

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.

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