

DISORDERING PATTERNS OF GUEST SPECIES IN ORGANIC ZEOLITES

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Guest molecular species present in organic zeolite crystalline frameworks are often disordered because of insufficient steric fit and non-stoichiometry of composition of the guest compound which may be two or multi-component. In addition to rather common order-disorder phenomena associated with local position and/or orientation of the guest, long range order-disorder effects may be observed. The present work reports on such non-local phenomena in some coordination complex type host materials of channel type crystal structure. Orientational ordering of guest molecules in a channel display interesting stepwise temperature behaviour, i.e. correlation of disorder to order transition between the channels appears in two steps. The temperature dependence of guest ordering within the range 100-350 K in a hexagonal host channel lattice has been determined by single crystal X-ray diffractometry (the crystal preserved its integrity on phase transitions). The host complex used is $\text{Ni}(\text{NCS})_2(4\text{-methylpyridine})_4$; the guest species being ortho- and meta-bromonitrobenzenes. The high temperature phase (above 282 or 320 K for ortho and meta isomers, respectively) are hexagonal with $a = b = 27.5 \text{ \AA}$ (approx.) which become doubled in the intermediate phase. The low temperature polymorphs are triclinic with some residual orientational disordering of the guest molecules. The phenomena seem to appear as common for this class of compounds.

Keywords: ORGANIC ZEOLITE, MOLECULAR INCLUSION, GUEST DISORDERING

INTERACTIONS INVOLVING FLUORINE: INPUTS TO DRUG POLYMORPHISM

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Crystal engineering essentially deals with the control of packing modes in crystalline solids using suitable functional groups via well-defined directional interactions like hydrogen bonds. However, among interactions involving halogens, which restrict the number of possible modes of packing, an *a priori* predictability of packing features is yet to be well understood. Especially interactions involving fluorine remain a dark area in crystal engineering and it is only through analysis of a large number of crystal structures of this category that any rationale for the propensity of $\text{F}\dots\text{F}$ to $\text{C-H}\dots\text{F}$ to $\text{C-F}\dots\pi$ be forecast. Several drug and drug intermediates belonging to isoquinoline, indole and other substituted methanols have been studied from single crystal x-ray diffraction by us to derive geometrical parameters for the above interactions involving fluorine. Analysis in terms of a newly defined slide parameter and orientational dependency suggest that $\text{F}\dots\text{F}$ interactions do occur as a special case of $\text{C-H}\dots\text{F}$ and $\text{C-F}\dots\pi$ is the most abundant interaction among halogens. Inputs to the possible exploitation of these interactions for polymorph generation have been derived.

Keywords: POLYMORPHISM, FLUORINE, DRUGS

SYNTHESIS AND USE OF POLY-PYRIDYL TECTONS IN CRYSTAL ENGINEERING

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In previous work we have reported the use of $\text{NH}\cdots\text{XM}$ ($\text{X} = \text{Cl}, \text{Br}$) supramolecular synthons based on anionic perhalometallate hydrogen bond acceptors and cationic N-H donors to allow controlled crystal synthesis. During the course of this work we have prepared several organic poly-pyridyl compounds. These compounds, when protonated, can be used as molecular building blocks, tectons, which offer a wide range of possible 1-D chain, 2-D or 3-D branched chain and 3-D motifs and geometries. This has been demonstrated through the synthesis of a range of 2,4,6-(py)-1,3,5-triazine derivatives, where py = 4-, 3- or 2-pyridyl. A range of salts involving these tectons and MCl_n anions have been prepared, where $\text{M} = \text{Fe}, \text{Sb}$ and Bi . These salts have been shown to produce 3-D layer type structures with several different structural motifs.

Keywords: PYRIDYL CRYSTAL ENGINEERING HYDROGEN BONDING TECTONS

ISOSTRUCTURAL IONS IN CRYSTAL ENGINEERING

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Supramolecular synthons such as $\text{NH}\cdots(\text{Cl})_2\text{Pt}$ may be exploited to prepare designed metal-containing hydrogen-bonded polymers, such as $\{[4,4\text{-H}_2\text{bipy}][\text{PtCl}_4]\}_n$. This project investigates the importance of hydrogen bonding in determining the aggregation of cation and anion tectons within a crystal lattice relative to shape (close packing), charge and other intermolecular forces. We seek to answer the question "Do hydrogen bonds control the long range aggregation or simply orient the molecular tectons locally?" The importance of hydrogen bonding in determining crystal aggregation is investigated using isostructural tecton ions. Isostructural tectons, such as the 2-, 3-, 4-picolinium, anilinium, and N-methylpyridinium cations, have the same molecular formulae, similar overall shapes, and the same net charge. They differ only in the position of the constituent atoms within the molecular structure and therefore in hydrogen bonding capability. Thus, the 4-picolinium cation has a singly protonated nitrogen atom within the aromatic pyridyl ring whereas the isostructural anilinium cation has a triply protonated nitrogen (primary amine) substituent on a benzene ring. Crystallisation of these tectons with metal salts, such as the square planar (MCl_4^{2-} , $\text{M} = \text{Pt}$) octahedral (MCl_6^{2-} , $\text{M} = \text{Pt}$) and tetrahedral (MCl_4^{2-} , $\text{M} = \text{Co}, \text{Zn}$) chlorometallates is reported. Crystal structures of $[\text{C}_6\text{H}_5\text{NH}_3]_2[\text{PtCl}_4]$, $[3\text{-Me}(\text{C}_5\text{NH}_5)]_2[\text{PtCl}_4]$ and $[4\text{-Me}(\text{C}_5\text{NH}_5)]_2[\text{PtCl}_6]$, are reported and the hydrogen bonding and packing patterns discussed and compared.

Keywords: ISOSTRUCTURAL, HYDROGEN BONDING, CRYSTAL ENGINEERING