

Halogen bonds in inorganic crystal design

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The electronic properties of organic halogens (C-X) differ substantially from those of inorganic halogens (M-X). The latter are directional nucleophiles, [1], whereas the former can be tuned to serve as directional electrophiles, [2], [3]. Thus, similar to D-H...A hydrogen bonds, C-X...X'-M halogen bonds can serve as directional, non-covalent interactions that can be applied to molecular crystal design.

These non-covalent interactions have been investigated through synthesis of compounds of general formula (n-halopyridinium)₂MX₄ (n = 3, 4; M = Co, Cu), which are propagated by N-H...X'-M hydrogen bonds and C-X...X'-M halogen bonds [X = Cl, Br, I, (≠ F); X' = Cl, Br, I]. The geometry of the hydrogen bonds vary in this series (linear, symmetrically and asymmetrically bifurcated), but halogen bonds have well defined geometries (linear for the organic halogens, bent for the inorganic). Normalised halogen bond distances, R_{XX'}, decrease: (i) with increasing negative electrostatic potential at the inorganic halogen, suggesting that these interactions are predominantly electrostatic in nature; (ii) with heavier organic halogens, which have positive axial electrostatic potentials. Competition between hydrogen bonds and halogen bonds has also been explored in mixed halide systems. These studies are supported by a CSD study showing the preferred geometries of over 300 C-X...X'-M halogen bonds.

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