better understanding of the electronic behaviour of the metal cence, 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 nonclassical hydrate complexes, and of mixed hydrate-diaryhybrid compounds in which the central metals are transition metal atoms. We will discuss different approaches applied to reach plausible spatial associations for these extra-large-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 modelled compounds. The validity of the determined molecular parameters has been checked against several external or indirect informations: extended Hückel calculations have been used to inspect the covalency of hydrides with the metal in ReH\(\text{II}^2\)-(P=CH2), or NMR dipole-dipole spin-lattice relaxation times \(T_1\) have been measured to estimate interatomic H-distance in [OsCl\(\text{II}^2\)-(P=CH2)](P=Ph)_2, [OsCl\(\text{II}^2\)-(P=Ph)](P=Ph)_2(C), and [OsCl\(\text{II}^2\)-(P=Ph)](P=Ph)_2(C). 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

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The ambivalent character of cyanide, \(CN^-\), is favourable for designing various multi-dimensional structures with appropriate coordination centres. Possible building blocks are cyanometallate \(M\)(CN)_n of octahedral (n=6), trigonal-bipyramidal (n=5), tetrahedral (n=4), square planar (n=4) and linear (n=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 variations with the topologies such as single and double 3D frameworks, single and interwoven 2D layers, host and guest 1D chains, and interchain cavities with definite crystal structures. Some of the 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.

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Symmetry considerations are particularly important in the organization of the cavities in lattice clathrates, a channel is often generated by a crystallographic helical axis. A classical example is the clathrate where a 61 axis relates two molecules linked together by H-bonds, in a way that leaves a channel around the helical axis, recent work on the dib clathrate family has shown a similar role of a 31 axis; moreover, the di-clathrate is located at a crystallographic 2 axis (Bishop, Inclusion compounds, 1991, Vol.5, 1). As intramolecular Clathrates, cyclocontanes (d1) involve several types of crystallographic rotation axes, of order 2,3,4,6. In the usual case, the two-fold axis relates two host molecules within a dimer. Here this symmetry element plays a significant stereochemical role by creating an intramolecular cavity which considerably enlarges the intramolecular cavity of the host.

With the clathrate \(\alpha\)-dicyclophane (Le Bas, 1995, Thèse de Doctorat d'Etat) we have the exceptional case in molecular clathrates where a high order molecular symmetry element (6-fold) 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 (cyanates, Distl et al. J. Chem. Soc., 1984, 67, 91). For p-cds the 7-fold host axis often generates severe disorder of the guest. A relevant problem pertaining to the criteria indicating 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 \(\gamma\)-cd \(\gamma\)-determined by Kamitori, J.A.C.S., 1987, 109, 2409) the coincidence of the host and guest crystallographic symmetry (four-fold) against the clathrate formation.

Chirality and enantiomeric discrimination is a particular case of molecular recognition. Two examples illustrate the distinction between intramolecular dissimilarity of the host and dissimmetry arising mainly from the (the crystal environment) in the case of the included compound 1,7-dioxaspiro[5.5]undecane \(\beta\) (Ryshkevich et al., Acta Cryst., 1992, C48, 1466), this host is enantioselective in a cis-symmetrically modified cyclodextrin where two out of the seven glucosidic units are substituted differently from all other. Combination of the two cases 7-fold symmetry with the classical glucose dissimmetry results in a total enantiomeric discrimination of the racemic host. 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 system with 7-fold symmetry the same phenomenon exhibits severe disorder associated with lack of chiral discrimination.

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