

PS06.06.12 MOLECULAR ARRANGEMENTS OF ALKYL-AMMONIUM SALTS AND AROMATIC ADDITIVES IN THE COMPLEX CRYSTALS. Keiichi Noguchi, Kulthida Vongbupnimit, Shigehiro Kamitori and Kenji Okuyama, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei Tokyo 184, Japan.

Recently, it has been found that some amphiphile molecules such as ammonium salts, phosphonium salts and other onium salts have the specific abilities to form complexes with aromatic molecules. In some cases, the formation of complexes can be prepared simply by mixing both powders of amphiphiles and aromatic molecules in a mortar (Toda, F. Tanaka, K., Okada, T., Bourns, S. A. & Nassimbeni, L. R., *Supramol. Chem.*, 1994, 3, 291-298). We have been investigating the crystal structures of various amphiphiles (host) and aromatic molecules (guest) by X-ray diffraction method in order to clarify the structural details and interactions between host and guest molecules (Vongbupnimit, K., Noguchi, K. & Okuyama, K., 1996, *Mol. Cryst. Liq. Cryst.*, in press). In the present work, the molecular arrangements in the complex crystals of dodecyltrimethylammonium chloride (DTAC) and four aromatic molecules, namely, hydroquinone(1), catechol(2), *p*-iodophenol(3), and *p*-phenyl-phenol(4) will be discussed.

All the four complex crystals show the smectic layer arrangement in which the host amphiphiles are mutually interdigitated and make some space for guest molecules between the parallel alkyl chains. Two types of molecular packings of DTAC and the guest molecules were observed. In the case of complexes 1 and 2, the aromatic ring of the guest molecule is parallel to the zigzag plane of the alkyl chain of the host molecule. Interaction between the guest molecules in these complexes is one-dimensional and very different from those in the guest crystals. On the other hand, the packings of host and guest molecules in the complexes 3 and 4 are found to be some kind of herringbone arrangement. A similar packing has also been observed in the crystal structures of the guest molecules. Also the transition temperature and the shape of the endothermic peak in DTA curves of complexes 3 and 4 are similar to those of their respective guest crystals. These results indicate that the specific interactions between the aromatic molecules in the guest crystals are kept even in the complex crystals. We termed the packing of 1 and 2 as 'host-dependent packing', and that of 3 and 4 as 'guest-dependent packing'.

PS06.06.13 NOVEL HYDROGEN-BONDED HOST LATTICES IN INCLUSION COMPOUNDS OF UREA AND PERALKYLATED AMMONIUM PENTABORATE SALTS. Thomas C.W. MAK* and Qi LI Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

As a sequel to our continuing research program in the rational design of new urea/thiourea-anion host lattices,^{1,2} two novel inclusion compounds containing hydrogen-bonded host networks constructed from urea and nonplanar pentaborate anions, (*n*-C₃H₇)₄N⁺[B₅O₆(OH)₄]⁻•4CO(NH₂)₂•H₂O (1) and (*n*-C₄H₉)₄N⁺[B₅O₆(OH)₄]⁻•2CO(NH₂)₂•B(OH)₃ (2), have been prepared and characterized by X-ray crystallography.

Compound 1 has a channel-like host lattice built of urea molecules, pentaborate ions and water molecules in a molar ratio of 4:1:1, and the (*n*-C₃H₇)₄N⁺ cations (represented by large circles) are arranged in a zigzag column within each channel (Fig. 1). Compound 2 features a two-dimensional open host network in which two channel systems extend parallel to the [101] and [010] directions, such that the (*n*-C₄H₉)₄N⁺ cations are accommodated in a stacked column within each channel of the first type (Fig.2) and in a zigzag column within each channel of the second type (Fig.3).

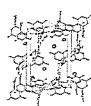
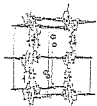
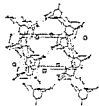


Fig. 1

Fig. 2

Fig. 3

1. Q. Li and T. C. W. Mak: *J. Incl. Phenom.*, 1995, 20, 73.2. T. C. W. Mak, W. H. Yip and Q. Li: *J. Am. Chem. Soc.*, 1995, 117, 11995.

PS06.06.14 STRUCTURE OF MACROCYCLE CONTAINING AZO AND AZOXY UNITS AND THEIR COMPLEXES. Yu.A.Simonov, Institute of Applied Physics, 2028 Kishinev, Moldova and J.Biernat and E.Luboch, Technical University of Gdansk, 80-952 Gdansk, Poland

Compounds containing the azo or azoxy units find application in the chemical sensors and the original materials for Langmuir films. A one step synthesis of both azoxy and azo crown analogues was performed by reducing bis(2-nitrophenoxy)-3-oxapentane with sodium stannite. According to X-ray analysis the 13-membered macrocycles have *cis* oriented phenyl residues in the azo compound (*L13*), whereas their orientation in the azoxy compound (*L13-O*) is *trans*. Their 16-membered analogues, (*L16*) and (*L16-O*) have been obtained. During the macrocycles interaction with NaI and KI the following complexes were isolated and structurally characterized: [Na(*L13*)²], [Na(*L13-O*)²], [K(*L16-O*)²]. From every crown ether molecule sodium atoms are coordinated by three oxygen and one nitrogen atoms placed in the antiprism corners. Na-O and Na-N distances are 2.31-2.58 and 2.50-2.59 Å, respectively. In both cases phenyl residues are in *trans*-position in respect to the -N=N- (-N=N(O)-) bond. Potassium atom in [K(*L16-O*)²] compound is ten-coordinated as a pentagonal antiprism. K-O and K-N distances are 2.83-2.92 and 3.01 Å respectively. Phenyl residues have *trans* orientation here. In all described sandwich-like structures intramolecular stacking interaction between phenyl moieties occurs. *L16-O* macrocycle forms the inclusion compound with NaI with the metal : ligand stoichiometry 1:1. Sodium atom coordination polyhedron is a pentagonal pyramid. In the crystal intermolecular stacking interaction was found.

PS06.06.15 MONOCLINIC THIOUREA INCLUSION COMPLEXES: IMPLICATIONS OF THE DURENE ADDUCT CRYSTAL STRUCTURE. John S Rutherford, Sultan Qaboos University, Sultanate of Oman, Emmanuel Marfo-Owusu, University of Transkei, South Africa and Peter S Ford and Judith A K Howard, University of Durham, UK.

The crystal structure of the durene (1,2,4,5-tetramethylbenzene) channel inclusion complex with thiourea, containing 11 molecules in the asymmetric unit, was determined using single crystal diffractometer data at 18°C, and refined to an R Factor of 0.104. The repeat distance along the channel is 37.33 Å, which corresponds to 4 durene molecules end-to-end, and to 3 complete turns of the thiourea chains. These two sublattices are each remarkably regular, constituting a "lock-in" commensurate superstructure in terms of the Rennie-Harris model [J. Chem. Phys., 96, 7117 (1992)]. The oblong cross-section of the durene molecules, as viewed along the channel axis, is accommodated by a herringbone arrangement of neighbouring channels. This effect is produced from the normally regular honeycomb host lattice through an antiparallel displacement of alternate sheets of thiourea molecules. Since the space group of this adduct is related to the rhombohedral aristotype through the following subgroup relations:

$$\begin{array}{cccc} R\bar{3}(bar)c & A2/a & P21/a & P21/m \\ I(1) & II(3) & III(6) & IV(18) \end{array}$$

(subgroup orders in parentheses), it can be deduced that monoclinic thiourea host lattices correspond to space group III, which actually occurs for the *trans*-1,2-dibromocyclohexane adduct. A phase transition directly from I to III is also consistent with the observed behaviour of the cyclo-hexane adduct at low temperatures [J. Solid State Chem., 10, 46 (1974)]. The intensity statistics expected for such lock-in superstructures will be discussed, as will possible extensions to the Rennie-Harris model.

[Crystal data: 2C₁₀H₁₄•9SC(NH₂)₂, monoclinic, space group *P21/m*, a = 18.595(4) Å, b = 15.324(3) Å, c = 18.780(4) Å, β = 105.07(3)°, Z = 4].