



[1] An IUPAC Task Group set up to examine the definition of halogen bonding has not reported yet, so that given here should be taken as temporary (see www.iupac.org/web/ins/2009-032-1-100 and www.halogenbonding.eu). [2] P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo *Angewandte Chemie International Edition* **2008**, *47*, 6114–6127. [3] P. Metrangolo, T. Pilati, S. Biella, G. Terraneo, G. Resnati *CrystEngComm* **2009**, *11*, 1187–1196. [4] A. Mele, P. Metrangolo, H. Neukirch, T. Pilati, G. Resnati *Journal of the American Chemical Society* **2005**, *127*, 14972–14973.

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Ionic, hydrogen or halogen bonds? Relevance for predicting crystal structures

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Describing a solid as a salt or a cocrystal and identifying the hydrogen or halogen bonds is central to crystallographic discussions, but there are borderline cases with proton disorder or long intermolecular distances. Is making these distinctions essential for predicting the crystal structures? This is investigated by modelling crystal structures using quantum mechanical calculations on the isolated neutral molecules or ions, and then modelling crystals as bound by the intermolecular electrostatic, repulsion and dispersion forces, with no explicit hydrogen or halogen bonding terms [1]. Crystal energy landscapes are calculated for three pyridinium carboxylate salts and the corresponding pyridine carboxylic acid cocrystals. The most stable crystal structures of the salt and cocrystal are compared with each other and the experimental crystal structures [2]. Despite the steric similarity of the neutral, COOH \cdots N(arom), and ionic, COO \cdots H-N+(arom), forms of the carboxylic acid pyridine heterosynthon, the relative energies of various crystal structures are sensitive to whether the solid is modelled as a salt or cocrystal. The hydrogen bonding appears to be sufficiently well described to predict the observed structures, although periodic electronic structures calculations are needed to confirm the proton disorder observed in one system. In contrast, many halogenated crystal structures have been correctly predicted by simply modelling the intermolecular interactions as the sum of electrostatic, repulsion and dispersion interactions, although modelling the anisotropy in the repulsive wall can be important [3], [4], [5].

The crystal energy landscapes show the variety of alternative crystal structures that are competitive with the observed structures in thermodynamic stability [6]. The range of compromises between all the intermolecular interactions within the crystal structures that are calculated to be thermodynamically favourable can be seen as a stringent test of whether the initial assumptions about the intermolecular forces are physically reasonable

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Halogen bonding involving metallate ions and anionic ligands

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The predominantly electrostatic nature of halogen bonds [1], [2] makes anions excellent halogen bond acceptors. Over the past 10 years we have studied the formation of halogen bonds in metal complexes, including metallate anions and related neutral complexes in which formally anionic ligands serve as the halogen bond acceptor.

The talk will provide a survey of halogen bonding across different anionic ligand types (and their corresponding metallate anions), focussing on halide ligands (X), which permit tunability of the acceptor group as well as the halogen bond donor [3], cyanide [4], [5] and thiocyanate ligands [5].

The relative strength of halogen bonds in the solid state has been established [1], [2], [3] and the determined quantitatively in solution [6]. The response of C–X \cdots X–M halogen bonds to changes in pressure and temperature have been studied in the solid state [7] as has the guiding role of such interactions (alongside hydrogen bonds) in solid state reactions [8].

A brief perspective on the scope of halogen bonding across a wide range of other ligands will also be provided [9].

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Electronic factors affecting the I–I bonds in the simplest polyiodides

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In the last decades, halogen bonding has acquired particular relevance for the building up of supramolecular patterns [1]. Heavier halides, especially iodines, are particularly sensitive to residual interactions, which allow formation of compounds of large nuclearities. In fact, anionic I_n^m species with n up to 29 and $m = -1, -2, -3$ have been reported [2], the simplest one being obviously I_3^- . Grouping of already electron rich atoms with similars, possibly with negative charge, is usually attributed to the high polarizability of the element. Calculations of the electron density are available, which highlight the points of its accumulation/depletion hence the capabilities of subsequent aggregations [3]. From the MO point of view, it is important to understand the electronic parameters which affect the stereochemistry of the higher nuclearity assemblies and, in particular, the variable strengths of the I-I interactions. The variability of the effects are already observed in the simplest linear systems I_3^- and I_4^{2-} , of which there are numerous crystal structures available. The I-I distances significantly vary depending on the nature of the counterion(s) and the overall packing arrangement. Thus I_3^- has not always the expected $D_{\infty h}$ symmetry but the two distances can become as different as 0.2 Å. Also for I_4^{2-} , which in principle consists of a central I_2 molecule residually interacting with two external I^- anions, it is evident that the three I-I separations depend on the crystal environment with possible loss of the highest symmetry. Here, we present a simple model based on experimental and theoretical data, which highlights how the mixing of the key σ orbitals is affected by a different distribution of the positive charges in various crystals [4]. To determine the latter, the Hirshfeld surface approach has been applied to some selected experimental structures where the differences are most remarkable [5]. Systematic DFT calculations (in vacuum and solvent) confirm that variously localized positive charges around the polyiodide can significantly affect the geometries of even the smallest I_3^- and I_4^{2-} units. The satisfactory results are interpreted in terms of a simple qualitative MO model, which monitors the σ orbital mixing for different positive charge distributions, hence the variable strength of the I-I bonding. The reciprocal validation between experiment and calculations and the predictability of the trends are the interpretational key to predict the variability of the halogen bonding in the smallest polyiodides and possibly in those of higher nuclearity.

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Computational and CSD analysis of $I_3^- \cdots I_3^-$ halogen bonds

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Iodide ions have a strong affinity to iodine molecules, forming polyiodide species such as triiodide (I_3^-), where the $I^- \cdots I_2$ interaction is extremely strong ($\sim 180 \text{ kJ mol}^{-1}$) [1]. These triiodide species can then form further interactions to neighbouring I_3^- ions, often forming infinite chains of ions [2]. These $I_3^- \cdots I_3^-$ interactions are surprisingly common, as seen from the number of crystal structures that contain this motif in the Cambridge Structural Database (CSD) [3]. Although the most

commonly observed chains are linear, or contain the triiodide ions oriented at 90° with respect to each other, as would be expected from the sigma-hole model of halogen bonding [4], a wide deviation from these angles has been observed. In this work we describe a detailed analysis of the relative orientations of I_3^- ions involved in interactions with neighbouring I_3^- ions, which we show with the aid of MP2 and density functional theory calculations is the result of the bending potential in $I_3^- \cdots I_3^-$ interactions being very low. Furthermore, we have found that the chemical environment of the ions plays a major role in stabilising the interactions. Although I_3^- is calculated as being stable in the "gas-phase", the presence of a surrounding electric field, as found in ionic crystals, is necessary for the stabilisation of $I_3^- \cdots I_3^-$ interactions.

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Perovskite oxynitride materials: anion order, Valence States and physical properties

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Oxynitrides represent a vast group of compounds to explore new materials with properties analogous to oxides [1]. The similarities in electronegativity, polarizability, ionic radii and coordination numbers of nitrogen and oxygen allow the formation of the same structural types when combined with cations, as well as the mutual substitution of both anions at the same crystallographic sites. This may result in the formation of solid solutions where the formal oxidation state of one or more cations changes according to the O/N ratio.

Oxynitride perovskites have been recently reported as non-toxic inorganic pigments, dielectric materials, visible light photocatalysts and colossal magnetoresistance materials among other applications. Perovskites of alkaline earth and early transition metals with formula AMO_2N ($A = \text{Sr, Ba}$) have been reported as dielectric materials ($M = \text{Ta}$) and visible active photocatalysts for water splitting ($M = \text{Nb, Ta}$). Perovskites of europium and Nb, Ta or W show a variety of electrical and magnetic properties that are tuned by the valence states of the cations, adjusted by the N/O ratio. They are prepared by treating precursor oxides in $NH_3(g)$ and the nitrogen stoichiometry is controlled by changing the temperature, flow rate and treatment time in the ammonolysis reaction. Depending on the electronic configurations of europium and the transition metal these compounds may show electronic conductivity and ferromagnetism that if coupled result in giant to colossal magnetoresistance [2,3]. Moreover microstructural inhomogeneities lead to non-intrinsic magnetocapacitance and non-ohmic conductivity [4].

The differences in electrical charge and electronegativity between nitrogen and oxygen direct the ordering of both anions in many oxynitrides [5]. In the above perovskites the ordering is driven by covalency and this lead to a preferred *cis* configuration of nitride anions in the octahedra MO_4N_2 and the formation of disordered zig-zag M-N chains [6]. The anion order remains at high temperature in the pseudocubic phase and directs the rotations of the octahedra in the room-temperature superstructure.

This lecture will present recent results on perovskite oxynitrides of europium, strontium and early transition metals focussing on the