

SUPRAMOLECULAR SELF-ASSEMBLY THROUGH DIFFERENT π -ARYL INTERACTIONS IN TWO ORGANOTELLURIUM COMPOUNDS

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$C_{12}[C_{16}H_{12}C_{12}]_2$ Te(IV)(1) and $Br_2[C_{16}H_{12}Br_2]_2$ Te(IV) (2). In both compounds the primary geometry about the Te(IV) atom is disphenoidal, with the halides in the apical positions and the lone pair of electrons and C atoms in the equatorial plane. In (1), the Te(IV) atom participates in a π -C₆H₅ interaction with one of the peripheric phenyl rings of a neighbouring molecule (Te⁺centroid = 3.757 Å), resulting in the self-assembly of a chain like supramolecular arrangement. The chains are packed by van der Waals interactions between the dangling phenyl rings of the second phenyl-chlorovinyl substituent. In (2) a Te⁺Br [3.253(1) Å] secondary bond links the molecules in a chain fashion. The adjacent chains are extended into a three dimensional supramolecular array by a Br⁻ π -C₆H₅ inter-chain interaction (3.680 Å). Due to the secondary interactions, which includes intramolecular Te⁺X secondary bonds, the polyhedron around the tellurium can be best described as a distorted pseudo-pentagonal bipyramid, with two halides in axial positions and the centroid of a phenyl ring in (1) and a bromine in (2) occupying the fifth equatorial position. Acknowledgements FAPESP, CNPq, CAPES.

Keywords: SELF ASSEMBLY, PI-ARYL INTERACTION, ORGANOTELLURIUM

PHASE TRANSFORMATIONS IN T-BUTYL CALIX[4]ARENE INCLUSION COMPOUNDS AT ELEVATED TEMPERATURES

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Thermal gravimetric analysis (TGA) studies have shown that upon heating a number of 1:1 t-butylcalix[4]arene (C4) inclusion compounds lose guest molecules and gradually convert to a stable 2:1 form. Remarkably this phase transformation occurs without loss of crystallinity. Single crystals (0.35 mm x 0.35 mm x 0.1 mm) of 1:1 C4-toluene (1) were mounted on goniometer heads and heated at 2° C/min (as in TGA studies). Those crystals that were removed at 150° C were completely transformed to single crystals of a 2:1 C4-toluene phase (2) (despite changes in crystal symmetry and unit cell volume). Those removed between 120° and 150° C were hybrid crystals. Diffraction studies revealed the simultaneous presence of domains of both 1 and 2, but only a single orientation of each phase. The 2:1 and hybrid crystals converted back to single crystals of 1 when heated overnight at 70° C in the presence of toluene vapor. Crystals heated beyond 150° C lost all guest molecules and were converted to a polycrystalline phase of neat, self-included C4 (3) which, upon further heating (above 240° C), were further transformed to a newly characterized low-density phase of neat C4 (4). Compounds 1, 2 and 4 all exhibit a similar layered structure with the C4 molecules arranged in an interlocked square-grid motif. In order to convert from 1 to 2 adjacent layers must shift by ~0.9 nm with respect to each other. It is remarkable that such large movements can be accomplished without destruction of the single crystals.

Keywords: INCLUSION COMPOUNDS, PHASE TRANSITIONS, HYBRID CRYSTALS

INCLUSION OF PARABEN MOLECULES IN HEPTAKIS(2,3,6-TRIO-METHYL)- β -CYCLODEXTRIN

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The aim of this study was to investigate the inclusion of methyl-, ethyl-, propyl- and butyl paraben in TRIMEB [heptakis(2,3,6-tri-O-methyl)- β -cyclodextrin] in the solid state. Powdered inclusion complexes were prepared by kneading. Thermal analysis and X-ray powder diffraction [XRPD] were used to confirm that complexation had occurred. Infrared spectroscopy was used to determine how the carbonyl stretching frequency was affected by complexation. X-ray diffraction from single crystals was used to determine structural and geometrical features. The thermal analytical results and XRPD patterns of the kneaded materials were different from those of physical mixtures, indicating complexation. The C=O stretching frequency of the complexed drug showed an increase frequency relative to the uncomplexed drug, which also indicated that the guest is included in the host. Preliminary X-ray photography revealed Laue mmm symmetry, corresponding to the orthorhombic system [space group $P2_12_12_1$]. Accurate cell data are listed below (in Å), with Z=4 complex units with 1:1 host-guest ratio in each case. Methyl paraben complex: a=10.718(1), b=26.353(1), c=30.018(2)Å; Ethyl paraben complex: a=14.886(2), b=22.024(3), c=27.602(2)Å; Propyl paraben complex: a=14.863(1), b=21.862(2), c=27.627(3)Å; Butyl paraben complex: a=14.866(2), b=21.967(2), c=27.635(4)Å. Physicochemical methods of analysis show that methyl-, ethyl-, propyl- and butyl paraben form well defined inclusion complexes with TRIMEB. All guests, except ethyl paraben, are orientated with their hydroxyl groups at the host secondary rim.

Keywords: CYCLODEXTRIN, INCLUSION COMPLEX, PARABEN

THE INFLUENCE OF INTERMOLECULAR INTERACTIONS ON THE SYN/ANTI FORM OF 2,4,6-TRIHYDROXYBENZOIC ACID - CRYSTALLOGRAPHIC STUDIES.

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2,6-Dihydroxybenzoic acid (DHBA) is known to form two polymorphs in which two different intramolecular hydrogen-bond schemes are observed [1]. 2,4,6-Trihydroxybenzoic acid (THBA), similarly to DHBA, has also two possibilities for intramolecular hydrogen-bond formation, one with two phenolic OH groups and second with one phenolic and one carboxylic OH group involved as donors in intramolecular H-bonds. To examine the influence of intermolecular interactions on the preferred form of the THBA molecule the crystalline complexes of THBA with weak heteroaromatic bases like pyrazine, quinoxaline and phenazine have been prepared and their crystal structure determined by X-ray analyses. Pyrazine and quinoxaline form with THBA 1:1 complexes where THBA carboxylic group adopts syn conformation. THBA molecule and the hydrogen-bonded to the carboxylic group aromatic base are nearly coplanar. While no stacking interactions are observed in the pyrazine complex, quinoxaline and THBA are arranged into infinite stacks where base and acid molecules alternate. When THBA is co-crystallized with the largest base, phenazine, the 1:2 complex is formed and the THBA molecule adopts anti form. The phenolic OH groups at position 2 and 4 act as donors in the hydrogen bonds to phenazine N atoms and THBA molecules fasten together the phenazine molecules arranged into infinite stacks. Contrary to THBA, the 1:1 complex is formed by DHBA with phenazine and the acid molecule is in the syn form.

[1]Gdaniec, M., Gilski, M., Denisov, G. Acta Cryst. C50, 1622 (1994); MacGillivray, L. R. Zaworotko, M. J. J. Chem. Crystallogr. 24, 703 (1994)

Keywords: MOLECULAR COMPLEXES INTERMOLECULAR INTERACTIONS CRYSTAL STRUCTURE