

MS31-P4 Halogen-bond mediated assembly of metal-containing architecturesMarijana Đaković¹, Željka Soldin¹, Ivan Kodrin¹, Christer B. Aakeröy²

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There is still a shortage of robust and transferable guidelines for deliberate supramolecular synthesis of metal-containing structures with precise and desirable metrics and topologies. Of the plethora of non-covalent interactions that can determine the assembly of a solid-state structure, the halogen bond is currently receiving considerable attention as a potentially important actor on the supramolecular stage. Similar yet different to its hydrogen bonding counterpart, the halogen bond is becoming a valuable tool in the crystal engineering toolbox.[1] In fact, in many organic materials the halogen bond is used as the primary intermolecular interaction to dictate supramolecular self-assembly due to its strength, directionality and possibility for electrostatic fine-tuning of both the donor- and the acceptor moiety.[2] On the other hand, relatively few metal-organic frameworks that rely on XBs have not received anywhere near the same attention. Therefore, we opted to employ a set of guidelines that has emerged from the engineering of organic solid-state systems and transfer them to the assembly of desirable metal-containing motifs. In this contribution we demonstrate how that principle can successfully be utilised in the rational design of a series of copper(II) and cadmium(II) coordination compounds. In addition, several structure-property correlations are presented (*e.g.* solubility, thermal stability, elasticity), and structural, thermal and spectroscopic data are complemented by CSD data mining. Extensive computational methods are used to facilitate the interpretation of the experimental efforts.

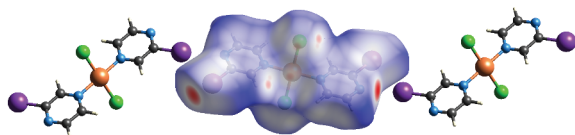
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Figure 1. Hirshfeld surface mapped with d_{norm} for visualizing halogen bonds in $\text{CuCl}_2(\text{I-pz})_2$.

Keywords: halogen bond, crystal engineering, coordination compounds

MS32. Halogen bonding in the solid state

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MS32-P1 Back to the Future: applying 2000's interactions to explain supramolecular arrangements in 1950's compoundsJoao L.F. Silva¹, Karina Shimizu¹, Maria T. Duarte¹

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The majority of papers published on halogen bonding are focused on molecules with isolated C-X bonds. In this work we tried to examine if the conclusions observed for this recent type of interactions also apply to a situation where two halogens are bonded to the same atom. To achieve this goal we choose a family of compounds, Cp_2TiX_2 , that was first prepared in the 1950's¹ and whose crystal packing could not at the time be analyzed in terms of halogen bonds.

As this type of interactions is the result of anisotropy in electron distribution around the halogen atoms^{2,3} we used DFT calculations to draw electron density maps for the various compounds. These maps showed that, in contrast with the halogens involved in isolated C-X bonds (the σ -hole model), the electron scattering is concentrated in the zone amidst the bonds, creating not only anisotropy but also asymmetry. Despite this asymmetry the parameters obtained for the type I halogen bonds encountered do not show large differences to those expected for C-X isolated bonds. However, the location of this large concentration of electronic charge in between the M-X bonds eliminates the possibility of type II halogen bonds.⁴

Another characteristic that is similar is the increase in significance of these halogen bonds with the atom polarizability: from fluorine (where they do not exist) to iodine (where all halogen atoms participate in $\text{X}\cdots\text{X}$ bonds).

In all compounds containing halogen atom there is always a competition between $\text{D-H}\cdots\text{X}$ and $\text{X}\cdots\text{X}$ interactions in the definition of the crystal packing. Independently of their relative number and significance, the presence of type I halogen bonds strongly affects the arrangement of the primary motif (chains of molecules formed through $\text{C-H}\cdots\text{X}$ hydrogen bonds) of these crystals: in the absence of $\text{X}\cdots\text{X}$ bonds the chains are parallel; when they are present the chains are antiparallel.

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