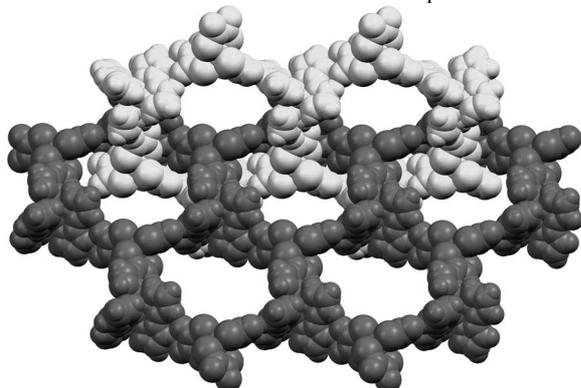


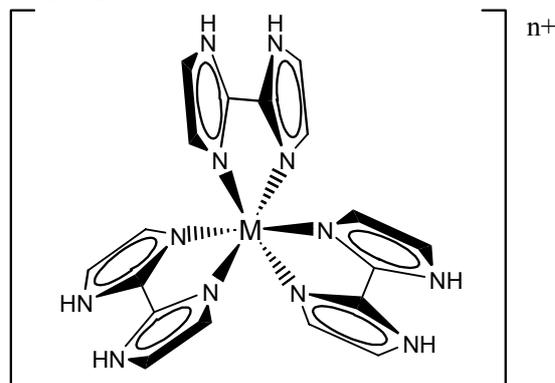
P.09.05.3*Acta Cryst.* (2005). A61, C361**Synthesis of 2D and 3D Nets Using Biimidazole Complexes**Alexandra M. E. Griffin, A. Guy Orpen, *School of Chemistry, University of Bristol, Bristol BS8 1TS*. E-mail: a.griffin@bristol.ac.uk

The use of hydrogen-bonding to control the arrangements of cations and anions has been well documented in previous research.[1]



[2] Here we report tris-chelated metal complexes containing the biimidazole ligand, which are capable of hydrogen-bonding to form three-dimensional and interpenetrated two-dimensional nets.

In particular $[\text{Ni}(\text{H}_2\text{biim})_3]^{2+}$ and $[\text{Cr}(\text{H}_2\text{biim})_3]^{3+}$ (H_2biim = 2,2'-biimidazole) have been crystallized with a variety of anionic tectons capable of hydrogen bonding to these cations.



[1] Podesta T. J., Orpen A. G., *CrystEngComm.*, 2002, 4, 336. [2] Angeloni A., Orpen A. G., *Chem. Commun.*, 2001, 4, 343.

Keywords: crystal synthesis, hydrogen bonding, biimidazole complexes

P.09.05.4*Acta Cryst.* (2005). A61, C361**Bio-mimicking Self Assembly in Materials: Role of Hydrogen and Halogen Bonding**Ashwani Vij, Joseph M. Mabry, Wade W. Grabow, Vandana Vij, *AFRL/PRSP-PRSM, 10 E. Saturn Blvd. Edwards, CA 93524*. E-mail: ashwani.vij@edwards.af.mil

Hydrogen bonding to an electronegative heteroatom is becoming an increasingly interesting area for chemists, biochemists and biologists. Because of such interactions, proteins can interact with drugs, which has enhanced our understanding of various biological processes within the body. We have made similar attempts to investigate the structures and properties of “big” small molecules, especially those containing silicon using a “macromolecular” approach to deal with data quality and diffraction issues. Halogen bonding in molecules containing silicon and tin is a favored process due to the capability of these atoms to expand their coordination spheres. Such an expansion of the coordination sphere can sometimes result in formation of unexpected crystal structures, which impart outstanding physical properties. If these systems contain fluorocarbons or fluorinated ligands, there are domains of hydrophobicity and hydrophilicity. The challenge is, however, to overcome the low temperature phase transitions to obtain meaningful

crystal structures without the destruction of crystal lattice. Data collection employing CCD or GADD detectors utilizing a sealed tube (Copper or Molybdenum) or rotating anode sources and structure solution/refinement strategies will be discussed, time permitting.

Distribution A: Approved for public release, distribution unlimited

Keywords: self assembly, biomimicking, halogen bonding

P.09.05.5*Acta Cryst.* (2005). A61, C361**Benzyltrimethylalkylammonium Haloplumbates: Organic/inorganic Composite Materials**Maciej Hodorowicz^a, Katarzyna Stadnicka^a, ^a *Faculty of Chemistry, Jagiellonian University, Kraków, Poland*. E-mail: hodorowm@chemia.uj.edu.pl

In due course of investigations of the relationships between sorption properties of benzylalkylammonium cations and their behaviour in the crystalline phases (the way of packing and the type of interactions), benzyltrimethyl-n-alkylammonium haloplumbates(II) with $n = 2 - 6$ and $9 - 10$ were tailored.

In recent years the chemistry of transition metal complexes has been developed towards the construction of different (unusual) structural models in order to rationalize the correlations between structure and physical properties. Halometallates(II) represent interesting systems for designing low-dimensional architecture with specific electronic, thermal, electrical, magnetic and polymorphic properties. Haloplumbates(II) form a particular class of these materials because the flexibility of Pb(II) coordination sphere and non-stereospecific nature of the halide anions. As mixed organic/inorganic materials benzyltrimethyl-n-alkylammonium haloplumbates(II) combine properties typical for organic molecular crystals with those associated to inorganic solids. The crystal structures of several benzyltrimethyl-n-alkylammonium haloplumbates(II) were determined by X-ray diffraction showing one-dimensional linear chains built of $-\text{[PbBr}_3\text{]}_n-$ mers. The studied structures could easily be modified by the size of ammonium cations, their packing properties and an ability to form weak hydrogen bond systems of C-H... π and C-H...X (X = halogene atom) type.

Keywords: haloplumbates, alkylammonium cations, structure

P.09.05.6*Acta Cryst.* (2005). A61, C361-C362**Crystalline Supramolecular Ladders via Co-Crystals**Tony N Sokolov, Tomislav Frišćić, Leonard R. Mac Gillivray, *Department of Chemistry, University of Iowa*. E-mail: tony-sokolov@uiowa.edu

Controlling the organization of molecules in organic solids is a topic of fundamental importance for the design of supramolecular materials. In this context, methods to dictate the organization of functional molecules in one dimensional arrays are emerging as an important area. The formation of such arrays may be achieved in either two ways: covalent functionalization of a substrate or co-crystallization. While substrate functionalization allows for the packing to be directed solely by the substrate, meaning that the bulk crystal is based purely on the substrate, the method also inherently requires further covalent modification to tune a desired property. In contrast, co-crystallization allows for the use of a “divide and conquer” approach, enabling the substrate to remain untouched while changes to the co-crystallizing agent tune a desired property. In this poster, we demonstrate the ability of 3-aminophenol (3AP) to function as a co-crystallization agent to direct the formation of infinite 1-D ladder-like assemblies in the solid state. The approach utilizes an O-H bond coupled with one N-H bond of 3AP to direct the face-to-face arrangement of a series of bipyridine units, by way of hydrogen bonds, while the second N-H bond of the amine interacts with a neighboring assembly. This approach has been extended to a series of three unsaturated homologues having the 4-pyridyl functionality; namely, 4,4'-dipyridyl(dpy), *trans*-1,2-bis-(4-pyridyl)acetylene(bpa), and *trans*-1,2-bis-(4-pyridyl)ethylene(bpe). X-ray crystal structure analyses of the co-crystals involving (3AP)-(dpy), (3AP)-(bpa), and

(3AP)-(bpe) confirms the 1-D ladder-like structures. Future work will involve studying the photophysical properties of such solids.

Keywords: supramolecular chemistry, cocrystals, infinite arrays

P.09.05.7

Acta Cryst. (2005). A61, C362

M-X...X'-C Halogen Bonds as Efficient and Reliable Supramolecular Synthons in Organic-inorganic Crystals

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The identification of non-covalent interactions in crystalline materials, the understanding of the role that these interactions play in directing supramolecular structures and the rationalisation within such structures of significant interactions with well defined geometry and reproducibility (synthons) is fundamental to crystal engineering, [1].

We have recently focused our attention in this area on the synthesis of molecular crystals in which the nucleophile-electrophile coupling between "inorganic" and "organic" halogens plays a vital role in the definition of the halogen bond synthon M-Cl...X-C (M = transition metal, X = Cl, Br, I), [2]. Theoretical calculations of the electrostatic potentials around the "organic" halogens rationalise the observed short directional interactions when integrated with previous studies of "inorganic" halogens as nucleophiles (in H-bond formation), [2,3].

Further studies have been made on halopyridinium salts of AuX₄⁻ (X = Cl, Br) where hydrogen bonds and halogen bonds cooperate in defining the crystalline structure. The nature of the halogen-halogen interactions is currently being studied via theoretical models, focusing on the evaluation of the interaction energies and of the individual components (electrostatic, charge transfer, etc.) of these interactions.

[1] Desiraju G. R., *Crystal Engineering – The design of organic solids*, Elsevier, 1989. [2] Zordan F., Brammer L., Sherwood P., *J. Am. Chem. Soc.*, 2005, **127**, in press. [3] Brammer L., Bruton E. A., Sherwood P., *Cryst. Growth Des.* 2001, **1**, 277.

Keywords: crystal engineering, halogen bonds, interaction energy

P.09.05.8

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Halogen Bonds in Inorganic Crystal Design

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The electronic properties of organic halogens (C-X) differ substantially from those of inorganic halogens (M-X). The latter are directional nucleophiles, [1], whereas the former can be tuned to serve as directional electrophiles, [2], [3]. Thus, similar to D-H...A hydrogen bonds, C-X...X'-M halogen bonds can serve as directional, non-covalent interactions that can be applied to molecular crystal design.

These non-covalent interactions have been investigated through synthesis of compounds of general formula (n-halopyridinium)₂MX₄ (n = 3, 4; M = Co, Cu), which are propagated by N-H...X'-M hydrogen bonds and C-X...X'-M halogen bonds [X = Cl, Br, I, (≠ F); X' = Cl, Br, I]. The geometry of the hydrogen bonds vary in this series (linear, symmetrically and asymmetrically bifurcated), but halogen bonds have well defined geometries (linear for the organic halogens, bent for the inorganic). Normalised halogen bond distances, R_{XX'}, decrease: (i) with increasing negative electrostatic potential at the inorganic halogen, suggesting that these interactions are predominantly electrostatic in nature; (ii) with heavier organic halogens, which have positive axial electrostatic potentials. Competition between hydrogen bonds and halogen bonds has also been explored in mixed halide systems. These studies are supported by a CSD study showing the preferred geometries of over 300 C-X...X'-M halogen bonds.

[1] Brammer L., Bruton E. A., Sherwood P., *Cryst. Growth Des.*, 2001, **1**, 277.

[2] Brammer L., Minguez Espallargas G., Adams H., *CrystEngComm*, 2003, **5**, 343. [3] Zordan F., Brammer L., Sherwood P., *J. Am. Chem. Soc.*, 2005, **127**,

in press.

Keywords: crystal engineering, halogen bonds, databases

P.09.05.9

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Control of Reactivity in the Solid State through Principles of Supramolecular Chemistry

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The crystalline solid state provides an environment that supports highly stereoselective reactions, wherein the stereochemistry of the product is largely controlled by the arrangement of molecules in the reactant crystal. However, the solid state has remained unexploited as a medium for synthetic chemistry, due to the difficulties related to achieving the crystal packing suitable for a reaction.

Our research group has approached the issue of controlling solid-state reactivity using principles of supramolecular chemistry, specifically template-controlled reactivity. Template-controlled solid-state synthesis uses linear templates, in the form of resorcinol, to direct solid-state [2+2] photodimerizations. The templates preorganize reactants within finite hydrogen-bonded molecular assemblies. Exposure of the assemblies in the solid state to ultraviolet radiation results in the stereospecific formation of a cyclobutane product.

The supramolecular nature of the lison between the reactant and the template provides the method with modularity that led us to explore the possibility to use the approach as a general way to conduct solid-state reactions. Specifically, we have addressed the construction of molecules with different sizes and shapes. In this contribution we report the construction of biologically relevant [3]- and [5]-ladderane frameworks, as well as the *ortho*-, *meta*- and *para*-[2.2]-cyclophane in quantitative yields and gram amounts.

Keywords: solid state reactivity, supramolecular assemblies, photochemistry

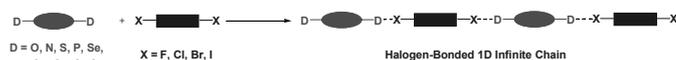
P.09.05.10

Acta Cryst. (2005). A61, C362

Halogen Bonding in Crystal Engineering

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Halogen bonding is the non-covalent interaction between halogen atoms (Lewis acids) and neutral or anionic Lewis bases¹. The main features of the interaction will be given and the close similarity with hydrogen bonding will become apparent. Some heuristic principles will be presented in order to develop a rational crystal engineering based on halogen bonding. The focus will be in particular on halogen bonded supramolecular architectures given by halocarbons and related structures. The potential of the interaction will be shown by useful applications in fields as diverse as synthetic chemistry, material science, and bioorganic chemistry.



[1] Metrangolo P., Neukirch H., Pilati T., Resnati G., *Acc. Chem. Res.*, 2005, in press.

Keywords: supramolecular chemistry, halogens, intermolecular interactions

P.09.05.11

Acta Cryst. (2005). A61, C362-C363

A Non-symmetric Disordered Tetramer: The Unusual Structure of 3(5)-ethyl-5(3)-phenyl-1H-pyrazole in the Solid State

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