

FA4-MS30-T01

Gels, Borromeanes and Self-Assembled Nanostructures from Competing Interactions to Ureas. Jonathan W. Steed. *Department of Chemistry, Durham University, South Road, Durham DH1 3LE.*
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A series of pyridyl-appended bis(urea) ligands form supramolecular gels in the presence of metal ions (metallogeles), particularly copper(II) and silver(I). The gels have been characterised by rheometry and SEM, and the effect of the metal ions on gel strength and morphology examined. The metal-induced gelation is linked to the competition between urea-urea and urea-pyridyl hydrogen bonding interactions. Crystals grown from these gels reveal a wealth of structural information about these systems that can be related to gel structure using powder X-ray diffraction data of their xerogels. Exotic species such as Borromean weaves and metallomacrocycles are all formed as alternatives to gelation.

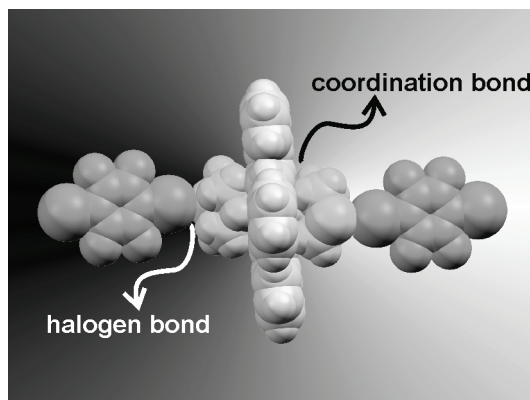
[1] *Angew. Chem., Int. Ed.*, 2008, 47, 5761–5764. [2] *Chem. Soc. Rev.*, in press.

Keywords: gel, Borromean, urea

FA4-MS30-T02

Halogen bonds: mechanosynthesis, unusual acceptors and metal-organic materials. Tomislav Friščić, William Jones. *Department of Chemistry, University of Cambridge, United Kingdom.*
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The past decade has witnessed an explosive growth of interest of chemists, materials scientists and biochemists in halogen bonds. As a result of such intensive research, halogen bonding is now becoming recognised as a versatile design element in crystal engineering. The presentation will provide a brief overview of the current status of halogen bonding in crystal engineering, and highlight several halogen-bonded systems that are being studied in our laboratory. We will describe the application of halogen bonding and isostructurality for the construction of cocrystal-based materials with controllable properties,[1] with particular attention given to systems involving halogen bond acceptors that are not compatible with hydrogen bonding, such as sulfur groups. The application of solid-state mechanochemistry for the synthesis of halogen-bonded architectures will be described,[2] and we will illustrate how the study of mechanochemical cocrystallisation using halogen bonds led to a better understanding of the mechanosynthesis of hydrogen-bonded cocrystals. Finally, the presentation will address our efforts towards the development of designs to construct halogen-bonded metal-organic materials.



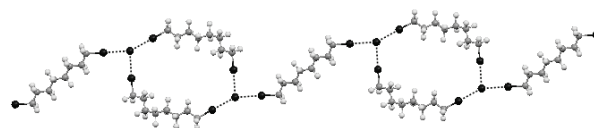
[1] Cinčić, D., Friščić, T., Jones W., *Chem. Eur. J.*, 2008, 14, 747. [2] Cinčić, D., Friščić, T., Jones W., *J. Am. Chem. Soc.* 2008, 130, 7524.

Keywords: halogen bonding, cocrystals, metal-organic compounds

FA4-MS30-T03

Halogen Bonding: A New Supramolecular Synthon in Anion Coordination Chemistry. Giancarlo Terraneo^{a,b}, Serena Biella^{a,b}, Pierangelo Metrangolo^{a,b}, Tullio Pilati^c, Giuseppe Resnati^{a,b,c}. ^aNFMLab - D.C.M.I.C. "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Italy. ^bCNST - IIT@POLIMI, Politecnico di Milano, Via G. Pascoli 70/3, 20133 Milan, Italy. ^cC.N.R. - I.S.T.M., University of Milan, Via C. Golgi 19, 20133 Milan, Italy.
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The halogen bonding (XB), namely the noncovalent interactions wherein halogen atoms function as electrophilic species [1], can be considered as a first choice intermolecular interaction for effective design of self-assembly processes, crystal engineering, and materials science [2]. The particular effectiveness of the interaction in self-assembly processes involving neutral species has received broad attention, on the contrary anion coordination and anion-templated assembly under XB control is a much less developed field [3]. In this contribution, we report some examples of anion binding driven by halogen bonding wherein halide anions act as halogen bonding acceptors. We will present how XB directs the self-assembly of anions forming discrete adducts and 1D, 2D, or 3D supramolecular networks. We will also describe how oxyanions, by far the most numerous class of anions in organic chemistry, can be used as new building block in crystal engineering based on halogen bonding. Some specific examples will be discussed in order to outline some general principles for the design of effective and selective receptors based on XB.



[1] Metrangolo P., Resnati G., *Science*, 2008, 321, 918. [2] Metrangolo P., Meyer F., Pilati T., Resnati G., Terraneo G., *Angew.*

Chem. Int. Ed., 2008, 47, 6114. [3] Metrangolo P., Pilati T., Biella S., Terraneo G., Resnati G., *CrystEngComm*, 2009, 11, 1187

Keywords: Halogen Bonding, Self-assembly, Anion Coordination

FA4-MS30-T04

The Electron-Pair Saturation Rule. A New Way of Looking at Crystal Packing. Paola Gilli, Valerio Bertolasi, Gastone Gilli. *Department of Chemistry and Centre for Structural Diffractionometry, University of Ferrara, Italy.*
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Packing forces can be divided in two large groups. The first is physical and includes: (i) *van der Waals (vdW)* forces as a balance of repulsion (exchange) and attraction (dispersive) interactions; and (ii) *electrostatic multipolar* forces as a sum of monopolar and dipolar interactions. The second is chemical and arises from: (iii) groups which are either Brønsted acids (proton donors, D–H) or Brønsted bases (proton acceptors, :A) and may interact by forming D–H⋯:A H-bonds; and (iv) groups which are either Lewis bases (electron donors, :D) or Lewis acids (electron acceptors, A) and may interact by forming D→A electron donor-acceptor (EDA) or charge-transfer (CT) interactions. This classification is quite useful in H-bond studies where directly leads to the *pK_a equalization principle* [1,2] for which really strong H-bonds occur only when the difference $\Delta pK_a = pK_a(D-H) - pK_a(A-H^+)$ tends to zero, but has proved to be inadequate for packing studies where the EDA/H-bond separation substantially hinders any unified treatment. The present contribution tackles this problem by the following strategy:

1. All possible EDA interactions have been rearranged following the seminal Mulliken classification [3];
2. The dichotomy between proton exchange and charge transfer is removed by reinterpreting the X/C–H⋯:Y H-bond as a donor-acceptor X/C–H←:Y adduct linked by a $\sigma^* \leftarrow n$ EDA interaction, analogous to that occurring in X/C–Hal←:Y halogen bonds; in this way all contacts (except vdW) become EDA interactions where the electron is the unified exchange particle;
3. These methods were applied to analyse 239 short contacts in the X-ray structures of picric acid and 14 of its adducts with nitrogen bases, finally leading to assess the novel electron-pair saturation rule for which ‘all electron donors of a closed-shell molecule, either non-bonding pairs of lone pairs or π -bonding pairs of multiple bonds, become spontaneously engaged in EDA interactions with the electron acceptors present, as far as these are available; when the acceptors are insufficient to saturate all donors, the latter are saturated in order of decreasing EDA interaction strength’;
4. Final results allow to reclassify attractive forces in two groups: (i) *physical* interactions due to *atomic* charges and dispersive forces and widely independent of the molecular constitution; (ii) *chemical* interactions (including EDA interactions and X–H⋯:Y and C–H⋯:Y H-bonds) which can be intended as holistic properties of whole molecules reacting among themselves by incipient (molecular interaction) or full (dative bond) nucleophilic addition to fulfil the saturation rule, that is to remove from the external molecular surface the maximum number of *points of residual reactivity* associated with bonding or non-bonding unsaturated electron pairs. It is

shown that this way of intending molecular interactions provides a particularly easy way to look at the crystal packing.

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Keywords: hydrogen bonding, EDA interactions, electron-pair saturation rule

FA4-MS30-T05

Hydrogen bonds and dynamics of crystalline amino acids: a synergetic effect of combining X-ray diffraction and single-crystal polarized Raman spectroscopy. Elena V. Boldyreva^{a,b}, Boris Kolesov^{a,c}.
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The properties of hydrogen bonds in crystals attract much attention, since they determine the crystal structures, their stability with respect to changes in temperature and pressure, non-linear optical properties, etc. Crystalline amino acids are also considered as biomimetics, and the knowledge of the dynamics of their crystal structures is helpful, to understand dynamics of biopolymers. Precise diffraction data can give valuable information on the position of atoms in the crystal structure and on the distribution of the electron density. At the same time, in case of static or dynamic disorder the diffraction techniques can give only averaged information, and are often not very efficient. It may be difficult, if at all possible to evaluate the parameters characterizing the barriers of rotation of hydrogen-bonded molecular fragments. A comparison of the relative strength of hydrogen bonds, if based on diffraction data, relies exclusively on the geometric parameters, what may be misleading. The exact position of H-atoms in a hydrogen bond may be difficult to find from X-ray diffraction data. At the same time, polarized Raman spectra measured from single crystals in several orientations at multiple temperatures and/or pressures may give an insight into fine details of the geometry and dynamics of hydrogen bonds and their role in phase transitions and solid-state reactivity. In the present contribution we shall illustrate this on several examples, including phase transitions in L-serine, L- and DL-cysteine, pressure-induced proton transfer in the crystals of oxalic acid dihydrate and several oxalates of selected amino acids, as well as the unique properties of selected hydrogen bonds in L-alanine on variations of temperature and pressure.

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Keywords: amino acids, hydrogen bonds, Raman spectroscopy, high-pressure crystallography, low temperatures