

between the host and guest molecules by the computational method (electrostatic surface charge distribution, heat of formation and so on) and we found the important contribution of CH- π interactions which probably act to stabilize the guest molecule inside the cavity of host molecule.

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MS11.01.06 INCLUSION COMPOUNDS: RELATING STRUCTURE TO THERMAL STABILITY. L. R. Nassimbeni, Chemistry Department, University of Cape Town, Rondebosch 7700, South Africa

Research on inclusion compounds has largely concentrated on the synthesis of novel host compounds, aimed at selective enclathration of targeted guest molecules. We have directed our program to the understanding of the intermolecular forces which are responsible for the process of molecular recognition between host and guest, in order to explain the physical properties of inclusion compounds.

We have synthesised a variety of host-guest complexes comprising bulky hosts containing the hydroxyl moiety, have elucidated their crystal structures and measured their thermodynamic stabilities with a variety of analytical techniques. The kinetics of enclathration of a gaseous guest by a solid host has been studied using a novel magnetic suspension balance, while the kinetics of thermal decomposition of labile clathrates has allowed us to elucidate the mechanism of the desolvation reactions. Competition experiments between close isomers of a guest have been carried out both in solution and with the host in suspension, and we have extended this principle to solid-solid systems.

The results of both the dynamic and equilibrium experiments are rationalised in terms of the molecular structures and the crystal packings of the host-guest compounds concerned.

MS11.01.07 MOLECULAR RECOGNITION OF ANIONS: HYDROGEN-BONDING PROPERTIES OF SULFATE, THIOCYANATE AND PICRATE ANIONS. Claudine Pascard, ICSN-CNRS 91198 Gif-sur-Yvette, France

Ions play an important role in biological systems, as substrates (ATP, peptidic side-chains..) or as structural elements at interfaces (membranes, micelles). Whereas the environment of cations is well studied, our goal is to analyse the structural characteristics of anion binding, very little¹ being written on this topic (aside of halogens).

The anions we started to study are geometrically very different: spherical, (sulfate dianion), linear (SCN) and flat (picrate). Sulfate plays a role in protein architecture, SCN has 2 acceptor centers and is very small, and picrate has a flat aromatic (hydrophobic) core. The method used was the search through Cambridge Crystallographic Data Bank, and we analysed the H-bonding possibilities of each anion observed in the retrieved crystal structures.

Discrete sulfate dianion principal characteristic is to form as many H-bonds as possible, short and direct, up to 12 per dianion. This quality gives sulfate a character of strong linker in forming molecular associations. The O-bonded sulfate (monoanion) is much less attractor and more directional. The H-binding property of SO₄²⁻ will depend on its complexing environment. SCN⁻ has a very unusual behaviour. To our knowledge, this systematic analysis of its binding properties is the first one based on experimental results: isolated, this linear anion binds by both ends to H-donors; when coordinated to a metal by one end, it can binds to H-donors by the other end. Metal cations fall into different classes whether they

bind to S or to N. Correlations between the charge (or size) of the cation and its position with respect to the anionic cylinder were found. Picrate forms strong hydrogen bonds which might involve the ortho nitro groups. The most evident result is the formation of intimate ion pairs. Other observed aggregation modes are infinite chains and macrorings.

The structural data assembled in these analyses can be useful to predict molecular associations, and in certain cases (sulfate¹), agree quite well with similar analyses in biological systems. Moreover, our results provide the first picture of the coordination behaviour of SCN⁻.

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PS11.01.09 MODEL STUDY OF THE RECOGNITION CENTER INVOLVING PYRIMIDINE BASES AND AMIDE GROUP OF AMINO ACIDS. I.K. Galetich and V.S. Shelkovsky, Institute for Low Temperature Physics and Engineering of the Academy of Sciences of Ukraine

In the frames of the problem of molecular recognition this work is aimed at the investigation of hydrogen bond formation of the amide group with nucleic acid bases in the crystal structure of a specific repressor-operator complex of bacteriophage 434. The interactions between the monomers of nucleic acids and proteins, which lead to hydrogen bonds formation, were studied on the systems (consisting of nitrogen bases 1,3-dimetUra and 1-metThy and acrylamide) which are good models of interactions, involving specific aminoacid side chains of Gln and Asn and free atomic groups of nucleic base Thy in single or double stranded DNA. Thermodynamic parameters of interactions were obtained using a method of temperature dependent field ionization mass spectrometry and theoretically by the atom-atom potential functions calculations. Under the mass spectrometric conditions the associates of molecules were formed in the gas phase; variation of the temperature allowed to obtain relative association constants and to calculate the enthalpies of associates formation (DH, kcal/mole) using Vant-Hoff plots. A good agreement between experimental and theoretical data for acrylamide complexes with 1,3-dimetUra (9.7 vs 10.1) and 1-metThy (6.8 vs 6.6) was observed. Proposed schemes of the energetically favourable hydrogen bonding are as follows: a) for the complex of acrylamide with 1,3- dimetUra: N1-H...O2 ; b) for the complex of acryl- amide with 1-metThy: O1...H-N2 or N1-H...O2. The data obtained enabled us to determine hydrogen bond for formation and mutual positions of molecules in the crystals and can be used for quantitative estimates of the probability of recognition.

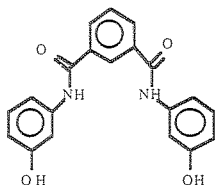
PS11.01.10 MOLECULAR RECOGNITION OF THE PHYTOHORMONE AUXIN AND RELATED COMPOUNDS. B. Kojic-Prodic, S. Antolic, S. Tomic and V. Magnus, Rudjer Boskovic Institute, P.O.B. 1016, 10001 Zagreb, Croatia

A molecular recognition approach was applied to the auxin family (indol-3-yl acetic acid, IAA), the most intensively studied plant hormone. The final goal of the research is to offer a mechanism of hormone binding to receptor(s) and to provide data for QSAR of indole and non-indole auxins. The study includes natural and synthetic alkylated and halogenated analogues of IAA. Both, active and inactive analogues have been included in the analyses. The problem has been tackled in three directions: analysis of the molecular geometry, study of electron redistribution by substitution effects, and correlation of the physico-chemical parameters with substitution effects and bioactivity. The analysis has been based on the results of X-ray structure analysis, computational chemistry, FT-IR, UV & NMR spectroscopies, physico-chemical parameters such as lipophilicity and acid-base properties of the

pyrrole NH, and bioactivity (including bioaffinity for some of them, Klaebmt, 1996). The 3D structure of the receptor has not been characterized yet. However, systematic analysis of a large number of substrates and inhibitors can provide information about the protein active site.

PS11.01.11 π - π STACKING IN MODEL DYE HOSTS. C.M. Murray, J.F. Malone, R. Docherty, A.J. Lavery, G. Stewart.

Weak hydrogen bonds e.g. C-H...O and weak interactions e.g. π - π stacking and T-bonding have been shown to have a role within crystal structure¹. The π - π stacking interaction, though weak, is significant in the structure of 1,3 Bis(((3-hydroxyphenyl)amino)carbonyl)benzene which is reported.



This interaction has been quantified using the HABIT program². Semi-empirical calculations of the heat of formation show agreement between the preferred conformation in the gas phase and the single crystal X-Ray diffraction structure. Similar structures retrieved from the Cambridge Structural Database confirm the importance of the π - π interaction for not only single molecule asymmetric units of this type but also asymmetric units which contain hydrated species or co-crystals. Quantification of the values is reported and the conformational preference is also investigated.

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PS11.01.12 STRUCTURE OF THE LEAD PICRATE COMPLEXES WITH 18-MEMBERED CROWN ETHERS IN THE CRYSTAL STATE AND IN ORGANIC SOLVENTS. N. K. Dalley¹, J. D. Lamb¹, A. Y. Nazarenko², E. B. Rusanov³. ¹Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, USA, ²Analytical Chemistry Department, Taras Shevchenko University, Kiev 252033, Ukraine, ³Institute of Organic Chemistry, NAS of Ukraine, Kiev, Ukraine

Despite the wide use of metal picrates for ion recognition studies, no structural data concerning lead picrate complexes with crown ethers have yet been published. Here we report molecular structures of Pb(18-crown-6)Picr₂ x CH₂Cl₂ (I) and Pb(cis-syn-cis-dicyclohexano-18-crown-6)Picr₂ (II). In both complexes Pb²⁺ is coordinated six O atoms of macrocycle, which has a distorted D_{3d} geometry (Pb...O separations are 2.64-2.84 Å). Both picrate anions in (I) and only one in (II) are monodentate with Pb...O = 2.47-2.48 Å, while the second one in (II) is bidentate (Pb...O = 2.56 and 2.88 Å). This correlates with the existence of different types of picrate - Pb²⁺ ion pairs in organic solvents in the presence of crown ethers, observed from spectral studies. The structural data together with our previously obtained structures of lead macrocyclic complexes enable us to discuss the features of ion recognition of Pb²⁺ by crown ethers.

Chemical Crystallography of the Future Open Commission

MS11.02.01 BEYOND ROUTINE STRUCTURE DETERMINATION - THE RENAISSANCE OF SMALL MOIETY CRYSTALLOGRAPHY. A. Alan Pinkerton, Department of Chemistry, University of Toledo, Toledo, OH 43606, USA

The introduction of area detectors, especially the CCD detector, into small moiety crystallography coupled with the availability of powerful, low cost workstations will have as large an impact on the discipline as that made by the introduction of automated diffractometers a quarter of a century ago. In the short term this will lead to a quantum jump in the number of routine structures determined each year. In the long term, crystallographers will devise new experiments and directions to take advantage of this technological advance. A number of potential new directions will be presented. This discussion will be based in part on experiences in my own laboratory and in part by gazing into a crystal ball (pun intended).

MS11.02.02 TIME-RESOLVED STRUCTURE ANALYSIS OF CRYSTALLINE-STATE REACTION BY A NEW DIFFRACTOMETER DESIGNED FOR RAPID DATA COLLECTION. Yuji Ohashi, Department of Chemistry, Tokyo Institute of Chemistry, Ookayama, Meguro-ku, Tokyo 152, Japan

The structural change of the reactant molecules can be directly observed by stepwise structure analysis using a new diffractometer in the process of the reaction. Since we found that the chiral cyanoethyl group bonded to the cobalt atom in a cobaloxime complex crystal was racemized by X-ray exposure without degradation of the single crystal form^[1], many solid-state reactions with retaining the single crystal form, crystalline-state reaction, have been observed^[2]. Recently several crystalline-state reactions which proceeds within ten hours have been found^[3]. In order to analyze the structural changes in such reactions, we have designed and constructed a new diffractometer for rapid data collection^[4]. The diffractometer, which has two imaging plates as detectors, enables us to collect the three-dimensional intensity data within two hours. Several examples of the direct observation of the structural changes by stepwise crystal structure analyses using the diffractometer will be shown and a new crystal chemistry based on the time-resolved structure analysis will be proposed.

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MS11.02.03 EXPERIMENTAL X-RAY DIFFRACTION EVIDENCE OF THE UNUSUAL BOND BENDING IN SMALL MOLECULES. M. Antipin*, and R. Boese,** Institute of Organoelement Compounds, Moscow, Russia.* Institute of Inorganic Chemistry, University of Essen, Germany**

Molecular structure and geometry are often the only kind of information that many chemists are interested in as a final result of the X-ray analysis. Meanwhile, much more information may be extracted now from X-ray diffraction data using modern opportunities of this method. Thus, multipole representation of the electron density distributions and its topological analysis allow to describe the nature of some chemical bonds in new terms of the bond paths, critical point positions etc. This approach was found to be very fruitful for description bonding in small cyclic or strained cage molecules, where so called bent bonds are present.

In the deformation electron density (DED) maps the bending