffraction.

A6-117

CRYSTAL STRUCTURE OF TTR COMPLEXED WITH AcCoA IN $P2_1$ FORM

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Tabtoxin Resistance protein (TTR) was found in *Pseudomonas syringae* pv. tabaci with the name derived from its detoxification reaction of Tabtoxinine-β-lactam. TTR, consisting of 177 amino acids residues, exhibits less than 12% sequence homology to other proteins with known structures at the protein level. X-ray crystallography method was used to determine the structure of TTR, which will illustrate the molecular mechanism of its detoxification, and will show possible significance to structural biology.

X-ray diffraction data of crystal of TTR complexed with AcCoA was collected in-house using a Rigaku 4.8KW, 1.54 Å wavelength X-ray generator and a MarResearch 345mm image plate. The data were processed using DENZO and was found to belong to spacegroup $P2_1$ with unit cell dimensions a=47.7 Å, b=66.6 Å, c=53.6 Å, $\alpha=\gamma$ =90°, β=103.7°. 2.25 Å resolution crystal structure of TTR complexed with AcCoA was solved by MR method, using the 1.55 Å resolution structure by MAD (space group is C2) as a model.

The structure is very similar to the C2 structure, with only 0.4 Å RMS between the Cα atoms of two structures. The structure shapes like a letter V, with an AcCoA binding between the two arms, which almost has no difference to the C2 structure. However, the distance between O atom of carbonyl group of AcCoA and –OH group in Tyr141 residue, which is directly related to the catalytic mechanism of TTR, is longer than that in C2 structure. The analysis of TTR structure will promote understanding of relationship between its structure and catalytic mechanism.

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PURIFICATION AND X-RAY CRYSTALLOGRAPHIC STUDIES ON MINI-INTEIN DnaB AND DnaE

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Intein, defined as in-framely embedded protein sequence that is removed by protein self-splicing, contributes another layer of complexity to the central dogma of Molecular biology. Post-translationally, the intein sequence undergoes rapid auto-splicing and couples to ligate flanking sequences to yield a functional external protein (extein) and an intein.

Naturally occurring inteins can be grouped into three categories: inteins that contain a homing endonuclease between the splicing domains, inteins that lack a homing endonuclease region (mini-inteins), and inteins in which the splicing domain is split, and are capable of splicing in trans. Though their amino acid sequences exhibit very little similarities in their splicing domains, they seem to share similar three-dimensional structure.

In order to gain structural insights into protein splicing, we have carried out X-ray studies on the recombinant mini-intein DnaE and DnaB, the naturally occurring intein from *Synechocystis sp.* and *Porphyra purpurea* with splicing activities. At present there are no structures available on such typical mini-inteins.

The inteins were overexpressed in *E.coli* and purified from the crude extracts by Impact system followed by anion-exchange and gel filtration. Crystals of both inteins have been acquired by methods of hanging-drop vapor diffusion. A set of data on DnaE was also collected at 115K using a Mar345 Image Plate with an in-house Rigaku rotating Cu anode X-ray generator at 2.9Å. It belongs to space group P3(1)21 with a cell parameter of a=b=58.535, c=70.197. Since no reliable models were available for both proteins, selenomethionine derivative have been prepared for DnaB and heavy metal derivatives for DnaE crystal are being tried for phase determination. Further, attempts are underway to obtain better quality crystal for high- resolution crystallographic studies.

ALLOSTERIC REGURATION AND CARBOXYLATION MECHANISM OF PHOSPHOENOLPYRUVATE CARBOXYLASE

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The crystal structure of active state (R-state) C_4-form maize PEPC (ZmPEPC) has been determined at 3.0 Å resolution. The structure includes sulfate ion at the plausible binding site of an allosteric activator, glucose-6-phosphate, while it includes no inhibitor, L-malate, at the inhibitor binding site found in *Escherichia coli* PEPC (EcPEPC). The crystal structure of inactive state (T state) EcPEPC has also been determined as the quaternary complex of Mn^{2+}, PEP analogue (DCDP; 3,3-dichloro-2-dihydroxy-phosphinoylmethyl-2-propenoate), and an allosteric inhibitor, L-aspartate, at 2.35 Å resolution.

From the structure comparison between R and T states PEPCs, the dynamic movements were revealed in ZmPEPC near the catalytic site. The functionally essential Arg647 (Arg587 in EcPEPC) in the unique sequence of GRGGXXGR^{647}GG was fixed by L-aspartate in EcPEPC. The residue moves 15 Å towards the active site in the R state ZmPEPC by release from the direct constraint of inhibitor molecule. Another essential residue, His177 (His138 in EcPEPC) moves 10 Å towards the active site in the R state ZmPEPC resulted from the binding of sulfate ion in the basic pocket of activator binding site.

Based on these molecular structures, the mechanisms for allosteric regulation and carboxylation reaction of PEPC will be proposed.

A6-120

STRUCTURE-BASED ANALYSIS OF FUNCTIONAL SITE OF A THERMOSTABLE ASPARTASE

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Aspartase catalyzes the reversible conversion of L-aspartate to fumarate and ammonium ion and plays an important role in the bacterial nitrogen metabolism. The crystal structure of the thermostable enzyme from *Bacillus* sp. YM55-1 was solved by the molecular replacement method using the *E. coli* enzyme as a search model and refined for the 2.5 Å low-temperature data with the R-factor of 21.9%. The present *Bacillus* enzyme is a homotetramer. It exhibits no allosteric effects, in contrast to *E. coli* enzyme which is activated by L-aspartate and divalent metal cation, but has 4-times higher activity than *E. coli* enzyme. The overall folding of the enzyme subunit is similar to those of *E. coli* aspartase and *E. coli* fumarase C which belong to the same family with the present enzyme. The structural comparison among these three enzyme revealed seven conformationally different regions. Four of the regions were located around putative functional sites, suggesting the involvement of these regions into functions characteristic of the individual enzymes. Moreover, the increase in the number of intersubunit hydrogen-bonds and salt-bridges was observed in the *Bacillus* aspartase relative to the other enzymes, which explains the thermostability of the present *Bacillus* aspartase.

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A6-121

CRYSTAL STRUCTURE ANALYSIS OF ANTIBODY ENHANCED AFFINITY TOWARD A MUTATED ANTIGEN BY PHAGE DISPLAY TECHNOLOGY

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It is known that an antibody recognizes its target antigen with high specificity and affinity. In some cases, however, an antibody can also recognize mutated antigens with subtle structural changes. In order to address the molecular mechanism of an antibody to recognize its target antigen, we have focused the interaction between hen lysozyme (HEL) and its monoclonal antibody, HyHEL-10. HyHEL-10 recognizes turkey lysozyme (TEL) with decreased affinity.

We attempted to isolate the mutant of HyHEL-10 grafting enhanced affinity toward TEL from phage display library mutated into four residues in complementarity-determining region 2 of heavy chain (CDR-H2) and the determine 3D-structures of complexes of isolated antibodies with HEL and TEL, respectively.

The clone mutated into three residues (Tyr53 Ser, Ser54 Phe and Tyr58 Phe), SFSF, was crystallized by vapor diffusion method. The analysis of crystal structures reveals that the interactions between CDR-H2 and antigen in SFSF-TEL complex differ from those in SFSF-HEL complex. These led to the change in conformations of loop regions of CDR-H2 and packing of CDRs. These results suggest that antibodies are possible to recognize different antigens in the change of packing of CDRs.

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A6-122

STRUCTURAL ANALYSIS OF HUMAN HEMATOPOIETIC PROSTAGLANDIN D SYNTHASE FOR ANTI-ALLERGIC DRUG DESIGN

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Prostaglandin (PG) D_2 is actively formed in a variety of tissues and is responsible for the symptoms in mastocytosis patients. PGD_2 released from mast cells is an allergic and inflammatory mediator, as demonstrated an allergic asthma model with the PGD receptor gene-disrupted mice. PGD_2 is formed from arachidonic acid by successive enzyme reactions: the oxygenation of arachidonic acid to PGH_2 via PGG_2 by PG endoperoxide synthase and the isomerization of PGH_2 to PGD_2 by PGD synthase (PGDS). We have determined the complex structures with PGH_2 analogue and Cibacrone Blue in the presence of Mg^{2+} and Ca^{2+}. The analogue-bound complex structures reveal the residue's rotation of R14 activated by Mg^{2+}. The Mg^{2+}-bound complex structure demonstrates a change of the crystal space group from $P2_1$ to $P1$ and dramatic improvements of resolution from 2.0 to 1.2 Å. Cibacrone Blue shows the mixture-type inhibition against the substrate and GSH. The K_d value for Cibacrone Blue in the presence of Mg^{2+} is raised up as four times stronger than the apo-form. The Cibacrone Blue bound complex structure shows the B-factor of GSH is more than 70 $Å^2$. We have to examine the presence of Mg^{2+} *in vivo* for the anti-allergic drugs.

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X-RAY CRYSTALLOGRAPHIC STUDIES ON S100 FAMILY PROTEINS

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The S100 protein family is a group of calcium-binding proteins, approximately between 9 and 13 kDa in size, which contain two EF-hand calcium-binding domains and share approximately 50% homology in amino acid sequence. Each member of the family exhibits a unique pattern of expression with some cells expressing multiple members of the family. S100 proteins can regulate a diverse group of cellular functions including cell-cell communication, cell growth, cell structure, energy metabolism contraction. S100A1, S100A2, S100A4 and S100P, four members of the S100 protein family, play some important roles in cell metabolism. S100 proteins all have a highly conserved calcium binding loop consisting of 12 amino acids and it is flanked by two -helices (that is, the EF-hand). The Ca^{2+}-binding site near the carboxy-terminus contains 12 amino acids and is common to all EF-hand proteins. The low-affinity Ca^{2+}-binding site near the N-terminal end is S100-specific, containing 14 amino acid residues. Three-dimensional structures of several members of the S100 protein family have been reported; these studies have provided interesting data on calcium-dependent conformation change, and the effects of mutation in the Ca2+-binding loops on function. To obtain more detailed information about the interaction of S100-target, and the significance of the 14 residue amino-terminal calcium-binding loop, we have crystallized all four human S100 proteins (S100A1, S100A2, S100A4 and S100P and their 3D structural analysis are in progress. After recombination, expression, and purification, we have obtained crystals of these four proteins from different crystal conditions, and some pre-liminary crystallography datas[Fig1].

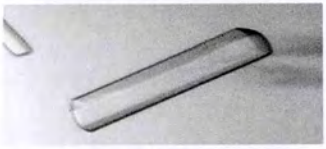
Buffer	NaAcetate
pH	4.6
Precipitant	PEG4k, $(NH_4)_2SO_4$
Additives	Ca^{2+}
Method	Vapor Diffusion
Space group	
Cell	

Crystal of S100A1

Buffer	TrisHCl
PH	8.5
Precipitant	PEG4k
Additives	Ca^{2+}
Method	Vapor Diffusion
Space group	P6
Cell	A=b=57.3Å c=104.7Å

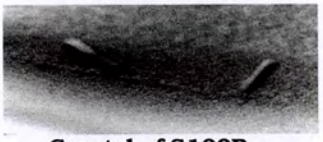
Crystal of S100A2

Buffer	TrisHCl
PH	6.0
Precipitant	PEG4k
Additives	Ca^{2+}
Method	Vapor Diffusion
Space group	P6 or P3
Cell	a=b=47.1Å, c=175.6Å



Cystal of Se-S100A4

Buffer	TrisHCl
PH	7.5
Precipitant	PEG4k
Additives	Ca^{2+}
Method	Vapor Diffusion
Space group	$P2_1$
Cell	a=b=77.74Å,c=78.42Å



Crystal of S100P

A6-124

CRYSTAL STRUCTURE OF A GCN5-RELATED N-ACETYLTRANSFERASE, TABTOXIN RESISTANCE PROTEIN, BOUND TO ACETYL COENZYME A - A MODE FOR THE SELF PROTECTION OF *Pseudomonas syringae* pv. Tabaci FROM ITS TOXIN

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Tabtoxin resistance protein (TTR) is an enzyme that renders Tabtoxin-producing pathogens, such as *Pseudomonas syringae*, tolerant to their own phytotoxins. We have determined the crystal structure of TTR complexed with its substrate, acetyl Coenzyme A (AcCoA), to 1.55 Å resolution using MAD phasing methods. The single domain protein includes the four conserved motifs of the GCN5-related N-acetyltransferase (GNAT) family, as well as a characteristic 'V' motif in which AcCoA is inserted between the two arms of the 'V'. Our high-resolution structure reveals a simple single-step catalytic mechanism whereby the pathogens can protect themselves via the transfer of an acetyl group to the toxin. We also report that our structure provides new understanding of the role of a critical tyrosine (Tyr141) residue that is found in the catalytic pocket of many GNAT superfamily members, including the histone acetyltransferases.

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CRYSTALLOGRAPHIC STUDY OF A CHIMERIC XYLANASE BETWEEN *Streptomyces olivaceoviridis* E-86 FXYN AND *Cellulomonas fimi* Cex.

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Xylanase hydrolyzes β-1,4-glycosidic bonds within the xylan backbone. Two family 10 xylanases from *Streptomyces olivaceoviridis* E-86 and *Cellulomonas fimi* have high sequence homology in the catalytic domain (38%) but slightly different substrate specificity against the xylan and xylooligosaccharides. A chimeric enzyme (OC1415) between the two enzymes showed the moderate catalytic activity between the two parent enzymes, but showed some different substrate specificity: OC1415 did not produce xylose. To investigate the structure-function relationship of family 10 xylanase, we conducted the X-ray structure analysis of OC1415.

Crystals were obtained by the hanging drop vapor diffusion method at room temperature using a 20 mg/ml protein solution and a reservoir solution composed of 28 % ammonium sulfate and 2% McIlvaine buffer. After two weeks, thin needle crystal cluster appeared. Diffraction experiment was conducted at Photon Factory. The data sets were processed and scaled using the programs DENZO and SCALEPACK. The crystals belong orthorhombic space group $P2_12_12_1$, with cell dimensions of a=48.48, b=57.19, and c=106.67Å. Collected native intensity data included 13,853 unique reflections with 88.3% completeness and an R-factor of 0.065 from 100 to 2.2 Å resolution. Structural analysis is undergoing by the molecular replacement method.

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A7 : Powder methods

X-RAY POWDER DIFFRACTION STUDIES ON $Cd_XSn_{1-X}Se$ SOLID SOLUTION

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$Cd_XSn_{1-X}Se$ compound with x= 0,0.25,0.3,0.75 and 1.0 are synthesized in a quartz ampoule by mixing tin, cadmium and selenium powders in their stoichiometric ratio by melt technique. The synthesized compounds are confirmed by X-ray diffraction powder pattern as homogeneous and polycrystalline in nature. The composition analysis of these materials are carried out by atomic absorption spectrometer. It is well known that CdSe exists in hexagonal and cubic system whereas SnSe crystallizes in orthorhombic structure. These two materials do not form continuous solid solution. The powder diffraction pattern for all the five samples are recorded in JOEL JDX 8030 powder X-ray diffractometer. The XRD data of CdSe and SnSe samples are indexed with the help of JCPDS files and the unit cell parameters are refined by least squares procedure. In the case of mixed compounds the XRD peaks are indexed with the help of a graphical method and using the software DICVOL91. The lattice parameters are refined using software UNITCELL and listed in the following Table.

Table: Refined unit cell parameters for $Cd_XSn_{1-X}Se$ compound

X	a	b	c	Crystal system
0.00	11.37(5)	4.44(2)	4.02(2)	Orthorhombic
0.25	12.21(1)	4.34(1)	3.94(4)	Orthorhombic
0.30	12.11(2)	4.751(7)	4.19(1)	Orthorhombic
0.75	12.57(5)	4.19(3)	3.91(1)	Orthorhombic
1.00	4.307(3)		7.03(1)	Hexagonal

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AB INITIO X-RAY POWDER DIFFRACTION STUDIES OF POLYMORPHISM IN Na_2O-Bi_2O_2-V_2O_5 TERNARY SYSTEM

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A new class of oxide ion conductors in solid solution of Na_2O-Bi_2O_3-V_2O_5 ternary system has been synthesized by solid state reaction. Two polymorphic modifications, α- $NaBi_3V_2O_{10}$ and γ- $NaBi_3V_2O_{10}$ which form at 600°C and 450°C respectively, have been subjected to ab initio structure determination via powder X-ray diffraction. α- $NaBi_3V_2O_{10}$ is triclinic, space group P $\bar{1}$, a = 7.1964(4) Å, b = 7.0367(3) Å, c = 5.5139(2) Å, α = 84.440(3)°, β = 113.461(2)°, γ =112.319(2)° and V =236.46(2) Å^3. Upon Reitveld refinement the structure refines to R_p = 9.94%, R_{wp} = 13.11%, $R_{(I,hkl)}$ = 8.73% for 30 parameters and 4871 data points. The structure is built from $(Bi_2O_2)^{2+}$ single chains that extend along the c axis with VO_4 units joining the chains along both a and b directions. γ- $NaBi_3V_2O_{10}$ is also triclinic, space group P $\bar{1}$, a =14.7132(3) Å, b =9.3429(2) Å, c = 10.3896(2)Å, α =69.855(1)°, β =128.030(1)°, γ =123.566(1)° and V = 937.37(2)Å^3. The final refinements gave R_p =3.84%, R_{wp} = 4.90%, $R_{(I,hkl)}$ = 2.44% for 107 parameters and 4850 data points. The structure depicts an entirely new motif, unlike the earlier polymorph, hitherto unknown in doped Bi_2O_3-V_2O_5 system. The structure is built of $(Bi_2O_2)^{2+}$ double chains extending along the [0 $\bar{1}$ 1] direction with VO_4 units joining these chains. Both structures depict, for the first time features which are not common to the Aurivillius family of compounds and are likely to display isotropic conductivity.

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ESTIMATION OF ERRORS IN THE MEASUREMENTS OF UNIT-CELL PARAMETERS: STATISTICAL UNCERTAINTIES OF PEAK POSITIONS OF POWDER DIFFRACTION LINES DETERMINED BY INDIVIDUAL PROFILE FITTING

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A formula for estimating a statistical uncertainty of peak position, determined by individual profile fitting, has been derived. A magnitude of the statistical uncertainty is given by (sum of peak profile intensities)$^{-1/2}$ × full-width at half-maximum × form factor × correlation factor × quality factor × the goodness-of-fit index. The form factor depends on a shape of diffraction profile, and it becomes smaller by 40% when the profile shape changes from Lorentzian to Gaussian. The correlation factor represents the parameter correlation between the peak position and the parameter for profile asymmetry, and it becomes unity when the profile shape is symmetric or the parameter for profile asymmetry is fixed during the least-squares fitting. The quality factor depends on a peak-to-background ratio. The formula was experimentally verified by using diffraction data sets of CeO_2 and Si powders. The statistical uncertainty is essentially based on the counting statistics and profile width. Therefore, the peak position of a strong and sharp peak in the low angle region can be determined more precisely than that of a weak and broadened peak in the high angle region. Precision of unit-cell parameters will be discussed in connection with the optimization of experimental conditions.

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RECENT ADVANCES IN STRUCTURE SOLUTION FROM POWDER DIFFRACTION DATA

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Crystal structure determination frequently is a prerequisite for the rational understanding of the solid state properties of new materials. Even though single crystal diffractometry is the method of choice when it comes to crystal structure determination, this approach is often impractical because of the difficulties involved in growing single crystals of appropriate size. High quality powder samples, on the other hand, are much easier to obtain. Using direct-space structure solution techniques, increasingly complex crystal structures can nowadays be solved directly from powder diffraction data. Combined with easy-to-use tools for model building and visualisation as well as molecular mechanics and first principles Density Functional Theory (DFT) calculations, crystal structure solution from powder diffraction data is becoming a routine task. To illustrate the applicability of direct-space Monte Carlo techniques to the crystal structure solution of organic and inorganic compounds, a variety of structure solutions with the program Powder Solve will be presented.

Recent advances include the determination of a preferred orientation correction during the structure solution search and the use of parallel tempering, a newly implemented global search algorithm. As a complementary technique, first principles DFT calculations have been used successfully to validate structure solutions and to aid the subsequent Rietveld refinement.

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A7-5

STRUCTURAL STUDIES OF CRYSTALLINE, MICROPOROUS $ALPO_4$-18 AND METAL SUBSTITUTED $ALPO_4$-18

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Zeolites and related materials show exciting applications in the field of catalysis in which their highly ordered framework structures containing pores play a major role. The chemistry of zeolites and other molecular sieves cannot be understood fully without the structural information since both are intimately related. $AlPO_4$-18 (AEI) is a crystalline, microporous aluminophosphate molecular sieve having a neutral framework charge. Incorporation of divalent metals like Mg, Zn, Mn, Ni etc. in the framework imparts acidic character to the framework. These metal substituted molecular sieves find exciting catalytic activity for conversion of methanol to light olefins. The structure of the neat $AlPO_4$-18 synthesized using tetraethylammonium hydroxide as the structure-directing agent is monoclinic. There are no structural characterization reports on the metal substituted $AlPO_4$-18 using powder X-ray diffraction technique. We report the structural characterization of metal (Mg and Zn) substituted $AlPO_4$-18 using powder X-ray diffraction and NMR techniques. The powder x-ray diffraction patterns of the metal substituted samples show remarkable decrease in crystallinity as compared to the neat AlPO, which decreases with the increasing concentration of metal atoms. Incorporation of the metal in the framework results in decrease in the symmetry of the sample as the space group changes from C2/c for the neat $AlPO_4$.18 in the monoclinic system to $P2_1$ for the metal substituted samples. Variation in the lattice parameters of the samples observed with the increasing metal concentration indicates metal incorporation in the framework.

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POWDER DIFFRACTION STUDIES OF HIGH-TEMPERATURE PHASE TRANSITION OF $CEALO_3$

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$CeAlO_3$ is one of the compounds of a series of perovskite-type rare-earth alminium oxide ($REAlO_3$). In these compounds the crystal symmetry and phase transition temperature systematically change according to the ionic radius of the rare-earth, but $CeAlO_3$ is an exception to this tendency [1,2]. We have been investigating the detailed structure and tried high-temperature synchrotron X-ray powder diffraction experiments. Experiments were carried out at the beam line 3A of Photon Factory. The synchrotron radiation from a bending magnet is monochromatized and horizontally focused by a Si(111) double-crystal monochromator. The wavelength is 1.38(A). The 3-circle-4-axis diffractometer with a Si(111) analyzer monochromator was used as a powder diffractometer. A high-temperature furnace with sample rotation system was used for sample heating. Powder diffraction profiles of selected peaks were observed changing sample temperature from 300K to 550K by theta-fix 2theta-scanning method. Analysis of obtained profiles by a profile-fitting program, 'PROFIT[3]' revealed existence of phase transition at about 546(K). The transition from orthorhombic to rhombohedral is consistent with other $REAlO_3$ but the temperature is much different from others.

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A7-7

INVESTIGATIONS ON THE SYNTHESIS, STRUCTURAL AND MICROSTRUCTURAL CHARACTERIZATIONS OF MG BASED K_2PtCl_6 TYPE (Mg_2FeH_6) HYDROGEN STORAGE MATERIAL PREPARED THROUGH MECHANICAL ALLOYING

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This paper deals with the formation of a new ternary hydride Mg_2FeH_6 (K_2PtCl_6 type) in a single step procedure following the process of mechanical alloying of initial stoichiometric ingredients Mg and Fe under hydrogen ambient. The optimum yield of formation of single phase Mg_2FeH_6 was achieved by hydrogen (~10 atm.) milling of constituent elements at a speed of 400 rev. min^{-1} for various milling duration. The structural characterization of the ball milled (2Mg+Fe) powder was carried out using Philips X-ray diffractometer by taking out the sample intermittently from the attritor mill in regular intervals of time. It was found that the Mg_2FeH_6 phase starts forming at a milling duration corresponding to 14 hrs. and the optimum Mg_2FeH_6 phase formation was obtained at 20 hrs. The proportion of this phase was estimated by employing Rietveld refinement analysis of the x-ray powder diffraction data and it was found to be 63%. This is the highest phase proportion reported so far for the Mg_2FeH_6 phase when formed from elemental Mg and Fe following the route of mechanical alloying. Together with Mg_2FeH_6 phase, some quantity of Fe (about 37%) is also present. It may be pointed out that Fe being a magnetic impurity can be removed leaving the Mg_2FeH_6 content to be nearly 90-100%. However, such purification was not done in the present investigation. In order to see further changes, we have also investigated synthesis of the material obtained by longer milling duration of 25, 28 and 30 hrs. The XRD patterns for the 25, 28 and 30 hrs. ball milled materials revealed that the intensity of Mg_2FeH_6 peaks get reduced in comparison to Fe peaks. This implies that beyond 20 hrs, there is no further increase in the phase proportion and the amorphization starts taking place. The post-sintering process of these mechanically alloyed samples did not improve the Mg_2FeH_6 phase proportion and yield as evidenced through XRD. The x-ray structural characterizations revealed that the as-milled Mg_2FeH_6 material (milling duration of 20hrs; under H_2 pressure ~10 atm., speed ~400 rev. min^{-1}) corresponds to the known face centered cubic structure with lattice parameter a = 0.6446(2) nm. The elemental (chemical) compositional analysis has been carried out for the mechanically alloyed Mg_2FeH_6 materials using EDAX technique. The results confirm the correct stoichiometric ratio of the initial mixture (2Mg+Fe). The surface morphologies of the (2Mg+Fe) mixture before and after mechanical alloying have been performed using scanning electron microscopic technique. The SEM explorations reveal the spongy like feature of Mg_2FeH_6 agglomerates.

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STUDY OF CRYSTAL STRUCTURE OF DOUBLE PEROVSKITE MATERIAL $Sr_2(FeMo)O_6$

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In this paper we report our recent results of crystal structure investigation by X-ray powder diffraction method for $Sr_2(FeMo)O_6$. The samples were prepared by conventional solid state reaction. The lattice constants were determined by WIN-METRIC programme on the basis of face centered cubic Bravais lattice's unit-cell. The simulated X-ray diffraction spectrum of this material was calculated. The obtained results show that the material has space group symmetry of Fm3m (225), with the lattice constant a = 7.8930 Å and chemical composition of $Sr_2(FeMo)O_6$. The crystal structure of this material has ordered structure of NaCl type with Fe and Mo being alternatively located in sites 4a (4b); strontium atoms are in sites 8c and oxygen atoms are in sites 24e. The distances of the atoms in unit cell were calculated. Magnetic properties and Raman spectrum of $Sr_2(FeMo)O_6$ were also studied.

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A7-9

COMPUTATION OF STRAIN TENSOR AND SHAPE OF CRYSTALLITES IN SILK I MODIFICATION OF *BOMBYX MORI*

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Using the X-ray powder data obtained from *Bombyx mori* Silk fibroin in Silk I modification, we have estimated the strains using profiles of several *(hkl)* reflections observed in the fibroin. For this purpose, we have used line profile simulation and matching with the experimental, on the basis of a paracrystalline one-dimensional Hosemann's model proposed by us[1]. The shape of the crystallite and size along different directions in the fibroin have also been estimated and presented here. From these results the strain tensor has been computed using the approach given by Wilke and Martis[2,3]. The effect of these strains on the molecular arrangement within the crystal structure and hence to identify the portion of the chain within the unit cell which participates in inducing the intrinsic strain during the formation of the fiber are being investigated.

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SYNTHESIS AND X-RAY POWDER DIFFRACTION STUDY OF DEFECT TETRAHEDRAL STRUCTURE COMPOUND $CUZNGA_3TE_6$

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Normal tetrahedral structure quaternary compounds crystallize either in stannite-type structure or wurtzite stannite-type structure where cations have ordered arrangement. Simple zincblende or wurtzite-type structures are observed for the compounds with no ordered cation arrangement. Not many 'defect-tetrahedral structure' quaternary compounds have been investigated so far. $CuZaGa_3Te_6$ was synthesized by the melt and anneal technique. X-ray powder diffraction data were collected in the 2θ range from 20° to 158° on a Siemens D500 X-ray diffractometer with a Cu-target source in conjunction with a scintillation detector and a graphite monochromator in the diffracted beam. The diffraction pattern was indexible on a body-centered tetragonal cell with a=0.5946(2)nm and c=1.1891(5)nm. The X-ray density, D_x was calculated as $5.81\times10^3 kg/m^3$. The compound 0may be crystallizing in a defect chalcopyrite-type structure, space group $I\bar{4}$ with Z=4/3.

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A7-11

RIETVELD REFINEMENT OF COPPER DOPED $LACU_XCO_{1-X}O_3$

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Perovskite type of oxides such as $La_{1-x}A_xBO_3$ with A=Ca, Sr, Ba and Ce and B=Co, Mn, Ni and Fe have been used as catalysts for the methane combustion and the activity increase is seen with increase in ionic conductivity with the introduction of oxygen and due to Ce^{III}/Ce^{IV} redox couple. $LaCo1_{-x}Cu_xO_3$ samples with copper content varying from 1-20 mol% were prepared using citrate complexation method and the Rietveld refinement of their powder XRD profiles was carried out using the program FULLPROF. The samples were scanned on STOE/STADI-P with transmission geometry. The program TREOR was used to index the powder pattern, which gave a hexagonal cell, and the refinement was started with the model having space group R3_c with constraints on the occupancy of copper and cobalt to be equal to one. The Rietveld refinement gave precise fitting for each sample with a reliability factor (R_{wp}) less than 4.8 – 6.7% and the goodness of fit varies from 1.18-1.22 for all the four samples. The substitution of cobalt by Cu^{2+} tends to increase the cation-oxygen-cation interactions. This substitution leads to a postive defectivity, which in turn should be compensated by oxygen vacancies in the absence of Co^{4+} species. The values of the Co-O bond distance for all samples varied in the range 1.931-1.932 Å which is lower than the expected on the basis of ionic radii which could be due to covalent contribution to the bond. The cooperative breathing modes of M-O bonds and the labile oxidation states are probably responsible for the catalytic activity, electrical conductivity and oxygen transport property of transition metal perovskite structures.

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A CLEVER METHOD OF QUANTITATIVE ANALYSIS OF ALUMINUM-RICH MULLITE

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Mullite is an important ceramic material. Its typical chemical composition is $3Al_2O_3 \cdot 2SiO_2$. In fact, frequently the actual chemical composition of mullite samples deviates from this ideal value owing to the different preparation technology, but its structure framework is still invariable. The quantitative analysis of mullite means to determine the content of mullite in a mixture system, which is composed of polycrystalline mullite and some amorphous products in preparation. The difficulty lies in that the intensities of diffraction peaks of the mullite phase are variable along with the different ratio of Al and Si atoms of the mullite phase.

Using structure parameters of different aluminum-rich mullites, we caculated their K(hkl) values. $K(hkl) = M(hkl)|F(hkl)|^2Lp(hkl)$. Here F(hkl) is the structure factor of (hkl) reflection, M(hkl) is the multiplicity factor and Lp(hkl) is the Lp factor. The K(hkl) value of every hkl reflection is variable along with the different ratio of Al/Si. We selected and analyzed those reflections, the K(hkl) value of which changes linearly along with the ratio of Al/Si. We found that the combination of the integrate intensity of three reflections I(100) + 0.56[I(120) + I(210)] is not variable. Provided the integrate intensity of these three reflections of samples is determined, the quantitative analysis of mullite can be completed rapidly and accurately.

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A8 : Aperiodic structures

A8-1

A DISSECTION OF THE GUMMELT DECAGON LEADING TO A CLASSIFICATION OF GUMMELT-TYPE PATTERNS

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Steinhardt *et al.* have proposed a model for the structure of decagonal Al-Ni-Co, built from overlapping clusters of a single type. The structure arises from a decoration of the decagons of a Gummelt covering. The unit (essentially a decagonal prism) was called by Steinhardt *et al.*, a "quasi unit cell". We propose a classification scheme for patterns derivable by decorating the Gummelt decagon. The classification makes use of the fact that G-patterns can also be derived from decoration of a *tiling* of the decagon. The corresponding tiling patterns employ three kinds of tile, and are a modification of the Penrose 'kite and dart pattern' The tiles are analogues, for decagonal quasiperiodic patterns, of the "asymmetric units" of a periodic pattern; and special points on the tiles are analogues of Wyckoff positions. This provides a simple mode of description and classification of all "Gummelt-type structures".

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THE MODULATED STRUCTURE OF COPPER-(4,4'-BIPYRIDYL SULFATE COORDINATION POLYMER COCRYSTALLISED WITH TERAPHTHALIC ACID

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Solvothermal reaction of copper sulphate, teraphthalic acid and 4,4'-bipyridine gave yellow crystals [Cu(C10H8N2)]4(SO4)2.2(C8H6O4), a 19.597(4), b 34.771(3), c 34.771(3), β 107.52(3) , C2/c, Z = 8] describable as a commensurate modulation of an idealised Z = 2 parent structure with aP = a/2, bP = b/2, cP = c. In the parent, polymeric chains of [-CuI-bipy-CuI-bipy-] are propagated by an n glide, 1/2+x,1/2-y,-1/2-z, and are cross linked (Cu-O-S-O-Cu) by the sulfate groups which lie on 2 fold axes. The teraphthalic acids lie on centres of inversion and hydrogen bond to the sulfates. The parent n glide cannot remain a symmetry element of the modulated structure. A (3+1) dimensional approach, modulation vector (ap*+bp*)/2, suggests the possibilty of a twinned triclinic crystal but observations of weak reflections with h even, k even, h+k=4n+2, preclude this option. A (3+2) dimensional approach with modulation vectors ap*/2, bp*/2 allows for space group C2/c with four options for the selection of the quarter of the parent structure symmetry elements to be retained. Reverting to the standard setting this allows four origin options for the asymmetric unit but origins 1/4,1/4,0 apart do not correspond to alternative origins for the asymmetric unit of the parent structure. In the correct model, the teraphthalic acids no longer sit on inversion centres. Some residual disorder about a 2-fold axis remains but an ordered structure in a lower symmetry space group was shown to be inappropriate.

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A8-3

STRUCTURE OF 3-MERCAPTO 4-N(4'-CHLOROBENZYLIDENE)-5-PHENYL, 1,2,4-TRIAZOLE

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Derivatives of 3-mercapto-5-phenyl 1, 2, 4-triazole have shown promise as antibacterial, antifungal and anti-inflammatory agents while they show very good therapeutic activity, they are also known to present a certain degree of mutogenic and carcinogenic properties. This may be due to the byproducts formed during their metabolism. The triazole derivatives are synthesized by the reaction of simple condensation of an amine and an aldehyde in alcoholic medium to form azomethine linkage(-N=CH-). The title compound, C_{15} H_{11} N_4 S Cl synthesized by the reaction 4-amino-3-mercapto-5-phenyl 1,2,4-triazole with 4-cholorobenzaldehyde in absolute alcohol has been screened for its antimicrobial activity.

The colorless platy crystals of the title compound were obtained using ethanol as the solvent. It crystallizes in monoclinic system, space group $P2_1/c$ with a=18.6686Å, b=4.0824Å, c=19.5796Å, β=102.3548°, V= 1457.65Å^3 and Z=4. The intensity data were collected on an Enraf Nonius CAD4 diffractometer. The structure was solved using direct methods and refinement by full matrix method using SHELX97. The final R value converged to 5.56%. The conformational analysis will be discussed in detail.

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MODULATED APERIODIC CRYSTAL STRUCTURE AND SUPERCONDUCTING MICROMECHANISM IN $YBa_2Cu_3O_x$ COMPOUNDS

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From the ESR experimental results, two different types of the Electron Spin Superexchange Couple Pairs [Cu-Y-Cu] in $YBa_2Cu_3O_x$ (YBCO) ceramics have been revealed: A singlet pair ($\uparrow\downarrow$) on the long diagonal of the twined Y-unit-cell by a distorted (a,b) angle $\Theta \approx 72°$ corresponds to the superconducting phase and a triplet pair ($\uparrow\uparrow$) on the short diagonal of the twined Y-unit-cell by $\Theta \approx 78°$ corresponds to the semiconducting phase. The persistence of the spin couple pairs as well as the superconducting micromechanism in YBCO correlates well with the modulated substructure system in the material. On the basis of the behaviour of the quasi-free electrons in the Y-unit-cell as a Nano Resonant Cavity of the short-range order structure of the material some important issues can be addressed. Some examples are the existence of the energy gaps, the fundamentals of the superconductivity in YBCO where the singlet pair ($\uparrow\downarrow$) revealed plays the role of the "Cooper Pair", an equation determining the superconducting transition temperature Tc, and an equation determining the temperature Tx of the conductivity maximum point in the semiconducting phase. The calculated results are in a very good agreement with the respective measured data.

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A DETAILED ELECTRON DIFFRACTION STUDY OF THE FERROELECTRIC AND FERROELASTIC α POLYMORPH OF $K_3MoO_3F_3$.

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$K_3MoO_3F_3$ is a representative member of the $A^{1+}{}_2B^{1+}M^{VI}O_3F_3$ (A, B = K, Rb, Cs; M^{VI} = Mo, W) family of elpasolite related oxyfluoride phases and undergoes two reversible structural phase transitions on cooling from the highest temperature, ideal cubic ($Fm\bar{3}m$) γ polymorph. The room temperature α polymorph of these phases is ferroelectric and ferroelastic. Problems associated with pseudo-symmetry and twinning have led to much confusion in the literature as regards the unit cell and space group symmetry of this polymorph. A detailed electron diffraction and XRPD study has been made of the ferroelectric room temperature α polymorph of $K_3MoO_3F_3$. It is shown that the true symmetry of this polymorph is neither tetragonal, trigonal or triclinic as previously reported but rather monoclinic $I1a1$, $a = 2a_p-c_p$, $b = 4b_p$, $c = a_p+2c_p$ when expressed in terms of the underlying elpasolite (ordered perovskite) parent structure type. The sharp satellite reflections characteristic of the monoclinic supercell are shown to fall on and to co-exist with a highly structured, continuous, three-dimensional diffuse intensity distribution (presumably arising from local O/F ordering and associated structural relaxation).

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A8-6

PURIFICATION AND STUDY OF ITS EFFECT OF POLYTYPISM IN SOLUTION-GROWN CADMIUM IODIDE CRYSTALS USING X-RAY DIFFRACTION.

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The Cadmium iodide has been purified using a zone-refining method fabricated by us. The crystals have been grown in two batches using unpurified and purified material. A comparative study has been made on these batches for polytypism using x-ray diffraction technique. Total number of polytypes involved are 360.

Formation of small period polytype 2H is governed by both temperature and impurities contained in the starting material. 4H is the most stable polytype. Higher occurrence of unidentified polytype in crystals of purified material has been attributed to free movement of edge dislocations during growth. The results have been examined against empirical considerations of earlier investigations.

THE QUASICRYSTAL-TO-CRYSTAL TRANSFORMATION - UNIT CLUSTER APPROACH FOR d-Al-Co-Ni.

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Experimental studies provided evidence for a transformation between decagonal quasicrystal phases and periodic approximants, leading to orientationally ordered crystalline nanodomain structures.

Theoretical work on the quasicrystal-to-crystal transformation is mostly concentrating on higher-dimensional models. Authors use the phason-strain formalism or general shears and rotations of the hyperlattice. These approaches, however, say little about real atomic-scale processes.

A geometrical model for the quasicrystal-to-crystal transformation of d-Al-Co-Ni was developed previously, based on computer simulations in direct and reciprocal space, with a mechanism involving only small atomic displacements[1].

Gummelt proposed a concept of non-periodic coverings, with one "unit-cluster" instead of tilings composed of two or more "unit-cells"[2]. Applying that concept to structure models of quasicrystal and approximant improves the transformation mechanism proposed.

It provides new relevance for tiling-flip mechanisms on the cluster-scale as a tool to study phason fluctuations. Monte Carlo simulations of continuously changing cluster coverings and the respective diffraction patterns are presented. Some of the outcomes shed new light on the transformation mechanism and on order / disorder processes evidenced in diffuse scattering.

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ROLE OF ANTIPHASE BOUNDARY ENERGY IN PERIODIC TO QUASIPERIODIC TRANSFORMATIONS IN SUPERLATTICES

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Results of the strip projection method have established that formation of planar defects is the initial stage of a periodic to quasiperiodic (P to QP) transition. While the crystal to quasicrystal transformation in certain systems initiates through the occurrence of periodically spaced faults, antiphase boundaries (APBs) play a similar role in periodic to quasiperiodic transformations in superlattices. Energy of the relevant planar defect is, therefore, expected to play an important role in the occurrence of periodic to quasiperiodic transformations of either kind. In the Monte Carlo simulation carried out in this work, the change in APB energy, accomplished by suitably altering the pair interaction energies, was found to explain the diffraction effects observed in the course of the transition - from periodic Al_5Ti_3 to a quasiperiodic superlattice structure to another periodic structure $Al_{11}Ti_7$ - observed in Al-rich single phase γ-TiAl alloys with varying compositions. The simulation results bring out salient features of the atomic arrangements in imperfectly ordered quasiperiodic and nearly quasiperiodic structures encountered in this transition.

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THE MULTIPLY TWINNED MODULATED STRUCTURE OF TRIETHYL PHOSPHINE SULFIDE

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The published structure (M. Van Meerssche & A. Leonard, (1959) Acta Cryst. 12 1053-1054) of S=P(C2H5)3 is described as having a 1:1 disorder in space group P63mc with Z = 2 with P31c describing a proposed ordered structure rather than P63. Synthetic precession photographs obtained from data collection on a Nonius CCD diffractometer clearly indicate a doubling of the a and b axes. The parent P63mc structure can also be described as a C centred orthorhombic cell of Ccm21 symmetry with ap' = 2ap + bp, bp' = bp, cp' = cp with four molecules per cell. The dominant modulation creating the extra reflections is a combination of displacements parallel to c and not an ordering of the ethyl ligands. This mode lowers the Ccm21 symmetry to Pnm21 with three fold twinning restoring hexagonal diffraction symmetry. Further modulations of the parent structure seem necessary, with partial ordering in a mode of Pna21 symmetry is a reasonable option. This suggests a probable six fold twinning since local symmetry of an average structure would then be lowered to Pn. Absences in the diffraction pattern suggest that the n glide is a dominant feature with adjacent layers displacing in opposite directions along c.

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A9 : Charge density studies

A9-1

CHARGE DENSITY DISTRIBUTION AND X-RAY ABSORPTION SPECTROSCOPY OF IRON-NITROSYL THIOLATE COMPLEXES

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The biomimic tri-, di- and mono- nuclear iron-nitrosyl complexes formed from the degradation of iron-sulfur protein are synthesized. The coordination sphere of Fe in the trinuclear complex and in the mononuclear one can be described as a tetragonal pyramidal $Fe(NO)(S)_4$ core. The dinuclear one consists of one dinitrosyl local tetrahedral $Fe(NO)_2(S)_2$ core and one trigonal bipyramidal $Fe(NO)(S)_4$ core. Electron density distributions of these complexes are studied in terms of a multipole model based on the X-ray diffraction data and are also studied by the molecular orbital calculations. Topological properties associated with the bond critical points (BCP), Laplacian of the electron density as well as electron density at the BCP of each chemical bond will be presented. The comparison between experiment and theory will be made. The intra-molecular chemical bond as well as the binding in the iron cores of trinuclear and dinuclear complexes will be discussed. The binding interactions between two Fe atoms with short Fe-Fe distance of 2.5772(3) Å and 2.6625(2) Å are good examples of metal metal interactions. The oxidation states and the net atomic charges of the Fe atoms as well as the magnetic properties are also interesting aspects of these complexes. The charge density investigation complimented by the X-ray absorption spectroscopy is expected to lead to the understanding of such properties.

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CHARACTERIZATION OF BR···BR INTERACTIONS IN TWO POLYMORPHS OF 4-BROMOBENZAMIDE CRYSTALS BY ELECTRON DENSITY DISTRIBUTION ANALYSES --- DATA COLLECTIONS ON A CONVENTIONAL IP WEISSENBERG CAMERA AT SPRING-8 BL04B2 BEAM LINE

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Short Br···Br contacts have been observed in many organic crystals and attracted great interests from the view point of the crystal formation. To elucidate the properties of this Br···Br interaction, we attempted electron density distribution analyses. 4-Bromobenzamide crystallizes into two crystalline forms (α- ,(I), and β-form, (II)). Both of them show short Br···Br contacts, while directions of these contacts are different.

The diffraction data of the crystals of these two-forms were collected at 100K using the IP Weissenberg camera, DIP-LABO, at BL04B2 in SPring-8 with radiation of 37.8keV(0.3282Å) to reduct absorptions of X-rays. An oscillation method was applied to the data collections. In order to achieve high completeness, some data sets were collected with different crystal orientations. Especially, for the crystal of (I), five data sets were collected for low and high angle regions with different exposure time. The data were processed by the program DENZO. Conventional and high order refinements were carried out by the program SHELXL-97. Now we are carrying on the structure analysis of (I) by the multipole expansion method. Current results are as follows; R_{int}, $R(F)$, $(\sin\theta/\lambda)_{max}$, reflections of $I > 2\sigma(I)$, unique reflections are 0.072, 0.042, 1.0, 6070 and 5143, respectively.

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A9-3

ARE SQUARATE AND CROCONATE DIANIONS AROMATIC? AN EXPERIMENTAL CHARGE DENSITY STUDY.

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The electronic charge density method of X-ray crystallography is employed to study diverse aspects of molecular systems. A comparative study of the structure and topography of charge density in the squarate and croconate dianions has been carried out based on low-temperature X-ray diffraction measurements. Both the dianion rings exhibit a high degree of planarity with uniform C-C bond lengths and angles typical of conjugated systems. Accordingly, the bond critical points in the two dianions carry similar densities as well as Laplacians. Deformation density maps reveal that the squarate ring is more strained than the croconate. Both the rings exhibit (3, +1) ring critical points (RCPs). The density and the Laplacian associated with the RCP of the squarate anion are 0.59 $eÅ^{-3}$ and 11.8 $eÅ^{-5}$ respectively, while for the larger croconate ring, they are nearly one-half these values. RCP parameters of the dianions have been compared with those of several aromatic as well as non-aromatic cyclic systems from literature. A plot of the Laplacian versus density at RCP of the squarate and the croconate dianions along with other cyclic systems of different sizes shows how one can distinguish, aromatic and nonaromatic systems. The aromatic rings fall in a region where the Laplacian is roughly proportional to the density while the non-aromatics show no definitive trend. The plot may be useful in the case of polycyclic systems where aromatic and nonaromatic rings coexist.

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OBSERVATION OF THERMALLY EXCITED 4f-STATE AND MECHANISM OF ELECTRON TRANSFER IN THE KONDO-CRYSTAL CeB_6 BY MULTI-TEMPERATURE X-RAY DIFFRACTION .

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Electron density distributions (EDD) in rare-earth complexes have been supposed to be almost impossible to measure by X-ray diffraction. However EDD in CeB_6 is highly interesting since 4f-electrons are spontaneously transferred from Ce to B_6 with a decrease in temperature by Kondo effect. Measurements at 298, 230, 165 and 100 K and a least-squares analysis assuming spin-orbit interaction for 4f-electrons revealed thermally excited 4f-state at 298 K and essential nature of the changing system beyond our expectation. It revealed that more 4f-electrons and B-2p electrons which contribute to B-B bonds within B_6 regular octahedra at corners of a cubic cell are transferred at lower temperature to B-B bonds connecting B_6 octahedra. The localized electrons permit small but significant expansion of the outermost lying Ce-5p(j=3/2) orbitals and enhanced anharmonic vibration (AHV) at low temperature, which explains the observed EDD quite well. The enhanced AHV in one of the most closest-packed crystals corresponds to an increase in entropy. Since the 4f-electron-transfer itself increases entropy, it cannot be stopped, though 4f-orbital becomes more stable at lower temperatures. The first excited $4f_{7}$ orbital has significant electron population at 298K corresponding to an energy gap of 470K and discontinuous change of crystal structure by it is also observed.

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A9-5 =A3-11

REFINEMENT OF CRYSTAL STRUCTURAL PARAMETERS AND CHARGE DENSITY USING CONVERGENT-BEAM ELECTRON DIFFRACTION

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We developed a new method to refine crystal structural parameters using convergent-beam electron diffraction (CBED), which is applicable to *nanometer-size* crystal structure analysis (K. Tsuda and M. Tanaka: Acta Cryst. A55, (1999) 939). The method is based on the fitting between theoretical calculations and experimental intensities of energy-filtered *two-dimensional* CBED patterns containing zeroth-order Laue-zone (ZOLZ) and higher-order Laue-zone (HOLZ) reflections. The use of HOLZ reflections is essential for the present method because small displacements of atoms can be sensitively detected using HOLZ reflections with large reciprocal vectors. For this purpose, we developed an energy-filter transmission electron microscope (JEM-2010FEF) and an analysis program (MBFIT) to refine structural parameters based on the dynamical diffraction theory.

Using this method, we have refined the atom positions and anisotropic Debye-Waller factors of the high-temperature phase of $LaCrO_3$. Clear anisotropy of the thermal vibration of the oxygen atoms has been successfully detected by electron diffraction for the first time. The low-order structure factors, which are sensitive to valence electrons, were refined together with these structural parameters, and were converted to deformation charge density. The result clearly shows charge transfer from La and Cr atoms to O atoms.

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A9-6

CHARGE DENSITY STUDIES BY THE MEM AND FLAPW

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The Maximum Entropy Method (MEM) is one of the powerful tools for the charge density study of crystalline materials. By the development of the MEM/Rietved Method, the new aspects of bonding nature for various crystalline materials have been revealed from synchrotron radiation powder data. In order to explore the origin of the bonding nature, a comparative charge density study between the MEM and the theoretical charge density should be one way to examine the characteristic feature of bonding electron distribution. In the talk, the charge density studies of $MgCu_2$, $PbTiO_3$ and $BaTiO_3$ by the MEM/Rietveld method and the Full Potential Linear Augmented Plane Wave (FLAPW) method will be presented to illustrate a usefulness of the comparative study of MEM and FLAPW method.

In the MEM charge density of the Laves Phase, $MgCu_2$, the strong covalent bonding was found for the Cu-Cu kagomé network, which is characteristic close-packed atomic arrangement of the Laves phase structure. This characteristic covalent feature was well reproduced in the theoretical charge density by the FLAPW method and identified as the result of the hybridization of Cu(p^3d^3) orbital. The results of the $PbTiO_3$ and $BaTiO_3$ will be also presented and discussed in connection with other ferro-electrical properties.

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A9-7

ELECTRIC PROPERTIES OF CRYSTALS USING X-RAY DIFFRACTION.

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Single crystal X-ray diffraction measurements at ambient or low temperatures allow obtaining an accurate description of the electron density distribution. We have been interested in determining electric properties from such data for materials with interesting electro-optical applications. The examples of spontaneous polarisation and pyro-electricity will be presented and we will discuss limitations due to fundamental and practical problems. Only in certain cases, will it be possible to give a rigorous definition of the spontaneous polarisation based on the charge density, independent of how accurate this may be.

A second part will concern diffraction measurements of piezo-electric coefficients. We have constructed an apparatus allowing us to apply electric fields to single crystals during the diffraction experiment. In order to minimise long-term modifications of the defect structure of the sample due to the field, a crenel shaped high voltage is applied. This technique is inspired by early work by Puget and Godefroy (1975) and I. Fujimoto (1982) and others. Our first results show that piezo-electric coefficients can be determined quite reliably from changes in Bragg angles. In principle we may analyse structure and electron density polarisations by measuring changes in the Bragg intensities. This is nevertheless highly delicate because of problems with reproducibility of the minute induced changes.

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A9-8

CHARGE DENSITY ANALYSIS OF 5-FLUOROURACIL AND 1,3-DIMETHYL-5-FLUOROURACIL

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Molecular recognition, self-assembly of complex molecules, coordination chemistry and generation of nucleotide structures are governed by weak intermolecular interactions. The study of interactions involving fluorine is of particular interest because of the unusual behavior of 'organic fluorine' in accepting hydrogen bonds. The charge density distributions in crystals of 5-fluorouracil and 1,3-dimethyl 5-fluorouracil have been analyzed using high-resolution X-ray diffraction data at 100K. 5-fluorouracil has dominant N-H...O interactions along with several weak C-H...O bonds. C-H...F and C-H...O interactions contribute to the packing in the crystal structure of 1,3-dimethyl 5-fluorouracil. Both structures have been evaluated in terms of critical points properties, ρ_b and Laplacian ($\nabla^2\rho$) distribution. C-H...F interaction appears in the structure of 1,3-dimethyl 5-fluorouracil indicating that the methyl substitution masks the propensity for the formation of strong N-H...O bonds present in the structure of 5-fluorouracil.

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X-RAY AND NEUTRON DIFFRACTION STUDIES OF SHORT SINGLE WELL N-H-O AND N-D-O HYDROGEN BONDS

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Short single well N-H-O hydrogen bonds are of considerable physical and biological interest. We have investigated those found in the mixed crystal 2[4,4'-bipy$H_{0.5}$][C_6H_2-1,2,4,5-$(COO)_4$-H_3] and in dinicotinic acid [C_5H_3N-3,5-$(COO)_2$-H_2] by variable temperature X-ray and neutron diffraction. The N--H--O distances are between 2.50 and 2.55Å and change only slightly with temperature. However the position of the hydrogen atom shows considerable temperature dependence with N-H ca. 1.2Å and O-H 1.3Å at 20K and the reverse holding for room temperature. This apparent 'proton translation' could be interpreted as due to the asymmetry in the H-bond potential well. To study this further large deuterated crystals of dinicotinic acid were prepared hydrothermally using deuterium oxide as solvent. This showed a lengthening of 0.04Å in the N---O distance and an even *greater* temperature dependence of the N-D and O-D lengths compared to the *protio* analogue. These novel findings contravene the conventional model of deuteration effects on low-barrier hydrogen bonding.

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A9-10

CHARGE ORDERING AND VALENCE-CONTRASTED DIFFERENCE-FOURIER MAPS IN Eu_3S_4

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Eu_3S_4 is a mixed-valence compound that has divalent and trivalent Eu ions in the ratio 1 : 2 and present an interesting example of the electronic arrangement and transport property. Synchrotron X-ray anomalous scattering technique was applied for the valence-difference contrast in the vicinity of Eu L_{II} absorption edge in order to determine the crystal structure and charge-ordering scheme for a low-temperature phase of Eu_3S_4. A vertical-type four-circle diffractometer was used for single-crystal work at wavelengths of λ = 1.63116 and 1.62977 Å in the beamline BL-10A, Photon Factory, Japan. The temperature dependence of 400, 040 and 004 intensities clearly showed that a room-temperature phase having a *bcc* Th_3P_4 structure (a = 8.516 ± 0.002 Å) transforms to a tetragonal $I\bar{4}2d$ cell (c/a = 1.004) at 188.5 K. The charge ordering was determined from the variation of residual factors in the least-squares refinement with a large difference in atomic scattering factors between Eu^{2+} and Eu^{3+}. The result indicated that the 4*a* site is occupied by only Eu^{3+}, while the 8*d* site is occupied by Eu^{2+} and half-remained Eu^{3+}. The existence of charge ordering was also supported by the difference-Fourier syntheses assumed that either Eu^{2+} or Eu^{3+} ions occupy all Eu sites.

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A CHARGE DENSITY STUDY OF XYLITOL AND RIBOTYL, TWO PENTOSE EPIMERS

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The two pentose isomers xylitol and ribitol differ significantly in their physico-chemical properties. Xylitol which crystallises in the acentric space group $P2_12_12_1$ is the higher melting, whereas the lower melting ribitol belongs to the centric $P2_1/c$. We have performed a determination of the crystal charge density of the two compounds using high resolution X-ray diffraction data in order to elucidate the differences in crystal structures of the two pentoses. High resolution ($\sin\theta/\lambda<1.1$ Å) X-ray diffraction data have been measured on both compounds. To obtain reliable parameters for the hydrogen atoms and investigate the deconvolution of thermal motion from the X-ray diffraction data, neutron diffraction data were measured at ILL. A topological analysis of the crystal charge density was conducted in order to unravel differences that can explain the different physico-chemical behaviour of the two pentoses. The analysis included a determination of the atomic basins defined by the zero-flux surfaces in the electron densities that was used to determine integrated properties of the atoms in the two compounds.

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A COMBINATION METHOD OF CHARGE DENSITY MEASUREMENT IN HARD MATERIALS USING ACCURATE, QUANTITATIVE ELECTRON AND X-RAY DIFFRACTION

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Current X-ray diffraction techniques for commonly imperfect specimens provide structure factors only on a relative scale, and the kinematic scattering condition breaks down for strong low Bragg angle reflections. Multiple diffraction is accounted for accurately in quantitative convergent beam electron diffraction (QCBED) data analysis, which provides absolutely scaled structure factors. Conventional single crystal X-ray diffraction has proved adequate in softer materials where crystal perfection is limited. In hard materials, the highly perfect nature of the crystals is often a difficulty. This is due to the inaccuracy of the corrections conventionally used to account for multiple scattering (extinction). The combination of accurate QCBED and X-ray diffraction structure factors provides more reliable analyses of experimental charge density in hard materials. The precision of the combination method is such that it promises to distinguish between rival many-electron theories used for structure calculations.

Our present study exploits the complementarity of synchrotron X-ray measurement for weak and medium intensities for α-Al_2O_3, and QCBED measurement of the strong low-angle reflections. The consistency of the QCBED structure factors determined from independent data sets at various accelerating voltages, thickness, and orientations and matched by both the Bloch-wave and the multi-slice methods confirms the validity of the technique.

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A9-13

TOPOLOGICAL ANALYSIS OF $NH_4[Ti(C_2O_4)_2]\cdot 2H_2O$

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High coordination number complex, $NH_4[Ti(C_2O_4)_2]\cdot 2H_2O$, is reinvestigated. Each Ti atom is coordinated by four oxalate dianions with a coordination number of eight in an approximate symmetry of D_4 geometry. Electron density distribution of this complex is studied in terms of multiple model based on the x-ray diffraction data. A theoretical calculation based on the periodic density functional theory (DFT in CRYSTAL98 program) will be reported for comparison. The result obtained from multipole refinement shows that the $d_{Z}2$ orbital is the most populated among all five d orbitals of Ti. Topological properties associated with the bond critical points (BCP), Laplacian of the electron density as well as electron density at the BCP of each chemical bond will also be presented. The BCP of C-O bond is apparently more positive closer to the carbon atom than to the oxygen atom. The delocalization of the oxalate ion will be demonstrated by the Fermi-hole function and the theoretical value. The isovalue surface of Laplacian for such a eight-coordinated Ti metal will be displayed.

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A10 : Education, computing and databases

A10-1

A DATABASE ON CRYSTALLOGRAPHIC AND MECHANICAL PROPERTIES OF POLYMERS

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It is well known that the properties of a material are closely related to the crystal structural characteristics. In this context, it is useful and convenient to compile together the crystallographic and other properties of interest. Polymers play an important role in aerospace engineering. A database entitled 'POLYSEARCH' has been developed to compile the crystallographic and tensile characteristics of polymers used in aerospace.

Details of the properties at ambient, high, low temperatures and high pressures are included. A category on miscellaneous properties such as glass transition, melting, decomposition temperatures, recommended limit of service temperature, density, names of suppliers etc., has also been included. POLYSEARCH is a user-friendly database with multiple access to any polymer. The package ChemSketch has been used to display the chemical and the molecular structure.

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A10-2

EMPIRICAL SUGAR BINDING SITE PREDICTION

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Carbohydrate – protein interactions are known to take part in a variety of biological activities, including cell recognition, growth control and apotosis. Detailed knowledge of structure based carbohydrate – protein interactions can be extracted from three-dimensional structures. To date, several tens of three-dimensional structures of carbohydratye - protein complexes have been determined. Considering the important roles of carbohydrate in the life system, the current methods in bioimfomatics and structural biology for carbohydrates are still immature.

We are developing a computer program system, which predict sugar binding site on protein 3D structures. This program system searches for the position of sugar binding sites by referring to empirical rules that are derived from known 3D structures of sugar-protein complexes. The system consists of programs for construction of empirical rules (scoring system) and programs for sugar binding site search. A total of 192 non-redundant sugar-protein complex structures were selected from PDB for empirical rule construction. The system was tested on several known sugar-protein complexes. Sixty-nine percent of the known primary sugar binding sites were successfully predicted.

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A10-3

MOLECULAR REPLACEMENT IN HEMIHEDRAL TWINNING

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Crystal twinning is rarely observed and causes difficulty in analyzing crystal structures. Especially, merohedral twinning that all reflections overlap with the other twin components is troublesome. However, when the crystal consists of just two components and the twin fraction is not equal to 0.5 (partial twinning), the intensity of each of components can be retrieved by considering the difference of the contribution to the diffraction intensity. If the value of the twin fraction is given, it is possible to restore the individual intensities by solving a set of simultaneous equation including the twin fraction and intensities. Unfortunately, the solutions of the simultaneous equation will be degenerated in the case of perfect twinning (i.e. the twin fraction is just equal to 0.5), and they can't be separated. In this study, a molecular replacement program (AMoRe) is modified so that it can solve the structure even in the case of perfect twinning. Since it is impossible to separate a reflection into each of components in the rotation function for perfect twinning, the modification was made only to the translation function. The outline of the changed algorithm and the result of the application for a model data set will be reported.

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TITAN2000: A PROGRAM TO AID STRUCTURE SOLUTION AND REFINEMENT WITH THE SHELX SUITE OF PROGRAMS

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The TITAN2000 program has been developed as a readily accessible tool to give classes of undergraduate students experience of the solution and refinement of small molecule crystal structures. It also has applications for crystallographers who do not have facile access to SHELX based molecular graphics programs. The program has been upgraded to run in the Windows 95/98/2000 or NT environments and provides a shell from which to launch the SHELXS[1] (solution) and SHELXL[2] (refinement) programs, such that the complete structural characterization can be accomplished within the program.

The program has evolved to provide an easy to use and relatively intuitive tool for the display and manipulation of output from the SHELX programs. This presentation will incorporate a demonstration of the operation of the program and will highlight features of the program from a teaching perspective.

1. Sheldrick, G.M. (1990) SHELXS A program for the solution of crystal structures from diffraction data. University of Göttingen, Germany.

2. Sheldrick, G.M. (1997) SHELXL-97 A program for the refinement of crystal structures. University of Göttingen, Germany.

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A10-5

SAMR-WEB: A SEMI-AUTOMATIC GRAPHICAL USER INTERFACE PROGRAM FOR THE MOLECULAR REPLACEMENT METHOD

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We have developed a graphical user interface program SAMR-Web which was designed as Internet-based tool for protein structure solution by the molecular replacement method (MR). The software is linked to Web sites of the Protein Data Bank (PDB) and the Swiss Model being an automated protein modeling server. Candidates of the model structure are searched in the PDB or the ExNRL-3D with a query sequence and an atomic coordinate of the search model including side chains is made by the comparative protein modeling method. The *SAMR-Web* then makes input data required for execution of the *EPMR* or *AmoRe* which are molecular replacement programs. The GUI is implemented in standard Perl and has been tested under Linux Redhat 6.2. The *SAMR-Web* required only minimal user inputs, including space-group symmetry, unit-cell parameters, reflection data and sequence file names and the number of copies of the search model in the asymmetric unit.

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A10-6

THE SEARCH/MATCH SYSTEM FOR POWDER DIFFRACTION DATA

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A new method for identifying components in crystalline mixtures from their X-ray powder diffraction data is presented. It can be run in Windows-9X. The reference database comes from the powder diffraction files (PDF) provided by the JCPDS-International Centre for Diffraction Data.

This method uses the weight factor for each diffraction peak as a criterion, and can not only give a list of possible phases but also the definite components of the unknown sample by a simulation process. Actual samples have been tested with high performance. The key points in this system are:

1. To compare the sample data with the database to make two filtrating--three most intensive peaks filtering and element filtering. The phases which pass filtrating were conceded as possible phase existed in the sample (Selected Phases).

2. Our program uses those SELECTED PHASES as the basic units to simulate the sample pattern with various combinations. Appearance of complete combinations by different methods would indicate real components of the sample.

3. Evaluation of the simulated patterns: The components of the simulated pattern, which has highest SIMILARITY, would be the components of the sample.

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A10-7

AB INITIO MO STUDIES ON THE ELECTRONIC STRUCTURE OF GLYPHOSATE.

P. Kaliannan and M. Mohamed Naseer Ali. Department of Physics, Bharathidasan University, Tiruchirappalli – 620 024, INDIA.

The herbicidal markets demand high performance products with stringent environmental acceptability requirements. Enzyme inhibition technique is one approach to meet out these challenges. Effective plant specific enzyme inhibitors offer the opportunity to satisfy the herbicide performance needs of the markets place while exhibiting favourably low mammalian toxicity properties. An attractive enzyme system on which to test this approach is EPSPS (5-enolpyruvyl shikimate – 3 – phosphate synthase) which is the target for N- Phosphono methyl glycine (glyphosate). Glyphosate is a non-selective herbicide that controls most of the world's worst weeds while exhibiting very low mammalian toxicity. In order to model a better inhibitor for this target enzyme we are in need of the detailed structural studies of the ternary complex of this enzyme. In the present study an effort is made to analyse the conformational features of glyphosate using quantum chemical calculations.

We have carried out a detailed ab initio MO calculations for this inhibitor as an initial step. The conformational energies, structural trends and exact locations of conformers in torsional space are studied at the HF level of theories with different basis set. We have also constructed the potential energy surfaces for glyphosate. The results of Mulliken population analysis and the behaviour of glyphosate in its torsional space will be discussed.

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A10-8

DEPOSITION AND PROCESSING OF PROTEIN DATA BANK ENTRIES AT OSAKA UNIVERSITY

M. Kusunoki, T. Kosada, R. Igarashi, Y. Kengaku, G. Kurisu and H. Nakamura, Institute for Protein Research, Osaka University, 3-2 Yamadaoka, Suita, Osaka 565-0871, Japan

The Protein Data Bank (PDB) is the sole international repository for three-dimensional structure data of biological macromolecules and is managed by the Research Collaboratory for Structural Bioinformatics (RCSB), USA. The RCSB is a consortium composed of Rutgers University, the National Institute of Standards and Technology, and the San Diego Supercomputer Center.

The coordinates of a biological macromolecule determined by X-ray crystallography or NMR spectroscopy are deposited with the PDB by the authors. The deposited data are validated and annotated by the PDB staff and are then released to the scientific community over the Internet (http://pdb.protein.osaka-u.ac.jp/). The Institute for Protein Research, Osaka University, Japan has started to serve as the deposition and processing center of PDB entries on July 1, 2000 for crystallographers and NMR spectroscopists in Asian and Oceanic regions. Since then, we have collected and processed 349 PDB entries as of August 14, 2001. We operate the ADIT (http://pdbdep.protein.osaka-u.ac.jp/), a Web-based PDB input tool,+ the same one used by the RCSB. We will describe our archiving activities of the PDB. The PDB activities at Osaka have been supported in part by Japan Science Corporation.

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A STATISTICAL AND MOLECULAR-MECHANICS ANALYSIS OF THE EFFECTS OF CHANGING DONOR TYPE ON BOND-LENGTH THE TWO SERIES $[Co^{III}N_nO_{6-n}]$ AND $[Ni^{II}N_nO_{6-n}]$ (n = 0 - 6): A NEW ROUTE TO BOND-STRETCH PARAMETERS.

Rosalie K. Hocking[a] and Trevor W. Hambley[a]. [a]Centre for Heavy Metals Research, School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

Changes in bond lengths across the series of complexes $[Co^{III}N_nO_{6-n}]$ and $[Ni^{II}N_nO_{6-n}]$, (n = 0-6) have been examined by a statistical analysis of the bond lengths in 256 Co^{III} and 205 Ni^{II} complexes. In both cases a systematic reduction in both metal-N and metal-O bond lengths is observed as oxygen donors replace nitrogen in the coordination sphere. In the case of Co^{III}, the reduction in bond lengths is linear across the series, whereas in the case of Ni^{II}, the reduction in bond-lengths is more asymptotic in nature. The trends across the two series were reproduced using molecular mechanics, however, the magnitude of the change was not initially predicted correctly in either case. Alterations to molecular mechanics parameters that reproduced the trends in the $[Co^{III}N_nO_{6-n}]$ series also resulted in an overall improvement in the predictions of Co^{III}-N bond lengths in a series of Co^{III} hexaamines. This improvement was taken as an indication that the bond-length reduction across the series is probably steric in origin. The systematic change to the strain in these systems enabled a map to be made of the energy surfaces describing the four interactions Ni^{II}-N, Ni^{II}-O, Co^{III}-N and Co^{III}-O. We find that many of these potentials exhibit an asymmetric character never before seen experimentally, and believe that this new method of determining bond stretch parameters may give molecular mechanics an improved reliability for predicting both structures and reactivity.

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A10-10

EFFECTIVE USE OF HOME PCS IN ADVANCED CANCER AND AID RESEARCH-PERSONAL EXPERIENCE.

S.Natarajan, Former Dean, Anna University.Chennai-60025.Res. 34/1 Second Main Road, Kottur Gardens, Chennai-60085.India.

In the era of drug design and macromolecular Crystallography the need for extensive use of computers is known to everybody. INTEL sponsored a programme to tap the potentials of home PCs all over the world and it is doing wonderfully well. As a retired teacher in crystallography I have volunteered my home PC for this purpose. There is a need to get more volunteers for this kind of projects all over the glob. In this regard my experience during the last few months under this project will be presented/shared.

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A10-11

APPLICATION OF η_{ij} MAPS

R.Sreekanth and S.S.Rajan, Department of Crystallography and Biophysics, University of Madras, Chennai-600 025,India.

A few new methods were earlier proposed from this laboratory (Srinivasan, R., Balasubramaniam, R. and Rajan, S.S. 1975) with a view to extract information on the nature of folding of protein chain and to analyze the distortions in helices present in the protein. The helical parameters for different stretches can also be found using these methods (Rajan, S.S. and Srinivasan, R.1977). These have now been applied to proteins solved at different resolutions to find the impact of resolution on the helical parameters and distortions in different helices. Studies were also made on the protein, lysozyme, solved at different humidity conditions to find the effect of humidity on helical parameters. The details will be presented.

References:

- Srinivasan R.,Balasubramaniam R. and Rajan S.S.(1975),J.Mol.Biol., 98 ,739.
- Rajan, S.S. and Srinivasan, R. (1977), Biopolymers, 16, 1617.

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ONTOLOGIES: ROSETTA STONES FOR GLOBAL KNOWLEDGE BASES

S.R. Hall, N. Spadaccini, D. du Boulay and I.R. Castleden, Crystallography Centre and the Department of Computer Science & Software Engineering, The University of Western Australia, Perth, Australia 6009.

Phenomenal improvements in instrumentation have made the efficient processing and communication of data one of our highest priorities. A key objective is the capture of computer-interpretable "knowledge" (i.e. meta-data). This is currently achieved in crystallography using customised software packages. From a longer-term and global perspective such approaches are restrictive in that, they are relatively inflexible (targeted at specific methodologies); non-extensible (new data types cannot be added easily) and the embedded knowledge is neither human-accessible nor re-useable (the meta-data are encrypted in imperative languages).

This talk will describe a generic object-oriented approach[1] to coalescing meta-data into textual data dictionaries (i.e. ontological descriptions). Some of the meta-data are methods and expressions that represent complex relationships between defined data items. These dictionaries may be compiled into computer code and used as an executable knowledge kernel for data manipulation, validation and interpretation.

A prototype crystallographic ontology, based on the widely adopted *Core CIF* dictionary, will be used to demonstrate the evaluation of quantities such as molecular geometry and structure factors.

[1] Spadaccini, N., Hall, S.R., and Castleden, I.R. "Relational Expressions in STAR File Dictionaries" 2000 *J Chemical Information and Computer Science* **40**, 1289-1301.

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A10-13

HYDROPHOBIC INTERACTION BETWEEN THE SUGAR MOIETIES OF CARBOHYDRATES AND AMINO ACIDS IN GLYCOPROTEINS AND GLYCAN-BINDING PROTEINS

T. Hema Thanka Christlet and K. Veluraja, Department of Physics, Manonmaniam Sundaranar University, Tirunelveli 627 012, India.

The carbohydrate-protein interactions in glycoproteins and glycan-binding proteins have been studied using the Protein Data Bank. The hydrophobic interaction between the hydrophobic plane in sugars, formed by three axial hydrogens in the stable chair conformation (pointing the same direction in β-sugars of Glc, Gal, Man), or the methyl group of acetamido sugars (NeuNAc, GlcNAc, GalNAc) and the hydrophobic/aromatic amino acids were computed. It is noted that in more than 50% proteins there is stacking/hydrophobic interaction between the glycan and the hydrophobic/aromatic amino acids. The angle between the stacking planes is in the range of $30^{\circ}\pm10^{\circ}$ or $80^{\circ}\pm10^{\circ}$ indicating the specificity of the stacking interaction. The methyl group in acetamido sugars also takes part in hydrophobic interaction with the hydrophobic/aromatic amino acids. To find the potentiality of various amino acids involved in hydrophobic interactions, a quantity called hydrophobic interaction index (HII) is computed for the two types of hydrophobic interaction. HII is maximum for Trp in both glycoproteins and glycan-binding proteins when the hydrophobic sugar plane is involved in the interaction. Leu shows lower HII in glycoproteins due to the fact that Leu residues do not occur frequently at the surface of the protein and the common occurrence of glycosylation is at the surface. The high HII value for Leu in glycan-binding proteins can be attributed to the predominant occurrence of Leu at the interior of the protein and extended binding site for the glycan in glycan-binding proteins. Ala and Val have high value for HII in glycoproteins because amino acids with small side chains are preferred around the N- and O-glycosylation sites. When the methyl group of acetamido sugars is involved HII is maximum for Trp and Leu in glycoproteins and glycan-binding proteins respectively. Thus it is concluded that stacking/hydrophobic interactions are one of the important and highly specific stabilising forces in the case of carbohydrate-protein interactions.

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Author Index

A3 : Crystallography in physics and earth sciences

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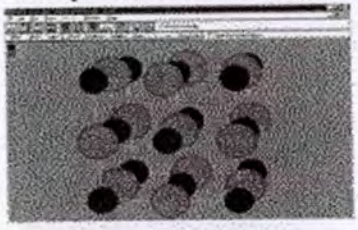

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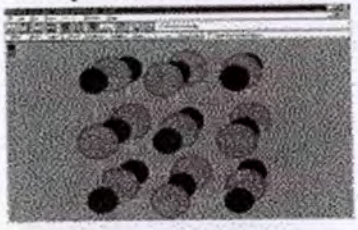

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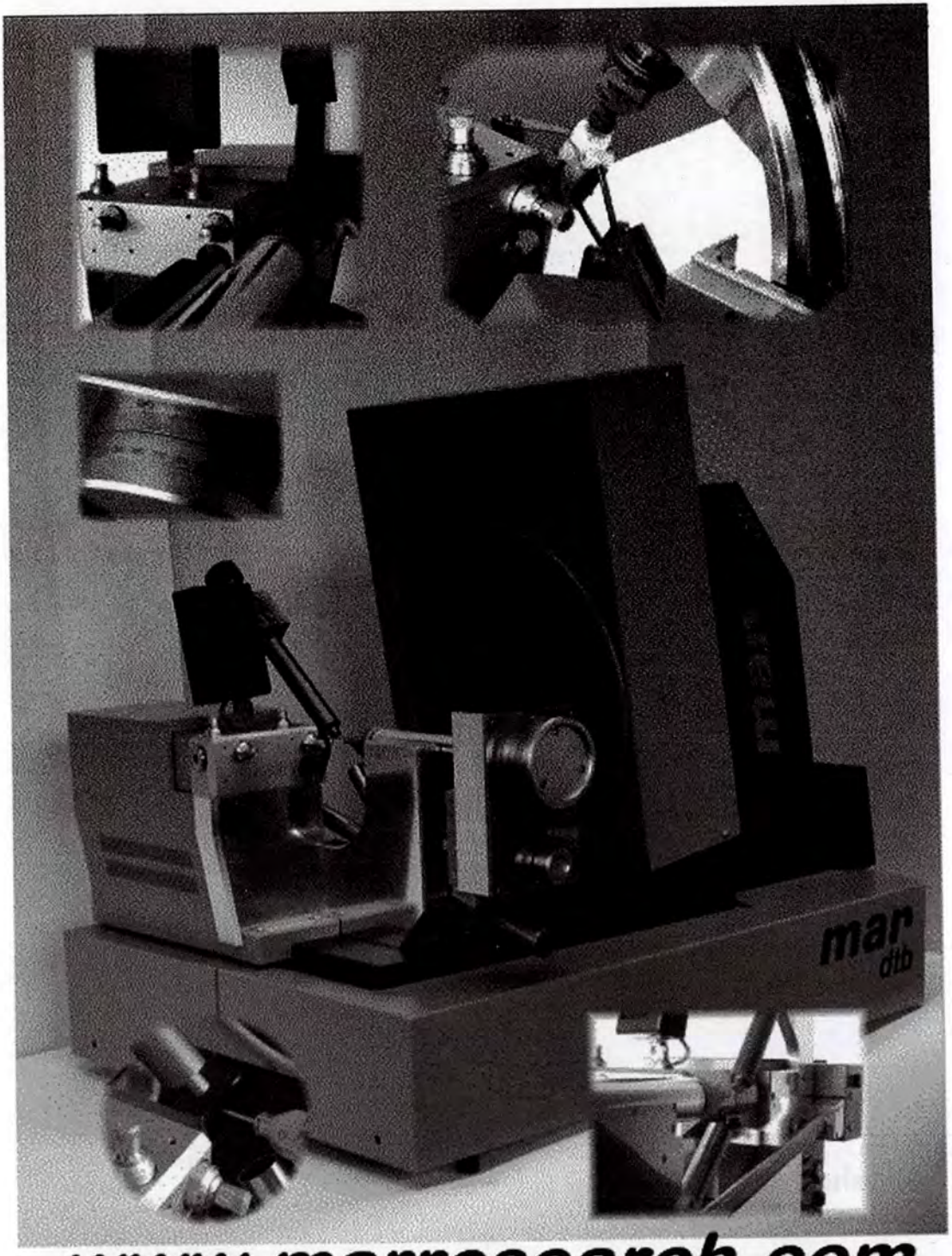

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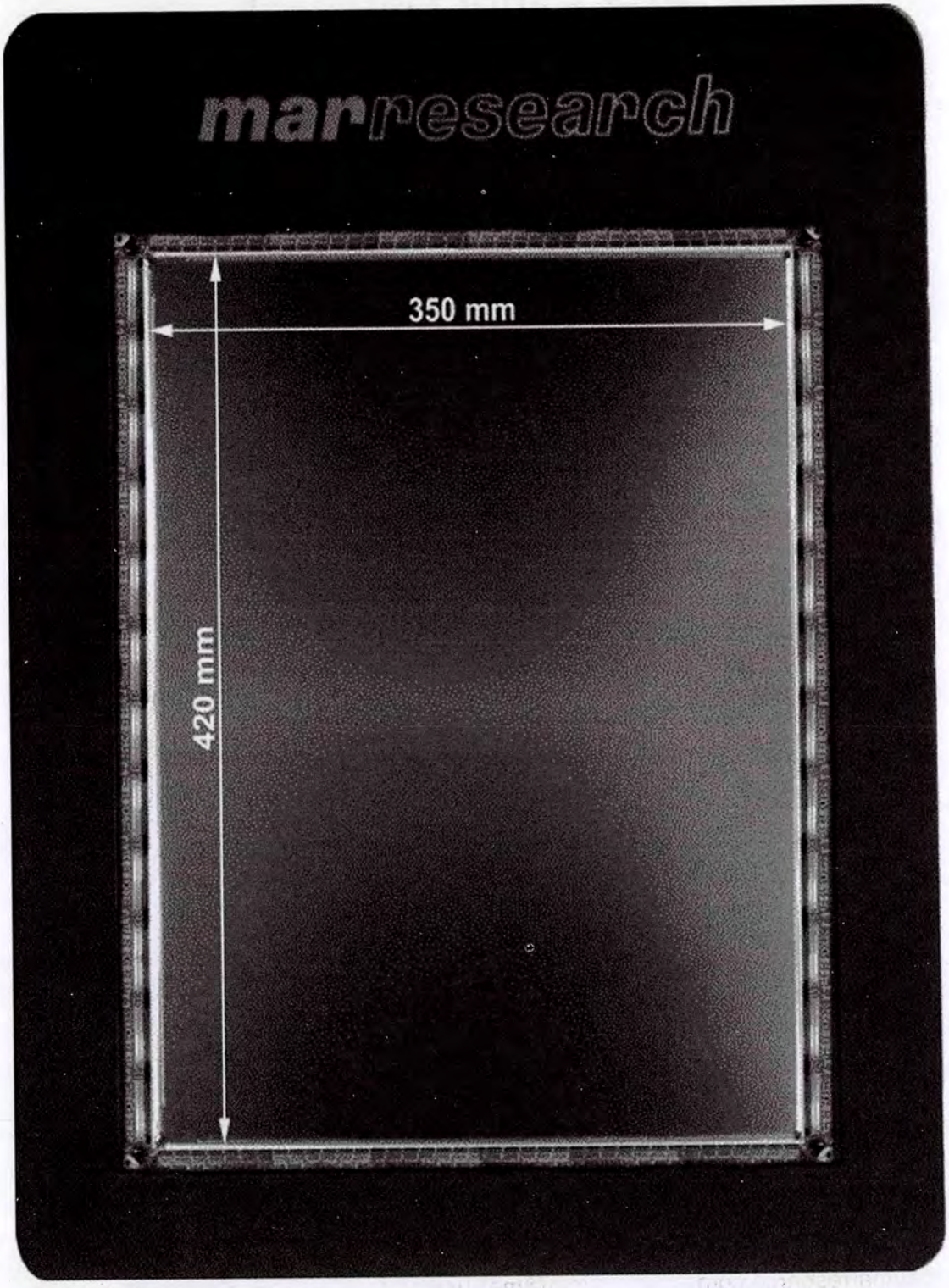
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