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## A coordination chemistry of anions through halogen bonding interactions

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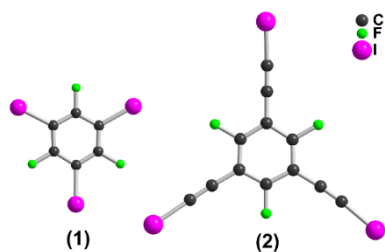
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While a IUPAC definition for hydrogen bonding was only released in 2011 after decades of discussions in the scientific community (Arunann *et al.*, 2011), it didn't take such a long time to come out with an analogous definition of halogen bonding (Desiraju *et al.*, 2013), following a revival of this interaction in the literature, which can be traced back to the early 1990s. The identification of this interaction is however not recent, as illustrated by the isolation of  $\text{H}_3\text{N}\cdot\text{I}_2$  adduct (Colin, 1814). Two centuries later, several review articles (Cavallo *et al.*, 2016; Gilday *et al.*, 2015; Fourmigué, 2009) have gathered together most available data. The halogen bonding interaction (noted XB) is essentially described as an electrostatic interaction between a charge concentration (Lewis base) and the charge-depleted area, called  $\sigma$ -hole, that a covalently bound halogen atom exhibits in the prolongation of this bond. Note that a charge-transfer covalent contribution can be found in the strongest halogen bonds, as illustrated for example in the triiodide anion following:  $\text{I}_2 + \text{I}^- \rightarrow (\text{I}-\text{I}-\text{I})^-$ . The setting of an halogen bond is characterized by a shortening of the interatomic distance, relative to the sum of the van der Waals (or ionic) radii of the interacting atoms, which is defined as the reduction ratio. The halogen bond donor

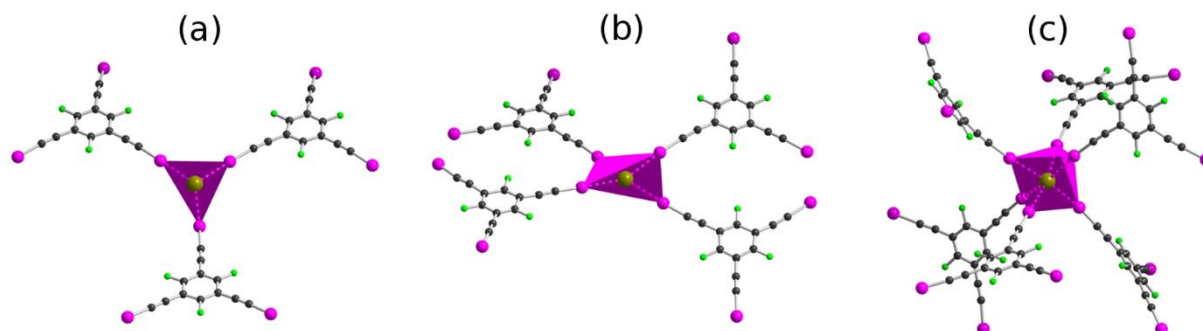
character of halogenated molecules is modulated by the nature of the halogen with  $I > Br \gg Cl \gg F$ , by the hybridization of the substituted carbon atom with  $C\equiv C-I > C=CH-I > C-CH_2-I$ , by the electron-withdrawing ability of the carbon substituents, with a strong activation in aliphatic and aromatic perfluorinated substrates such as  $F_{2n+1}C_n-I$  or  $C_6F_{6-n}I_n$ . Besides, dihalogens ( $I_2$ ,  $Br_2$ ,  $Cl_2$ ), interhalogens ( $I-Cl$ ,  $I-CN$ ) and N-iodoimides (N-iodosuccimide, N-iodosaccharin) are also strong halogen bond donors. All Lewis bases are potentially XB acceptors and among them, anionic species, and particularly halide anions ( $Cl^-$ ,  $Br^-$ ,  $I^-$ ) thanks to a maximal charge concentration (Metrangolo *et al.*, 2008a; Cavallo *et al.*, 2010).

The paper by Szell *et al.* (2017) in this special issue of *Acta Cryst. B* deals with such a crystal engineering approach through the formation of co-crystals associating ammonium or phosphonium halide salts with neutral, halogenated, activated halogen bond donors such as *sym*-triiodotrifluorobenzene **1** or more specifically here its extended analog, the 1,3,5-tris(iodoethynyl)-2,4,6-trifluorobenzene) **2**. While ditopic halogen bond donors such as diiodoacetylene ( $I-C\equiv C-I$ ) or *para*-diiodotetrafluorobenzene most often lead to 1D systems in the presence of halide anions, it was expected that threefold symmetry molecules such as **1** or **2** would provide higher symmetry structures (trigonal, hexagonal, cubic) that would express the presence of the molecular threefold symmetry of the halogen bond donor.



Earlier reports (Metrangolo *et al.*, 2008b) have shown indeed that "mutual induced fitting process elicits the tridentate coordination profile of both 1,3,5-trifluoro-2,4,6-triiodobenzene (**1**) and  $I^-$  ions resulting in cation-templated anionic (6,3) networks", with the small cations ( $Me_3S^+$ ,  $Me_4P^+$ ,  $Et_4N^+$ ) sitting within the pores of the honey-comb network. With  $Et_4N^+I^-$ ,  $Et_4P^+I^-$  and solid solutions thereof, the adducts even crystallize in the R-3c trigonal space group, while with larger cations (Metrangolo *et al.*, 2008; Triguero *et al.*, 2008), the (6,3) networks were maintained but strongly corrugated. In a search for larger pores, the extended halogen bond donor **2** was recently designed (Liefbrig *et al.*, 2013) and further used here with another set of cations of varying size and shape (Szell *et al.*, 2017). Remarkably, besides the above described honey-comb networks with tricoordinated halide anions (Figure 1a), the adduct with the larger  $EtPh_3P^+Br^-$  salt crystallizes in the cubic Pa-3 space group, with a six-fold coordination around the bromide anion (Figure 1c), as already observed with the smaller  $Et_3BuNBr$  salt (Liefbrig *et al.*, 2013) which crystallizes in the cubic Ia-3 space group. Furthermore, the XB interaction of

acetonitrile acting as XB acceptor toward one iodine atom of **2** leaves only two iodine atoms (out of three) to interact with the halide anion, and leads to another set of structures with then a four-coordinated bromide anion (Figure 1b).



**Figure 1**

Detail of the coordination sphere of the bromide anion in three adducts of (**2**) with respectively: (a)  $\text{Et}_3\text{BuN}^+\text{Br}^-$ , (b)  $\text{MePh}_3\text{P}^+\text{Br}^-$ , and (c)  $\text{EtPh}_3\text{P}^+\text{Br}^-$ .

These beautiful examples illustrate a charge-inverted coordination chemistry, where the metal cation is replaced by the halide anion, where the ligands are replaced by the halogen bond donors. The essentially electrostatic nature of the XB interaction has important consequences on the coordination number and geometry. Indeed, in classical coordination chemistry, the overlap interactions of the ligands orbitals with the  $nd$ ,  $(n+1)s$  and  $(n+1)p$  orbitals of the metal center, together with the electron count, determines the favored coordination number and geometry. This does not hold in the present situation, where many examples exhibit very acute  $\text{I}\cdots\text{X}^-\cdots\text{I}$  angles, as observed for example in the di-coordinated bromide anion ( $74^\circ$ ) in the 1D chains formed from *para*-diiodotetrafluorobenzene adduct with  $\text{Me}_4\text{N}^+\text{Br}^-$  (Grebe *et al.*, 1999), or with the tricoordinated bromide anion in the honeycomb network formed out  $\text{Bu}_4\text{N}^+\text{Br}^-$  and **2** (Lieffrig *et al.*, 2013) where the sum of the three  $\text{I}\cdots\text{Br}^-\cdots\text{I}$  angles does not exceed  $246^\circ$ . It appears indeed that in all these systems, the sizeable dispersion forces associated with the indirect  $\text{I}\cdots\text{I}$  contacts can favor these apparently surprising organizations around the halide anion. Another remarkable point is also the coordination number around the halide anion, often found at 2 or 3, but easily extended to 6 as observed in the cubic structures described here (Szell *et al.*, 2017, Lieffrig *et al.*, 2013), and even to 8 in the co-crystal formed out from  $\text{CBr}_4$  as halogen bond donor and  $\text{Me}_4\text{N}^+\text{Br}^-$  (Lindeman *et al.*, 2003). Note that in the latter and despite an apparent crowding around the bromide anion, the reduction ratio for the  $(\text{Br}_3\text{C}-)\text{Br}^-\cdots\text{Br}^-$  distance still amounts to 0.88, indicating a sizeable halogen bond interaction.

Last but not least, the paper by Bryce *et al.* in this issue also combines these crystal structures analyses with complementary solid state NMR investigations. The formation of the honey-comb network from  $\text{Et}_3\text{BuN}^+\text{Br}^-$  and **2** is indeed associated with a clear and substantial shift (+18/35 ppm) in the resonance of the carbon directly bonded to iodine, as a result of halogen bond formation, in agreement with established trends in  $^{13}\text{C}$  shifts of aromatic *ipso* carbons upon halogen bonding (Moss *et al.* 2005; Viger-Gravel *et al.* 2013). These last results illustrate how the halogen bonding interaction, whose renewal in the 1990's was essentially rooted in crystal engineering studies, is now diffusing in all areas of chemistry (Cavallo *et al.*, 2016), from theoretical and analytical investigations (in gas, liquid and solid state) to the optical, magnetic and conducting properties of crystalline materials, from soft matter issues (liquid crystals, polymers and gels) to biomolecular systems and their relevance to the pharmaceutical field.

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