

04.X-1 MOLECULAR COMPOUNDS AND COMPLEXES-CURRENT DEVELOPMENTS IN PERSPECTIVE. By Frank H. Herbstein, Department of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel 32000.

Crystalline molecular compounds and complexes contain two (or more) components (in the phase rule sense) linked by secondary interactions such as hydrogen bonding, charge transfer (CT) or van der Waals forces. Early examples are chlorine hydrate (Davy, 1811; Faraday, 1823), quinhydrone and quinol - sulphuretted hydrogen (Wohler, 1844 and 1849) and anthracene picrate (Fritzsche, 1858). These, and others, remained poorly understood chemical curiosities until von Stackelberg (gas hydrates), H.M. Powell (clathrates, CT compounds) and other workers determined key crystal structures almost forty years ago, demonstrating the essential role of secondary interactions. Classification of the many examples in terms of secondary interactions followed. In this classical period discovery of new examples was somewhat random, emphasis being placed on the crystalline nature of the substances, a continuing situation now accompanied by two developments of growing chemical importance. The first, exemplified by Pedersen's discovery of the crown ethers (1967), refers to the clathration of molecules (or ions) by molecules, giving entities which can be identified in crystals but also persist (more or less) in solution. Much effort has gone into the design of appropriate hosts. The second concerns the study of complicated molecules whose parts interact by secondary forces, e.g. the donor-acceptor cyclophanes of defined geometry with intramolecular CT interactions. One general theme, with broad implications in biology, is that of "MOLECULAR RECOGNITION"; another is the use of molecular compounds and complexes for the study of phase transitions and disorder phenomena. Finally one notes that DNA is a polymeric hydrogen bonded complex, and that organic conductors stem from charge transfer molecular compounds.

04.X-2 INCLUSION COMPOUNDS - AN OVERVIEW. By Wolfram Saenger, Institut für Kristallographie, Fachbereich Chemie, Freie Universität Berlin, Takustr. 6, D-1000 Berlin 33.

In this talk, the formation and structure of inclusion compounds will be reviewed as well as their growing utilization in industry.

An inclusion compound is defined as a complex where a guest molecule fits into a host cavity and is associated only by non-covalent forces. The best known inclusion compounds are iodine blue, the ice and urea clathrates, intercalation complexes and adducts formed by zeolites and by cyclodextrins. In addition, there is a wide variety of other inclusion compounds ranging from inorganic to organic hosts to more complex systems such as enzyme-substrate and DNA intercalation complexes, and new host compounds are being tailored according to the spatial requirements of certain guest molecules. Due to limitations of time, only some examples of this fascinating class of compounds will be discussed, with emphasis on structural aspects.

Literature:

J.L. Atwood, J.E. Davies, D.D. MacNicol "Inclusion Compounds", Vol. 1-3, Academic Press, New York (1984).

04.X-3 CRYSTALLINE COMPLEXES INVOLVING AMINO ACIDS AND PEPTIDES. By M. Vijayan, Molecular Biophysics Unit, Indian Institute of Science, Bangalore - 560 012, India.

The first systematic attempts to utilise the X-ray analysis of molecular complexes involving amino acids and related model compounds have been concerned with interactions between basic amino acid side chains and the phosphate group in protein-nucleic acid association. These attempts were closely followed by detailed structural studies on complexes between nucleotide bases and their derivatives on the one hand and amino acids and their derivatives on the other, in an attempt to elucidate the elementary patterns of interactions between bases and amino acid side chains. In the meantime, the X-ray analysis of crystalline complexes involving amino acids and peptides, among themselves as well as with other biomolecules, was developed, largely in our laboratory, as a useful tool for characterising the atomic details of the possible non-covalent interactions important in the structure, assembly and function of proteins.

The X-ray work on amino acid and peptide complexes has been concerned largely with hydrogen bonded and ionic interactions (salt bridges). The results of this work emphasize the high directionality and specificity (implying recognition) of such interactions. For example the positively charged guanidyl group of arginine can, and does, take part in four types of specific interactions, two involving two parallel hydrogen bonds and the other two two convergent hydrogen bonds. The carboxyl group takes part in a specific interaction involving two parallel hydrogen bonds in favourable situations. The lysine side chain, by itself, cannot take part in a specific interaction, but it forms characteristic interaction patterns with, for instance, the carboxyl group.

In all the amino acid complexes, the unprotected amino acid molecules align themselves into head-to-tail sequences in which the α -amino and the α -carboxylate groups are brought into periodic hydrogen-bonded proximity in a peptide-like arrangement. Such sequences, the ubiquitous occurrence of which cannot be explained exclusively in terms of simple electrostatic interactions, have been suggested to be of probable relevance to prebiotic condensation during chemical evolution. A careful examination of the crystals of amino acids, their racemates and complexes indicate that these sequences are an intrinsic feature of amino acid aggregation. A detailed analysis of the relevant peptide structures, the X-ray determination of a dipeptide-dipeptide complex and theoretical modelling studies show that head-to-tail sequences remain the most prominent feature of peptide aggregation which is governed essentially by interactions involving main chain atoms. The comparison of complexes between L amino acids and those between a L amino acid and a D amino acid provides insights into the effect of chirality on molecular aggregation. The difference between the aggregation patterns observed in LL and LD complexes are also of probable relevance to chiral selection during chemical evolution.