

07-Crystallography of Organometallic and Coordination Compounds

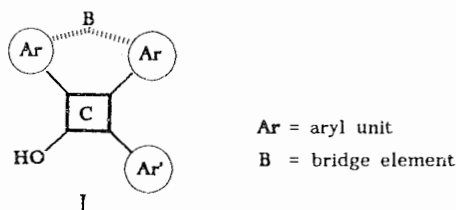
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07.01 -- Molecular Recognition and Inclusion Compounds

MS-07.01.01 NEW SUPRAMOLECULAR ARCHITECTURES: INCLUSION STRUCTURES, BINDING MODES, AND MOLECULAR RECOGNITION. By *Ingeborg Csöreg*,^{*} Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, Sweden, and *Edwin Weber*, Institut für Organische Chemie der Technischen Universität Bergakademie Freiberg/Sachs., Germany.

Engineering of supramolecular crystalline complexes is an important problem connected with the development of new technologies, including chemical sensor devices and non-linear optical materials. This involves specific interaction and orientation of molecules in particular aggregate patterns. Moreover, the possibility of studying the structural basis of molecular recognition and selectivity by using synthetic hosts as models for biological systems has provided an impetus for much of this research. X-ray diffraction studies may provide a clearer insight into the structural principles of non-covalent interactions being essential here.

In order to learn the rules which govern the interactions between groups of different molecules in different geometric environments, we have developed a new family of host molecules, represented by the general formula I.



This particular design involves a basic triaryl-methanol frame where two of the aryl residues are bridged, thus giving rise to a distinct molecular shape. The structural modifications include variation and substitution of the aryl groups and/or modification of the bridging unit, yielding the structures shown in Figure 1.

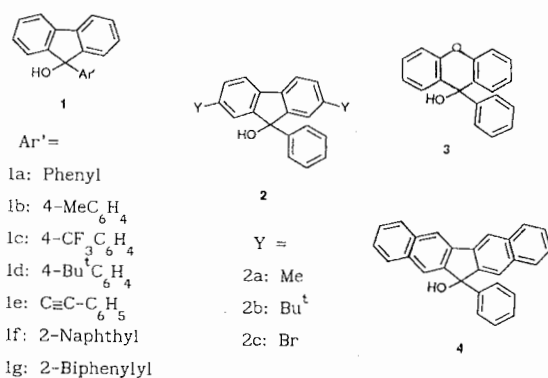


Figure 1.

These hosts form crystalline inclusions with a variety of uncharged organic molecules depending on their structural parameters. Crystal structures of selected inclusion compounds of hosts 1-4, in particular with alcohols and heterocycles, such as dioxane, thioxane, morpholine and piperidine as guests, and also of unsolvated hosts, will

be presented. Versatility in binding modes and packing relations, as well as general features in complexation and molecular recognition, will be discussed.

MS-07.01.02 INCLUSION PROPERTIES OF CALIXARENES, By G.D. Andreetti, Institute of Structural Chemistry, University of Parma, Viale delle Scienze, 43100 Parma, Italy

Calixarenes have received wide attention in recent years in the fields of inclusion chemistry and of molecular recognition (J. Vicens and V. Böhmer, *Calixarenes*, a versatile class of macrocyclic compounds, Kluwer Academic Pub., 1991). They offer good examples of intramolecular cavity complexes formed by neutral molecules and by ions. There are no reports of complex formation by n.m.r. studies and for such compounds the crystal structure analysis is the unique tool to show the topology and the nature of intermolecular and intramolecular interactions which drive their formation. An attempt has been made to correlate the molecular parameters concerning the cavity topology, size and substituent distribution with conformational preferences and complexing properties. Most of the results concern the description of the static structure of complexes and only recently some details have been collected with respect to the dynamic structure of solid state complexes obtained by neutron scattering (F. Uguzzoli, Neutron scattering studies on calixarenes, European meeting on substituted calixarenes, Belfast, 1991) The conformational preference in functionalized calixarenes will be discussed in connection with the requirements of the *cone* conformation in connection with the inclusion process. The calixarene based cation carriers and receptors will receive attention in relation to the applications of these compounds in sensors technology and in the discussion of Cram's complexation principles. Theoretical models for the host-guest interactions will be discussed and related to thermochemical measurements and to phase transitions studies.

MS-07.01.03 RELEVANCE OF X-RAY CRYSTALLOGRAPHIC RECOGNITION OF CLASSICAL AND NON-CLASSICAL HYDRIDES IN TRANSITION METAL COMPLEXES. By F.J. Lahoz, Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain.

Within the general field of organometallic and coordination chemistry the study of the structure and chemical reactivity of molecular transition metal hydrides (with *classical* M-H bonds) is an area of current great interest due to the capacity of these compounds to act as catalyst precursors or active intermediates in homogeneous catalytic processes. A significant discovery in this domain was made in 1984 when G.J. Kubas demonstrated the existence of coordinated molecular hydrogen in certain metal complexes. These η^2 -H₂ complexes, commonly referred as *non-classical hydrides*, opened up the possibility of obtaining a more detailed following of the oxidative addition of hydrogen to the metal, decisive step in many catalytic cycles and provided an opportunity of studying a new type of chemical bonding to metals (σ -bond complexes).

Current work in this area is leading to the preparation of a considerable number of complexes containing η^2 -H₂ ligands or where both type of ligands -*classical and non-classical hydrides*- are simultaneously present in the molecules. Although several spectroscopic techniques have been used to evidence the presence of both type of ligands, this information quite commonly results partial in the elucidation of the molecular structure of these compounds, making this assignment non-definitive.

Furthermore, the spatial localization of these hydrogen atoms results of crucial interest to understand or predict their interaction with reacting substrates or with the ancillary ligands of the complex and, eventually to suggest reasonable proposals for the catalytic mechanisms. This structural information is also important to get a

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better understanding of the electronic behaviour of the metal centre, obtainable from the detailed knowledge of its coordination environment.

In our presentation, we will report several structural studies, carried out by conventional X-ray diffraction methods, of *classical or non-classical hydride* complexes, and of mixed hydride-dihydrogen compounds in which the central metals are transition metal atoms. We will discuss different approaches applied to reach plausible spatial assignments for these extra-light-atoms and to carry out their conventional free-atom refinement. Our experience indicates that special effort should be dedicated to the precise localization of the atom positions, as their subsequent refinement has been observed to be very sensitive to this step.

The molecular parameters obtained are compared with reliable data from neutron diffraction analysis of related complexes. The validity of the determined molecular parameters have been checked against several external or indirect informations: extended Hückel calculations have been used to inspect the coplanarity of hydrides with the metal in $\text{RuH}(\eta^2\text{-H}_2)\text{I}(\text{PCy}_3)_2$, or NMR dipole-dipole spin-lattice relaxation times (T_1) have been measured to estimate interatomic H-H distances in $[\text{OsCl}_2(\eta^2\text{-H}_2)(\text{PzH})(\text{PiPr}_3)_2]$, $[\text{OsCl}(\eta^2\text{-H}_2)(\text{biim})(\text{PiPr}_3)_2]\text{Cl}$, and $[\text{OsH}_3(\eta^2\text{-PyS})(\text{PiPr}_3)_2]$. Examples reported will include complexes of different nuclearities, with metals from the second and third rows.

MS-07.01.04 DESIGNING MULTI-DIMENSIONAL HOST STRUCTURES OF CYANOMETALLATE SYSTEMS; STATIC AND DYNAMIC BEHAVIOUR OF GUEST MOLECULES IN CRYSTAL. By T. Iwamoto, Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Japan.

The ambidentate character of cyanide anion, CN^- , is favourable for designing various multi-dimensional structures with appropriate coordination centres. Possible building blocks are cyanometallates $\text{M}(\text{CN})_n$ of octahedral ($n=6$), trigonal-bipyramidal (5), tetrahedral (4), square planar (4) and linear (2) configurations to extend 3D frameworks, 2D networks, or 1D chains with other joining coordination centres and/or complementary ligands modifying and/or reinforcing the cyano-linked multi-dimensional structures. Structural varieties with the topologies such as single and double 3D frameworks, single and interwoven 2D layers, bent and straight 1D chains, 1D honeycomb channels, have been materialised for the systems involved with such cyanometallate moieties as $\text{Ni}(\text{CN})_4$, $\text{Cd}(\text{CN})_2$, $\text{Cd}(\text{CN})_4$, $\text{Hg}(\text{CN})_4$, $\text{M}(\text{CN})_4$ ($\text{M}=\text{Cu}, \text{Hg}, \text{Zn}$), $\text{Cd}_2(\text{CN})_7$, $\text{Cd}_3(\text{CN})_8$, $\text{Ag}(\text{CN})_2$, $\text{Ag}_2(\text{CN})_3$, etc. The inclusion compounds are formed by accommodating various kinds of guest molecules in the cage, interlayer, intralayer, intermesh, channel and interchain cavities with definite crystal structures. Some of them mimic the mineral structures of cristobalite, pyrite, clay, zeolite, etc. Single crystal X-ray diffraction is essential to ascertain the static inclusion structures, some of which are accompanied with orientational disorder of not only the guest but also the linking cyanide. Solid state NMR supplies information advantageous to understanding disorder and dynamic behaviour of the hosts and guests. The structural features of these inclusion compounds are reviewed comprehensively, in particular on the developments in Australia, Canada, Japan and other territories.

MS-07.01.05 SYMMETRY AND MOLECULAR RECOGNITION IN CLATHRATES. G. Tsoucaris and G. Le Bas, CNRS UPR180, Univ. Paris XI, Chatenay-Malabry, France.

Symmetry considerations are particularly important in the organisation of clathrates. First, a distinction should be made between *lattice clathrates* and *intramolecular clathrates*. In the former, the cavities are created within the crystal as large intermolecular voids between several host molecules. In the latter, the host molecule already comprises an intramolecular cavity and is capable of inclusion in solution.

In general, crystal symmetry elements play a most important role in the organisation of the cavities. In lattice clathrates, a channel is often generated by a crystallographic helical axis. A classical example is the urea clathrate where a 6₁ axis relates urea molecules linked together by H-bonds, in a way that leaves a channel around the helical axis. Recent work on the diol clathrate family has shown a similar role of a 3₁ axis; moreover, the diol host molecules are located at a crystallographic 2 axis (Bishop, Inclusion compounds, 1991, Vol.5, 1). As intramolecular clathrates, cyclodextrins (cd) involve several types of crystallographic rotation axes, of order 2,3,4,6. In the usual β -cd clathrates, a two-fold axis relates two host molecules within a dimer. Here this symmetry element plays a significant stereochemical role, by creating an intradimer cavity which considerably enlarges the intramolecular cavity of β -cd. With

the clathrate α -cd.cyclopentanone (Le Bas, 1985, Thèse de Doctorat d'Etat) we have the exceptional case in molecular clathrates where a high order molecular symmetry element (6-fold axis) coincides with the same crystallographic element.

Certain hosts forming intramolecular clathrates exhibit high non crystallographic symmetry. This is the origin of problems related to pseudosymmetry and disorder. In some cases the non crystallographic symmetry is nearly perfect (anion cryptates, Dietrich et al, Helv. Chim. Acta, 1984, 67, 91). For β -cd's the 7-fold host axis often generates severe disorder of the guest. A relevant problem pertains to the criteria indicating that the refinement of the disordered molecule is carried out to the end with the given data.

An important aspect in modern molecular science is the question of molecular recognition. Clathrates provide examples where the host/guest recognition is based upon crystal symmetry. Thus in the complex γ -cd .12-crown-4 (Kamitori, J.A.C.S., 1987, 109, 2409) the coincidence of the host and guest crystallographic symmetry (four-fold axis) governs the clathrate formation.

Chirality and enantiomeric discrimination is a particular case of molecular recognition. Two examples illustrate the distinction between intramolecular dissymmetry of the host and dissymmetry arising mainly from the crystal environment. In the case of the included compound 1,7-dioxaspiro (5,5) undecane 1 (Rysanek et al, Acta Cryst., 1992, C48, 1466), this volatile pheromon has been introduced in a dissymmetrically modified cyclodextrin where two out of the seven glucosidic units are substituted differently from all others. Combination of the above lack of 7-fold symmetry with the classical glucose dissymmetry results in a total enantiomeric discrimination of the racemic guest. This last molecule is located exactly in the center of the host cavity. We have here an example of chiral influence within a dissymmetric intramolecular cavity. We mention that in the natural β -cd with 7-fold symmetry the same pheromon exhibits severe disorder associated with lack of chiral discrimination.

The influence of crystal environment dissymmetry will be illustrated with an example of asymmetric synthesis which occurs within a native β -cd clathrate. Phenyl ethyl malonic acid undergoes thermal decarboxylation at 100°C leading to an enantiomerically enriched product (Arad-Yellin et al, Weizmann Institute, personal communication). Crystal structure determination has shown a different microenvironment of the two carboxylic groups; this is considered as the origin of the asymmetric synthesis.