



[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 heterosynthion, 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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