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Chapter 7

Halogen Bonding in Crystal Engineering

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/48592

1. Introduction

The structural features of a molecule are determined by the covalent bonds within the molecule. Modification of the structure requires the breaking and creation of covalent bonds. Similarly, the intrinsic reactivity of a molecule arises from the covalently bonded functional groups and active sites on a molecule. Again, changing the properties requires modifications of the covalent bonds. Even if the ability of a molecule to react is dependent on the covalent molecular structure, the reaction itself is typically launched by non-covalent intermolecular contacts. The reacting molecules need to "see each other" and they need to be brought close enough to each other for the reaction to take place. In other words, the non-covalent interactions provide the glue that brings and holds molecules together, thus making the intermolecular interplay possible. Supramolecular chemistry and processes such as self-assembly and crystallization are strongly guided by non-covalent interactions. These interactions cover a range of different types of intermolecular forces including Columbic interactions, hydrogen bonds, π-interactions, metallophilic interactions, agostic interactions, and halogen bonds. Building predesigned supramolecular entities and molecular assemblies imposes some requirements on intermolecular contacts. They must be sufficiently strong and they must have directional preferences. If these conditions are met it is possible to design molecular building blocks with suitable acceptor/and donor sites for different types of contacts and also to build molecular assemblies in a controlled way.

2. Crystal engineering

When the properties of a molecule are tailored in a conventional way by creating or removing covalently bound functional groups or active sites on a molecule, the physical or chemical properties obtained are solely the intrinsic properties of the molecule designed. An alternative approach to modifying the functionality of molecular material is to link molecular units together to create coordination polymers or extended molecular systems. In such systems the interactions between the building units give rise to new properties that do

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not exist in the building block molecules. This is the very essence of crystal engineering. Desiraju has stated that "crystal engineering is the rational design of functional molecular solids" and defines crystal engineering as "the understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding in the design of new solids".[1] In other words, the goal is to create functional systems by assembling molecular units into extended molecular structures. Over the past few decades vast numbers of papers (Fig. 1) and textbooks have been published on this topic.[2–4]

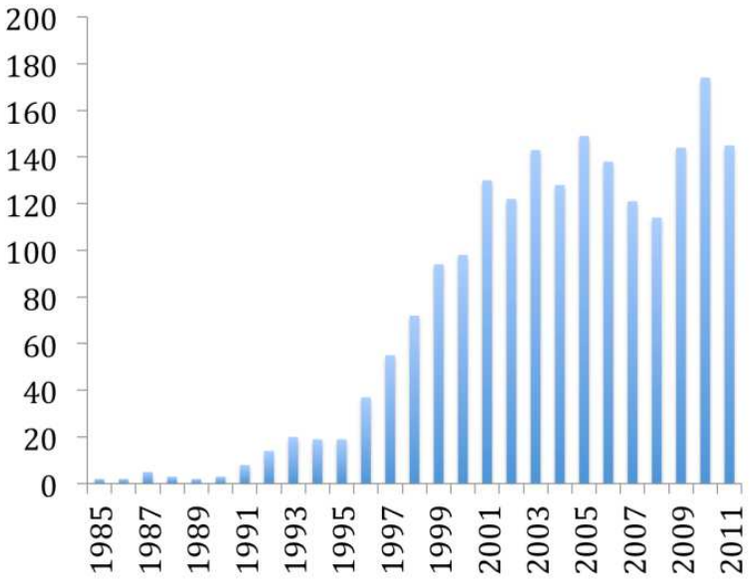

Figure 1. The number of crystal engineering publications since 1985 (ISI WoK, March 2012, topic ="crystal engineering"). These figures include only those publications whose topic includes "crystal engineering". The true number in this field including all related publications is much larger.

As mentioned above, bringing molecules together in a predictable way requires that the intermolecular forces are directional and strong enough to maintain a certain molecular architecture. Non-covalent interactions such as hydrogen bonds, halogen bonds, π···π interactions, metallophilic interactions, and agostic interactions all have directionality to at least some extent. Especially hydrogen bonds, halogen bonds and π···π interactions are relatively strong electrostatic forces with strong directionality. The bond energies of very strong hydrogen bonds range between approximately 65 and 170 kJ/mol, strong bonds between 15 and 65 kJ/mol, and weak hydrogen bonds around 15 kJ/mol or less.[5] The π···π interactions are somewhat weaker with interaction energies up to 50 kJ/mol.[6,7] The strength of the halogen bonds is comparable with the hydrogen bonds ranging between weak (ca. 5 kJ/mol) to strong (180 kJ/mol) contacts.[8] In addition to strength and directionality, the third requirement is that the intermolecular interactions should be selective. If the molecular building blocks contain different types of active sites the contacts must be predictable. Aakeröy et al have shown that even closely related interactions such as hydrogen bonds and halogen bonds can be used side-by-side in the same structure in a hierarcial way to build predictable molecular assemblies.[9,10] The challenge in this kind of combination is that the halogen bond donor (typically iodine or bromine) can interact not

only with the halogen bond acceptor (electron-pair donor) but also with the hydrogen bond donor. An example of the coexistence of halogen bond and hydrogen bond is shown Fig. 2. In this example two-point N-H···O hydrogen bond contacts and one point I···N halogen bond contacts between the 2-aminopyrazin-1-ium and 2,3,5,6-tetrafluoro-4-iodobenzoate are used to build linear chain structure.[10]

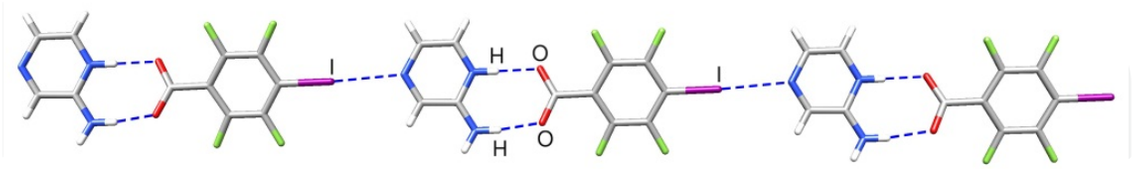

Figure 2. Halogen bond and hydrogen bond contacts in the linear chain assembly of 2-aminopyrazin-1-ium and 2,3,5,6-tetrafluoro-4-iodobenzoate.[10]

Building predictable assemblies and extended molecular systems is possible only after the very natures of the different types of interactions are understood. When the potential and limitations of these contacts are recognized, they serve as a versatile toolbox for crystal engineering. The following sections will focus on one of the "new" intermolecular contacts i.e. halogen bonds. In fact this is not a new discovery. The first observations about halogen bonds were published as early as 1863. This intermolecular force was, however, almost forgotten for years. But because of the interest in crystal engineering it was "rediscovered" and for the past decade it has become topic of growing interest.

3. Halogen bonds (XB)

The definition of halogen bond is not as well established as the definition of hydrogen bond although these interactions have a lot of similarities. Both contacts are electrostatic intermolecular interactions involving an electron donor and an electron acceptor. In hydrogen bonds D-H acts as a hydrogen bond donor, i.e., the electron acceptor. The hydrogen bond acceptors are, then, electron donors such as oxygen or nitrogen atoms (Fig. 3).

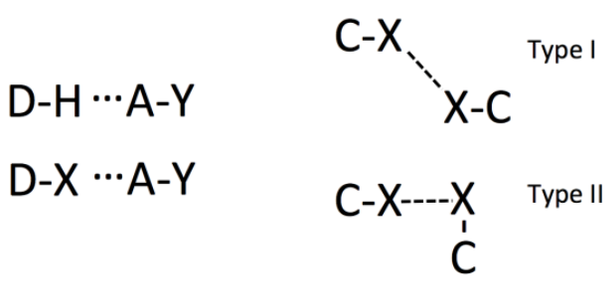

Figure 3. Comparison of the hydrogen bond (top left) and the halogen bond (bottom left). (D = donor, A = acceptor). Classification of the halogen bonds based on the geometry (right).

Because of the similarities involved, the same terminology has also been adapted in halogen bonds. The halogen in D-X acts as the halogen bond donor (electron acceptor). While electron donors such as nitrogen, oxygen, sulfur etc. act as the halogen bond acceptors (Fig.

3). The key to the halogen bonds is the polarizability of the halogen atom. Therefore, the strongest halogen bonds are formed by the most easily polarizable halogens, and the strength of the halogen bonds typically decreases in the order I > Br > Cl > F.

Halogen bonds are commonly defined as electrostatic interactions between Lewis acids (the halogen atom) and neutral or anionic Lewis bases and abbreviated as XB, where X refers to the halogen and B the Lewis base.[11] The strong directional preferences of a halogen bond arise from the tendency to maximize the main two directional attractive contributions to the interaction energy i.e. electrostatics and charge transfer. These, in turn, minimize the exchange repulsion that is also strongly directional. Optimizing the electrostatic and charge transfer aspects have been successfully used in designing of drugs, liquid crystals, organic semiconductors, magnetic materials, nonlinear optical materials, and templates for solid synthesis.[12–16] Conventionally, halogen bonds have been divided into two classes, TypeI and Type II (Fig. 3), based solely on the bonding geometry.[4] A few theories and concepts have been proposed for rationalizing the XB in greater detail. The most familiar one is the σ-hole theory. Other theories such as the lump-and-hole theory and the concept of amphoteric halogen bonds have been used to cover the "blind spots" in the σ-hole theory.

4. σ-hole theory

In most cases, the σ-hole theory has successfully explained the contradictory nature of halogen bonding. Conventionally covalently bonded halogens are seen as negatively charged entities. How, then, is it possible that they can participate in inter-atomic interactions as electron acceptors? In the σ-hole theory the σ-holes are defined as regions of positive electrostatic potential on the outer sides of halogen atoms, centered close to the extension of the halogen atoms' covalent bonds (Fig.4).[17]In general three factors determine the σ-hole's presence or absence and their magnitudes: a) the polarizability of the halogen atom, b) its electronegativity, and c) the electron-withdrawing power of the remainder D of the D-X molecule.[17] When the halogen is more polarizable and has lower electronegativity, the potential of the σ-hole can become more strongly positive. So the positivity of the σ-hole increases in the order F ‹ Cl ‹ Br ‹ I.

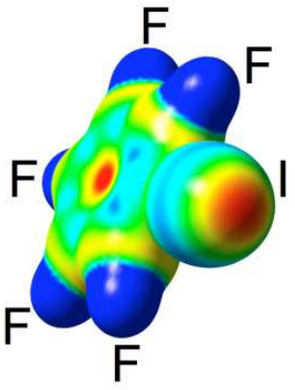

Figure 4. Regions of concentrated negative electrostatic potential (blue) and regions of depleted potential (red) on pentafluoroiodobenzene.

Apparently, the σ-hole determines the existence and, the strength of the halogen bonding. Since the σ-hole is located on the extension of the covalent bond along the D-X axis, it generates the directional preferences of the halogen bonding. When the halogen atom in D-X···A acts as the halogen bond donor, the D-X···A angle is close to 180° (Fig. 3 and Fig. 4). If the halogen acts as the halogen bond acceptor (electron donor), the angle is close to 90° because the electron density around the halogen atom is concentrated at an angle of 90° from the D-X bond (Fig. 3).

5. Lump-hole theory

The σ-Hole theory has satisfactorily explained most halogen bonding interactions, but it fails in some cases. For example, CH_3Cl can form a halogen bond with OCH_2, which is impossible according to the σ-hole theory because of the lack of a positive potential region around the Cl.[17,18] In lump-hole theory there are no true positive regions of the halogen bond donor. The charge density is, however, polarized and there are regions of charge depletion and charge concentration on the donor and acceptor. When these two interact, the areas with charge concentration on the halogen bond acceptors are interacting with the charge depleted areas of the halogen bond donor. Based on lump-hole theory, the participation of fluorine in halogen bonds can be also explained, since a true positive σ-hole is not needed.

6. Amphoteric character of halogen bonds

The amphoteric character of halogen bonding was first proposed by Nelyubina et al. in 2010.[19] They were unable to find a true σ-hole in halogen bonds between I_2 and I^-. Rather, the I in both I_2 and I^- had regions of electron density accumulation and depletion. When the I^- and I-I were interacting, both of them acted as donors and acceptors of electron density simultaneously. Nelyubina et al. defined this type of halogen bond as an 'amphoteric' interaction.

7. The effect of the halogen bond acceptor

When fine-tuning halogen bonding interactions it is, at least in principle, possible to modify the properties of both the halogen bond acceptor and the halogen bond donor. According to the σ-hole theory, the XB acceptor should be rich in negative electrostatic potential, or the acceptor is at least expected to be charge concentrated, which is required by lump-hole theory. Even according to the concept of amphoteric halogen bonds, the acceptor should be able to act as an electron donor. Probably the most commonly used halogen bonding acceptors are covalently bonded halogens and nitrogen atoms.[8,11,20–24] Metal halides, oxygen, sulfur, selenium and even silicon have, however, been reported to have the capacity to act as halogen bond acceptors with suitable donors.[25–31]

8. C-X/N/S/O…1, 2-diiodoterfluorobenzene systems

One of the most commonly used XB donor is 1,4-diiodoterfluorobenzene due to its strong positive σ-hole on the iodine atom.[28,32,33] Similarly, 1,3-diiodoterfluorobenzene has been

widely used as the Lewis acid in halogen bonds.[22,34,35] In the present study, however, we focus first on the XB systems with the less commonly used isomer of diiodotetrafluorobenzene, i.e., 1,2-diiodoterfluorobenzene (1,2-TFIB).[33,34,36–39] We will use 1,2-TFIB as the "probe donor" to study the halogen bonding interactions with different type of XB acceptors and to elucidate how the halogen bonding acceptor affects the properties of halogen bonding.

Cauliez. et al, used thiocyanate anion as the XB donor to construct co-crystals with 1,2-TFIB (Fig. 5).[34] Halogen bonds were observed between the neutral iodinated species (XB donor) and both the S and the N end of the thiocyanate anions, demonstrating the bidentate nature of SCN^-. Both C-I···N and C-I···S presented strong linearity, and relatively strong halogen bonding interactions. On the other hand, the C-S···I and C-N···I angles follow roughly the directions of the free electron pairs on the acceptor atoms, providing an example of how the electronic structure of the XB acceptor affects the overall geometry of the molecular assembly. In this particular structure, weaker C-I···F interactions were also observed. In these contacts the fluorine atoms of the halogenated benzene acted primarily as XB acceptors. In addition to the XBs mentioned above, series of F···π, I···π, π···π, and F···H hydrogen bond contacts contributed to the crystal structure of the co-crystals of thiocyanate and 1,2-TFIB.

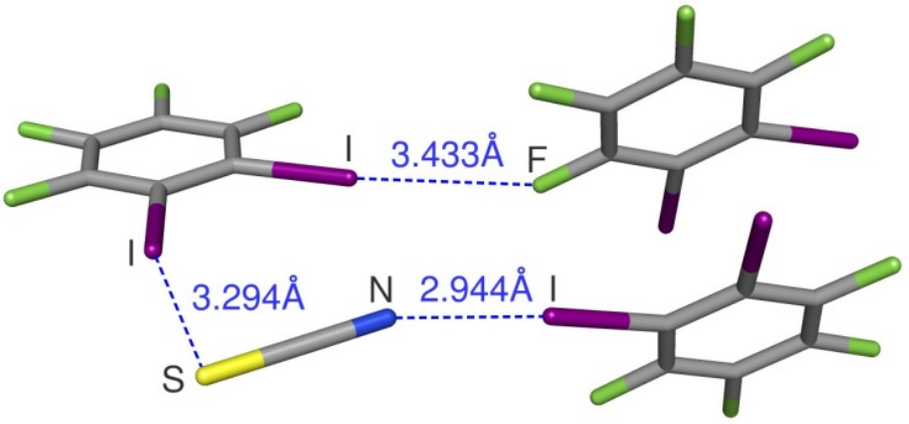

Figure 5. The halogen bond contacts in the co-crystal of the thiocyanate anion and 1,2-TFIB.[34]

A zigzag chain structure have also been obtained through C-I···N, and C-I···S halogen bonds in co-crystals of thiomorpholine (TMO) and 1,2-TFIB (Fig. 6).[33] Like thiosyanate, the thiomorpholine is able to act as a bidentate N, S halogen bond acceptor.[33,34] The co-crystal of TMO and 1,2-TFIB have been obtained by a simple mechanocemical synthesis i.e. by grinding the components together. The interesting feature of this stepwise co-crystallization process is that it is proposed to be guided by the competition of the strong and weak halogen bonds. The initially formed finite molecular assemblies are held together mainly by the stronger N···I bonds. These intermediates are then polymerized into infinite chains by cross-linking through weaker S···I interactions.

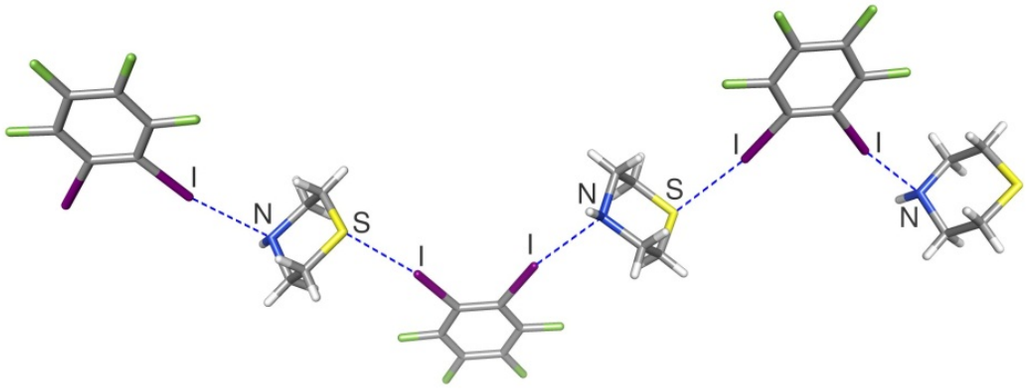

Figure 6. The zigzag chain of TMO/1,2-TFIB co-crystals.[33]

Yet another zigzag chain structure has been obtained by co-crystallizing 1,2-TFIB with phenazine through C-I···N halogen bonds (Fig. 7).[36] Here the C-I···N halogen bonding is slightly weaker than that of the example shown in Fig. 6. This was most probably caused by the steric effect of the XB donor. It demonstrates that the overall geometry of the XB acceptor has an effect on the halogen bonding. The directionality of XB is clearly shown in the example on Fig. 7. The angle of the C-I···N is 169°, which is almost linear.

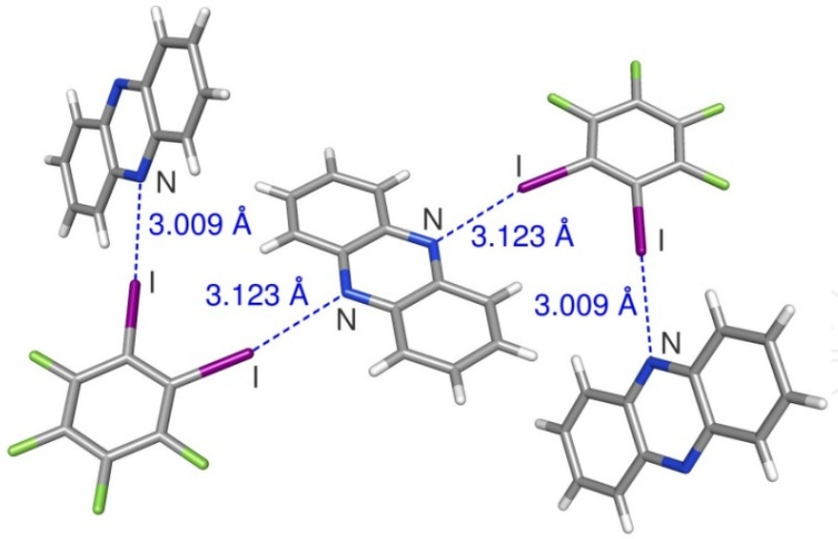

Figure 7. C-I···N halogen bonding in the zigzag chain structure of the co-crystal of 1, 2-TFIB with phenazine.[36]

The co-crystals of 4,4′-bipyridine and (1,2-TFIB) (Fig. 8) provide another example of C-I···N contacts. In this structure the C-I···N bonds linked the bipyridine (XB acceptor) and 1,2-TFIB together into two independent and almost perpendicular wave-like chains.[39]

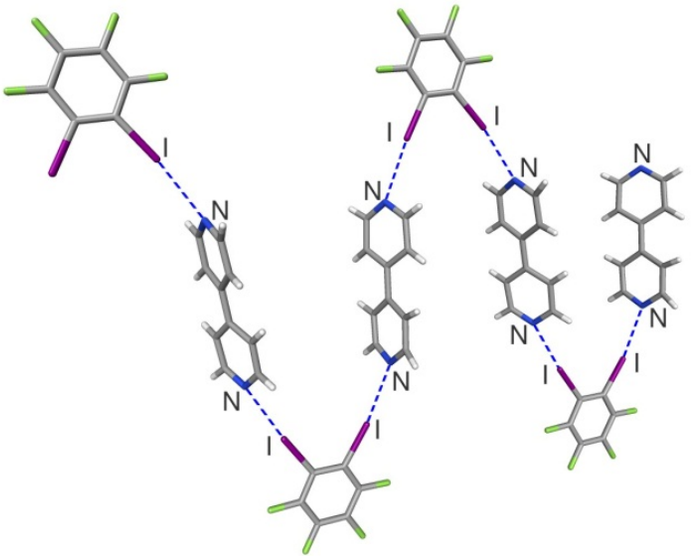

Figure 8. Co-crystals 4,4′-bipyridine and (1,2-TFIB). The I···N distances range from 2.909 to 2.964 Å.[39]

The co-crystals of 2-mercapto-1-methylimidazole (mmim) and 1,2-TFIB show nicely the bonding preferences of XB (Fig. 9).[38] The mmim molecule and 1,2-TFIB form a complex, in which N-H···S bound imidazole dimers are connected through C-I···S interactions to a pair of 1,2-TFIB molecules, forming infinite chains. The C-I···S bonds are different in strength (the C-I···S distance of the weaker one was 3.843 Å, while the stronger one was 3.291 Å) and the bonds involving sulphur can be defined as trifurcated bonds. They consisted of two halogen bonds and one hydrogen bonds. The sulfur acts as the electron donor for both bonding types. In principle, the iodine could be also a hydrogen bond acceptor. However, it is solely devoted to the halogen bond, while the hydrogen bonds are formed only between the sulfur and NH of the imidazole ring.

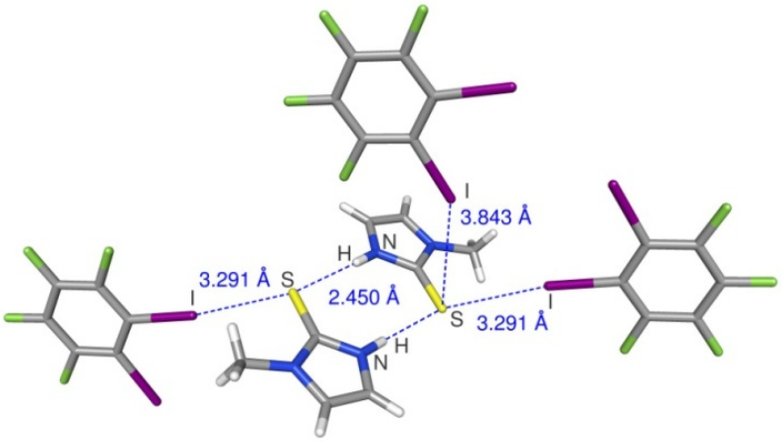

Figure 9. The halogen and hydrogen bonds in the structure of (mmim)·(1,2-TFIB).[38]

As mentioned previously, oxygen can also be used as an XB acceptor to construct supramolecular structures. Co-crystals of the nitroxide 1,1,3,3-tetramethylisoindolin-2-

yloxyl (TMIO) and 1,2-TFIB are formed under standard sublimation conditions.[37] The formed 2:2 cyclic tetramer structure (Fig. 10), $(TMIO)_2 \cdot (1,2\text{-}TFIB)_2$, showed that each nitroxide oxygen atom, when serving as the XB acceptor, set up bifurcated halogen bonding with two iodine atoms from two 1,2-TFIB molecules, respectively. Again, the N-O···I angle follow the direction of the free electron pairs on the oxygen atoms, thus encouraging the tetrameric assembly of molecules. The O···I contacts in this motif were clearly shorter than the van der Waals contacts (down to 81.2%-83.1%), with strong directionality (C-I···O angles range from 170.30°-179.2°).

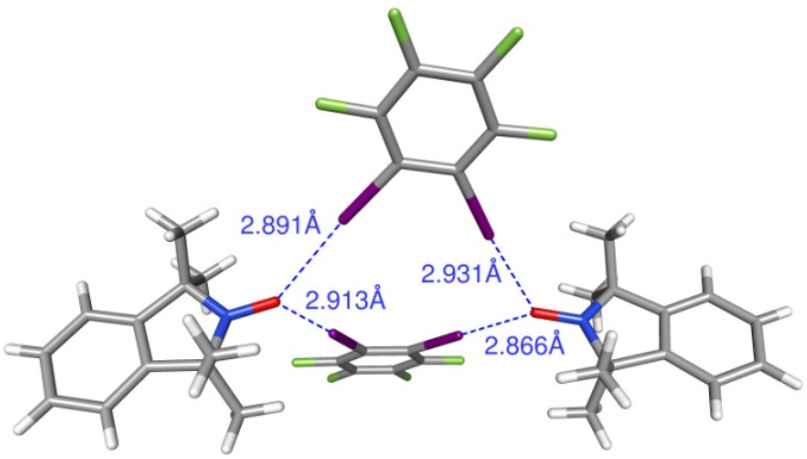

Figure 10. The tetrameric unit $(TMIO)_2 \cdot (1,2\text{-}TFIB)_2$ (red = oxygen, purple iodine).[37]

As the examples above show, the 1,2-TFIB can be used as the XB donor with various acceptors. If, however, there are no other acceptors available, the "amphoteric" nature of 1,2-TFIB is revealed. When the 1,2-TFIB is crystallized from methanol, a structure with series of weak XB bonds can be obtained (Fig. 11).† The iodines form XB contacts, functioning as both the donors and the acceptors. The I···I distances are relatively long, ranging from 3.258 Å to 3.740 Å. Nevertheless, the distances are less than the sum of the van der Waals radii, and the directionality support the existence of the halogen bonds. The I···I contacts resulted in a zigzag structure that is further expanded through the F···F, F···I, and F···π halogen bonds. The F···F and F···I contacts are weak with long distances consisting of 2.783-2.924 Å and 3.258 Å for F···F and F···I, respectively. It should be noted that, to judge from the C-F···F angle (147.3°), the F···F contacts showed some amphoteric character. In the case of C-I···F, the fluorine atom behaves more clearly as the halogen bond acceptor, due to the existence of the negative lateral sides of the fluorine atom caused by the aspherical charge density distribution.[40]

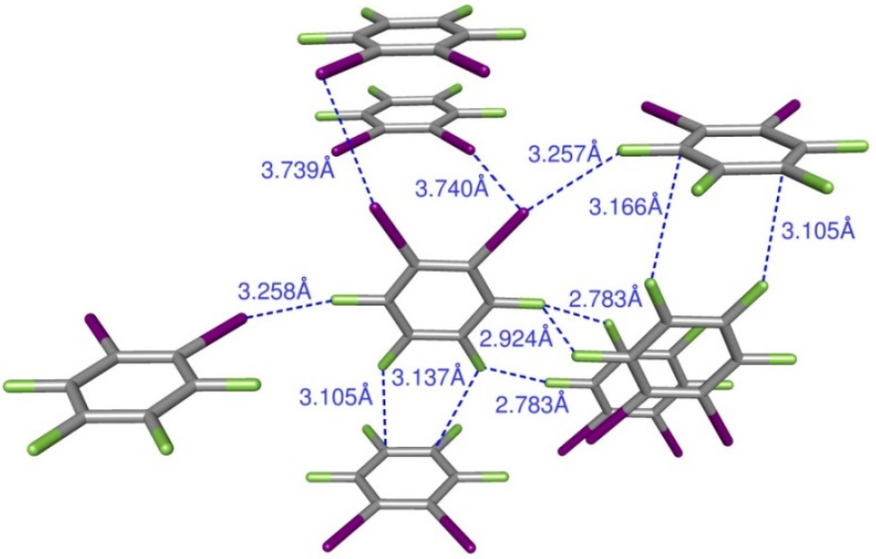

Figure 11. Halogen bonding interactions in the crystal structure of 1,2-TFIB. †

9. X/Se···X system (X=Cl, Br, I)

As early as in 1984, a study of Cl···Cl halogen bond in crystal structures of six dichlorophenols was carried out by Thomas and Desiraju.[41] This study was extended in 2011 by Mukherjee and Desiraju to 3,4,5-trichlorophenol and 2,3,4-trichlorophenol.[42] In the crystal structure of 3,4,5-trichlorophenol (Fig. 12), one Cl atom forms bifurcated halogen bonds with another chlorine and oxygen, respectively. This Cl, however, functions as XB acceptor with the other Cl, while at the same time, it serves as the XB donor for the oxygen atom, thus showing its dual nature.

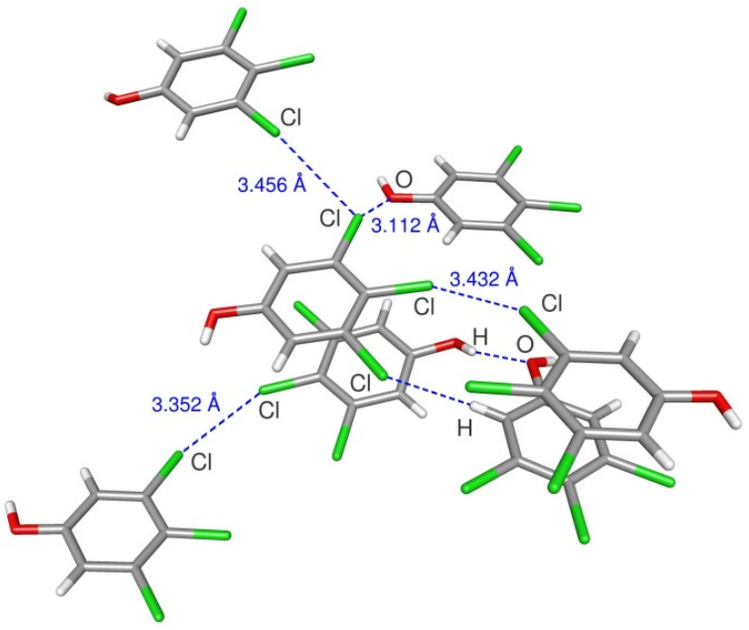

Figure 12. Halogen and hydrogen bonding in the crystal structure of 3,4,5-trichlorophenol.[42]

Crystals with a zigzag sheet packing structure have been obtained by crystallizing 1-butyl-4, 5-dibromo-3-methylimidazolium iodide (Fig. 13).[43] The two bromine atoms of the cation act as the XB donors, while the iodine anion is the XB acceptor. The crystal structure shows that the iodide anions in the c-axis direction are positioned either at the top or the bottom of the zigzag structure, suggesting that the size of the halide anion has a strong effect on the zigzag sheet formation.[43]

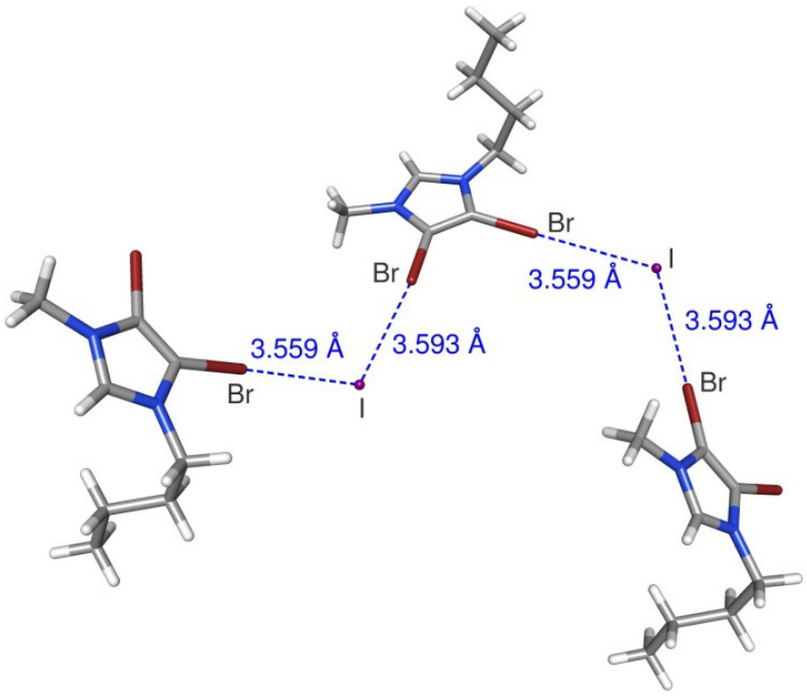

Figure 13. Halogen bonding interactions in crystal structure of 1-butyl-4,5-dibromo-3-methylimidazolium iodide.[43]

The structure of co-crystal of 1,2-diiodoimidazole with 1,3,4-triiodoimidazole (Fig. 14) was studied by our group.‡ In this structure the two 1,2-diiodoimidzol molecules are linked by a I···I halogen bonding interaction (3.916Å), forming a dimeric unit. This unit is further connected with other 1,3,4-triiodoimidzole molecules, expanding the structure along crystallographic directions a, and b. The N-H···N hydrogen bonds expand the structure further in direction of c axis, constructing a 3D network. The bonding preferences of different interactions can be clearly seen in this structure. Halogen bonds are formed only between the iodine atoms, and each iodine atom of diiodoimidzol is trifurcated. In addition, it demonstrated the dual character of iodines, serving both as XB donors and as acceptors.

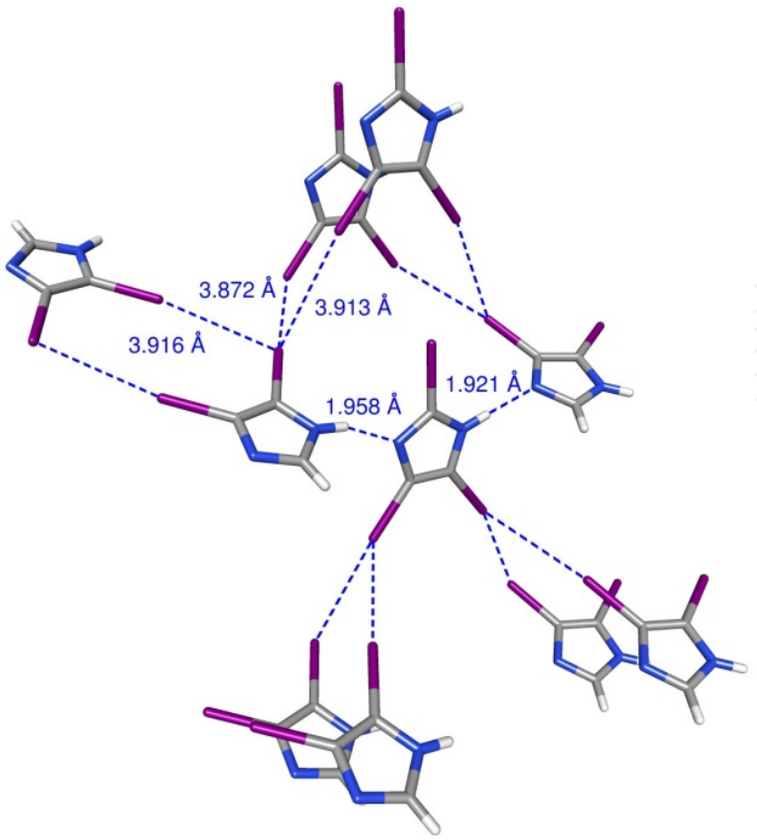

Figure 14. Hydrogen and halogen bonds in the co-crystal of 1,2-diiodoimidazol and 1,3,4-triiodoimidazol.‡

Halogen bonds involving selenium as the XB acceptor have not been widely studied.[29] The chain structure formed by connecting di-ter-butyliodophosphane selenide molecules through Se···I halogen bonding is one example of such a system.[29] In this structure the Se···I distance was found to be only slightly shorter than the sum of the van der Waals radii of selenium and iodine. Another example of Se···I interaction can be found in the crystal structure of iodoisopropylphosphane selenide.[29] In both structures, selenium is also involved in Se···H hydrogen bonds, providing another example of the interplay between the closely related electrostatic interactions.

10. M-X/N/NCS/CN…X systems

Simple metal bound ligands, capable of donating electrons, can also be used as XB acceptors in the construction of supramolecular structures.[44] Metal complexes are of particular interest because of the possibilities of using halogen bonds as a tool in the modification of the redox, magnetic, optical, and chemical reactivity of the metal complexes.[44–46]

The palladium pincer complex {2,6-bis[(di-t-butylphosphino)methyl]-phenyl}palladium (PCPPd) halides, PCPPdX (X=Cl, Br, or I) have been studied by Johnson and Rissanen as the XB acceptor in systems with I_2 as XB donor.[47] The all three crystal structures have similar basic features (Fig. 15). However, the halogen bond strength was found to increase in the

order Cl ‹ Br ‹ I, suggesting that the XB interactions are mainly electrostatic as expected.[47] The other intermolecular contacts were relatively weak. It is, however, worth mentioning that in PCPPdI·I_2 the Pd···I-I···π interaction also appeared to result in the formation of a chain-like structure. This was not observed in the other two structures.

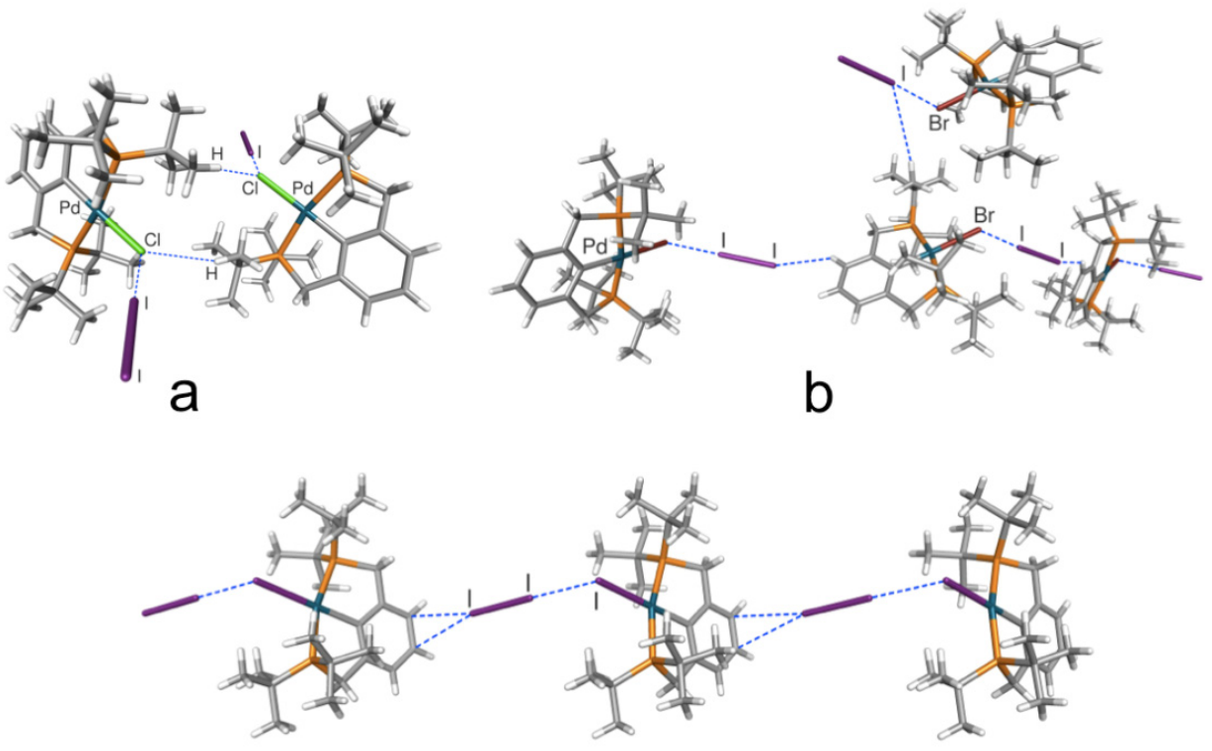

Figure 15. Crystal structures with halogen bonds in PCPPdX···I_2 (X=Cl, Br, or I). (a) PCPPdCl···I interactions, (b) PCPPdBr···I interactions, (c) PCPPdI···I interactions.[47]

The bonding preferences of halogen and hydrogen bonds can also be found among the assemblies of metal complexes. The co-crystals of [RuI_2(H_2dcbpy)$(CO)_2$] (H_2dcbpy = 4,4′-dicarboxylic acid-2,2′-bipyridine), I_2 and methanol is an example of such system (Fig. 16).[48] The two [RuI_2(H_2dcbpy)$(CO)_2$] complexes are held together strongly by the hydrogen bonds between the carboxylic acid groups. The iodide ligands bonded to the ruthenium centers are involved only in halogen bond, thus extending the structure into a chain of metal complexes. The halide ligands are linked by halogen bonds through two I_2 molecules. It is worth noticing that the halogen bonds between the I_2 molecules are bifurcated, and the solvent molecule is supporting the structure via hydrogen bond. The I-I···I bond angle was nearly linear (167°) for the first I_2, but due to the bifurcated nature only 137.8° for the second I···I_2 contact, which differs from the conventional XB bond angles.

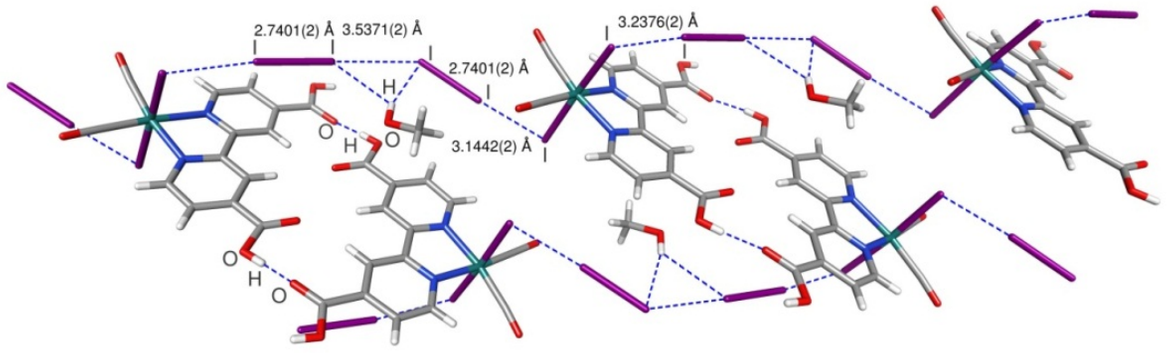

Figure 16. Halogen and hydrogen bonds in the structure of $[RuI_2(H_2dcbpy)(CO)_2]\cdot I_2$.[48]

Any ligand possessing a free electron pair can be seen as a potential halogen bond acceptor. The N-bound thiocyanate in *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) provides an example of such a ligand. The structure of the $[RuI_2(H_2dcbpy)(CO)_2]\cdot 2I_2$(Fig. 17) adduct have been obtained at room temperature by mixing I_2 and the complex in methanol.[49] In this structure, the sulfur atom of one of the thiocyanate ligands forms bifurcated halogen bonds with two I_2 molecules. Based on the distances, these bifurcated bonds are weaker than the non-bifurcated one.

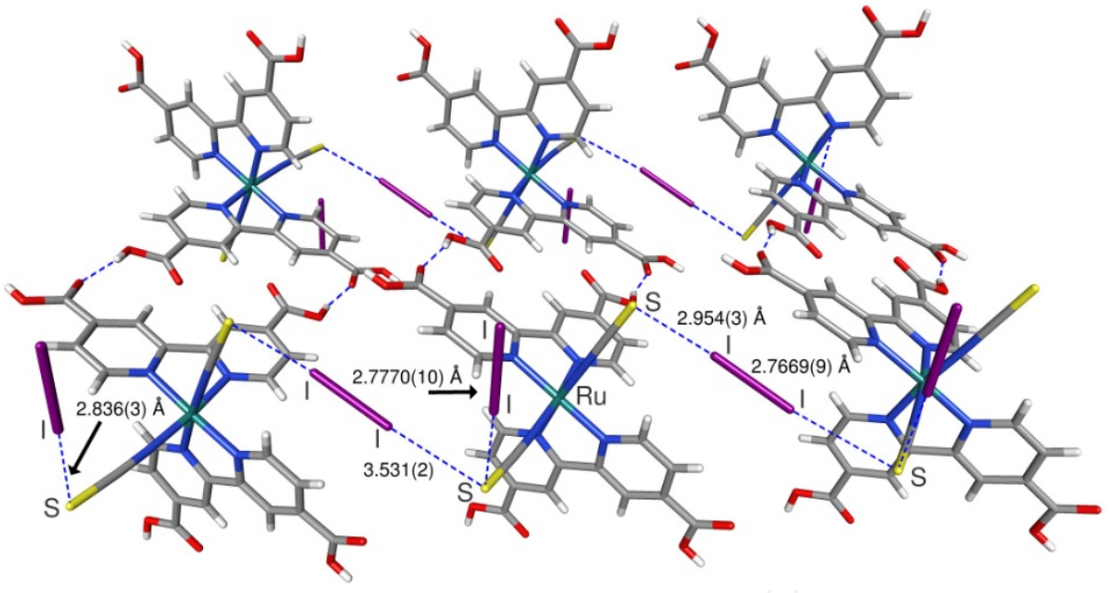

Figure 17. Halogen bonding interactions in $[RuI_2(H_2dcbpy)(CO)_2]\cdot 2I_2$.[49]

Ormond-Prout, Smart, and Brammer proposed that halogen bonds can be used to predict and control the process of self-assembly and to fine-tune the electronic properties of cyanometallates.[50] To confirm this assumption they synthesized two types of halopyridium hexacyanometallate salts, $(3\text{-XpyMe})_3[M(CN)_6]$ and $(3, 5\text{-X}_2\text{pyMe})_3[M(CN)_6]$ (X=Cr, Fe, Co).[50] The authors harvested a total of ten crystals, and found out that five out of each family of compounds were isostructural, while other structures were the solvates, $(3\text{-IpyMe})_3[Fe(CN)_6]\cdot 2MeCN$(2·2MeCN) and $(3,5\text{-Br}_2\text{pyMe})_3[Cr(Cr(CN)_6]\cdot$(10·4$H_2O$). The

halogen bonding distances in these structures were shorter than the sum of the van der Waals radii. In the case of (3,5-Br_2pyMe)$_3$[Cr(Cr(CN)$_6$]·(10·4H_2O), a weak additional C-Br···O halogen bond was found, which can be attributed to the competition between the halogen bonding and the O-H···N hydrogen bonding. The close-to-linear geometry of the CN···X halogen bonds found in the all structures suggests that these interactions predominantly involved the exo lone pair of nitrogen atom. However, the structures contained another type of halogen bonds with less linear CN···X contacts (CN···X ‹ 105°). Such angles indicate that the triple bond between the C and N contributes to the halogen bonding interaction leading to X···π contact (Fig. 18). In this series the strength of the halogen bonds was found to be dependent on the metal center (Cr ‹ Fe ‹ Co). This is a good example of how the metal center can be used for modification of halogen bonds. In this particular example, the primary reason for the different behavior of the different metals has been attributed to the metal-cyanide π-back-donation.[50]

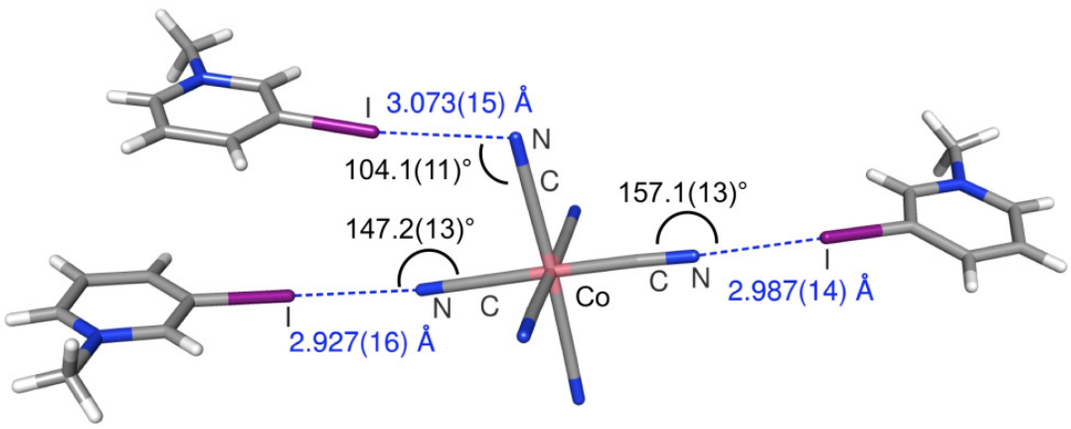

Figure 18. Halogen bonding contacts in (3-IpyMe)$_3$[Fe(CN)$_6$]·2MeCN.[50]

11. Hydride-halogen systems

In addition to the more conventional electron donors, the hydride, R-H$^{\delta-}$, has also been proposed as potential XB acceptors.[51] This type of halogen bonds, R-H$^{\delta-}$···XR$_X$, has been investigated computationally by analyzing a series of model systems. The results indicate that H$^{\delta-}$ is a potential electron donor for halogen bonds.[51–53] The halogen bonding interaction between LiH or HBeH and either XCF_3 or XCCH (X= F, Cl, Br, I) has been studied with high-level quantum mechanical calculations, quantum theory of atoms in molecules (QTAIM), and natural bond orbital (NBO) methods. The most important finding of these studies has been that the hydride-halogen bond formation causes the elongation of R$^{\delta+}$-H$^{\delta-}$ bond due to the involvement of hydride in the halogen bond. It has been suggested that the interaction is inductive in nature, and the formation of hydride-halogen bond results in the charge transfer from the hydride to a halogen-donor molecule.[51]

12. Modification of the halogen bond donor

The modification of the halogen bonds acceptor molecule for halogen bonding has been reviewed in many papers. As the above examples show a variety of acceptors can be used for halogen bonds. In general, it can be said that a good halogen bond acceptor is a strong electron donor. Much less have been written about the modification of the XB donor. [21,54]

Some of the strongest halogen bond donors are dihalogen molecules, which form strong halogen bonds.[55] This is of course due to the polarizing effect of the other halogen atom. All dihalogen molecules can act as halogen bond donors and the order of the XB bond strength follows the order I_2> Br_2> Cl_2> F_2. This is again the result of the polarizability of the halogens increasing in the same series.[20] The bond strength can be increased further by substituting the second halogen atom in dihalogens with fluorine, which polarizes the other halogen even more strongly. [56,57] The lighter dihalogens are volatile and so the crystal structures of such systems are rather rare. However, some of these structures have been characterized in gas phase by rotational spectroscopy.[58] The results indicate that for Cl_2, ClBr, ClF and ICl the covalent halogen-halogen bond strength increase in the order Cl_2 < BrCl < ClF < ICl. When combined with the known crystallographic data the increasing strength of the halogen bond donors for dihalogens can be given: F_2< Cl_2< Br_2< I_2< IBr < ICl. This order seems to be independent on the halogen bond acceptor.[54]

Polyhalides is another well known group of XB donors.[59] In these systems the halogen bonding typically occurs solely between the polyhalogenides and do not include other molecules. This is especially true with the polyiodides.[59] The polyiodide networks are often complicated three-dimensional networks, layers, or chains. The properties of these compounds have been intensively studied. There are even examples of systems where some of the iodines can be released into solution without breaking the crystal structure.[60] The removal of iodines have then been used to change the nonlinear optical properties of the compound.[9]

In the polyhalides iodine and bromine can often act both as halogen bond donors and as acceptors, and occasionally, the same atom can act both as acceptor and donor.[59] Amphoteric halogen bonds have also been found within polyhalide networks, though they are not very common.[8] In addition to the homonuclear polyhalides, mixed polyhalides are also known. The most common type is the mixed trihalide.[61,62]

Fig. 19 shows the typical features of the polyiodides. In this example, there are two crystallographically different I_3^- units, one of which has two nearly identical I-I bonds. The second I_3^- has unequal I-I bonds and it is closer to a I_2-I^- motif. The two I_3^- units are then linked via I_2 molecule. This is a typical example of a polyiodide structure. In this particular network the I_2 molecule acts as a halogen bond donor and the I_3^- units act as acceptors.[12]

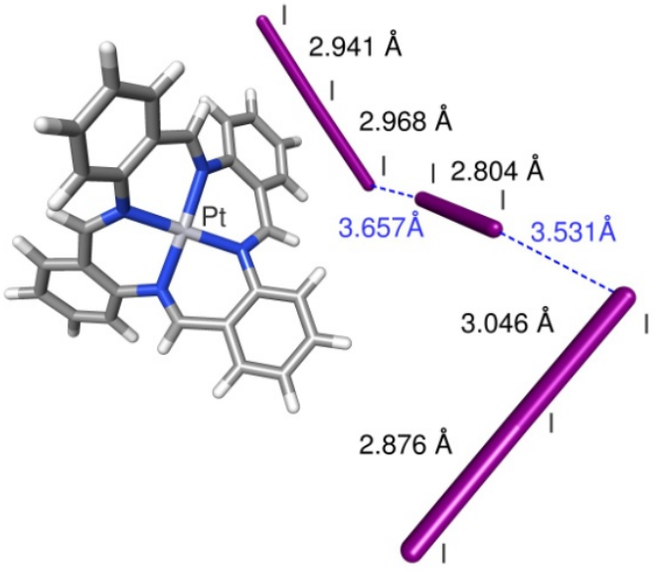

Figure 19. An example of a polyiodide network of $(C_{28}H_{20}N_4\ Pt)^{2+}$ $(I_8)^{2-}$.[63]

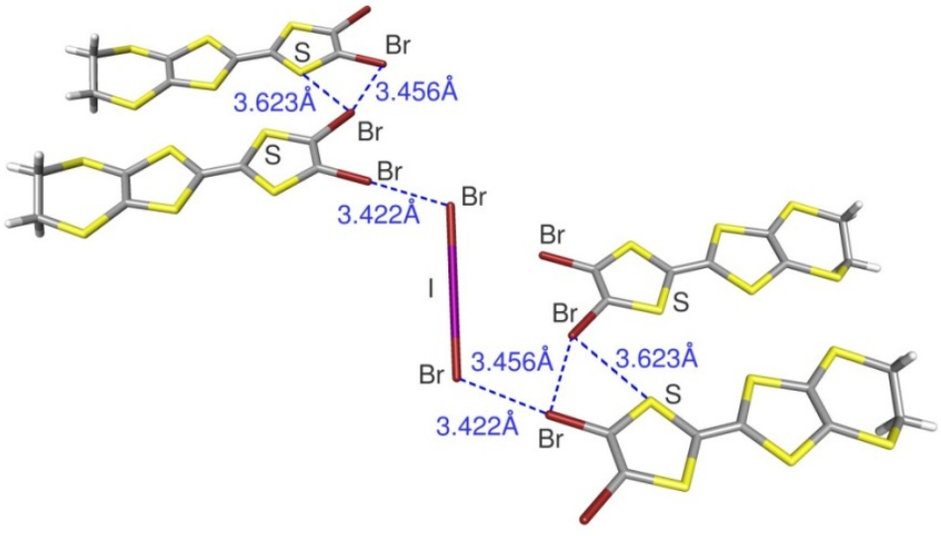

Figure 20. The halogen bonding in $(C_8H_4Br_2S_6)_2$ IBr_2.[64]

Fig. 20 provides an example of a structure containing a mixed trihalide. The structure contains halogen bonds between the trihalide and two dibromo tetrathiofulvalene molecules. Additionally, there are also bifurcated halogen bonds between the bromine and sulfur atoms of the tetrathiofulvalenes. The very similar halogen bond distances between the trihalide (Br-I-Br) and Br-atoms of tetrathiofulvalene indicate that the bond strengths are nearly identical for both of the Br···Br contacts. In this case the Br-atoms dibromo tetrathiofulvalene act as the halogen bond donors and the trihalide as the acceptor.[64]

Organic compounds containing a C-X bond are often relatively easy to modify, which makes them attractive halogen bond donors. As discussed earlier, among the most commonly used

XB donors are fluorinated iodobenzenes.[22,47,65] There is obviously a large number of halogen containing organic compounds that could be used as halogen bonding donors. For the purpose of crystal engineering, the interesting parameters of these compounds are the geometry and expected strength of the halogen bonds. If the halogen atom is only singly bonded to a carbon atom, the formed sigma hole will be pointing in the opposite direction of that bond.[22] Hence, the direction of the halogen bond is clear and easy to predict. However, controlling the strength of the halogen bond donor requires further information. Numerous studies of this topic have been published, especially on aromatic halogen bond donors.[24,55–57,66] On the basis of both the existing experimental and theoretical studies, it can be stated that electron withdrawing substituents increase the strength of the halogen bond donor, while the electron-donating groups reduce it.[24,55,66]

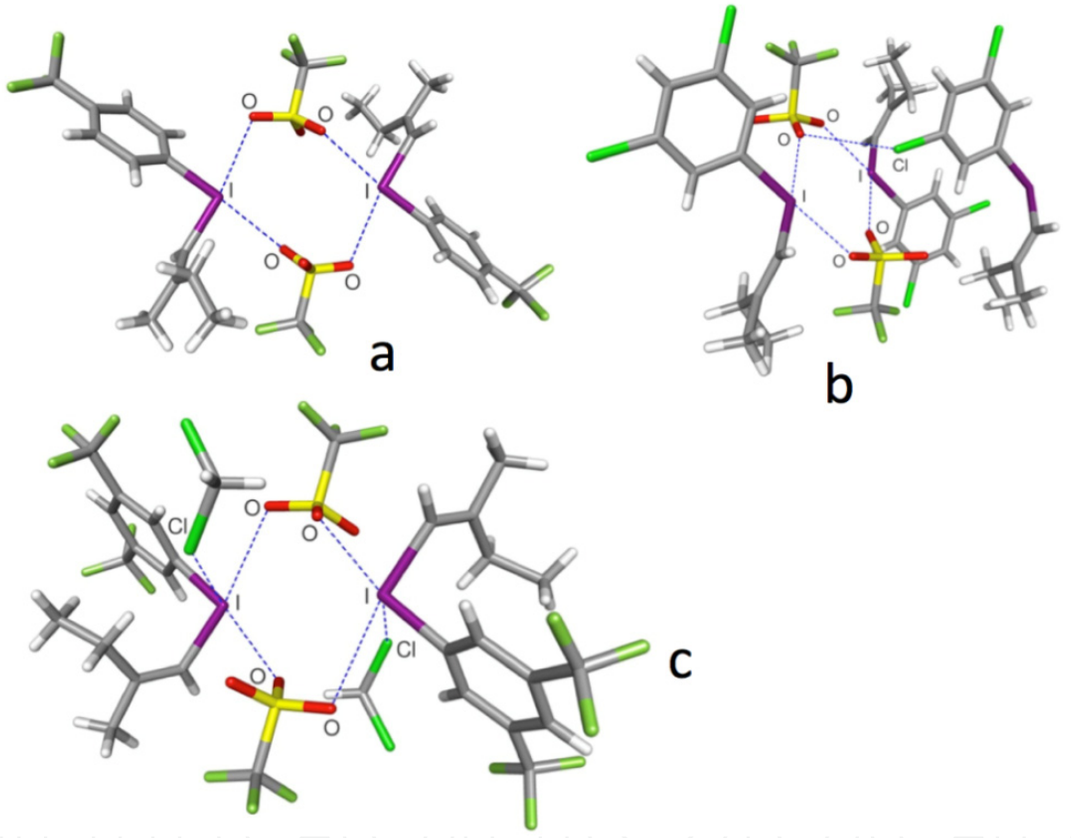

Figure 21. Halogen bonding of the iodine atoms for ($C_{12}H_{13}F_3I^+$)($CF_3O_3S^-$) (a); ($C_{11}H_{12}Cl_2I^+$)($CF_3O_3S^-$) (b) and 2($C_{13}H_{12}F_6I^+$) 2($CF_3O_3S^-$) CH_2Cl_2 (c) [67]

In Fig. 21 there are three structures each of which contains the same basic building blocks of the alkenyl(aryl)iodonium trifluoromethanesulfonate salts, while one of them also contains dichloromethane. From the point of view of halogen bonds, these provide a useful illustration of the effects that the electron withdrawing groups have on the halogen bonding donor. In the first compound (a) there is one $–CF_3$ substituent on the aromatic ring. The halogen bonds are formed between the iodine of alkenyl(aryl)iodonium cation and oxygen atoms of the triflate. The I-O distances are 2.910 Å and 2.991Å. In the second structure (b) there are two chlorine substituents on the aromatic ring, which makes it more electron-deficient than the previous one.

There are now two crystallographically independent dimers (only one is shown in Fig. 21.) that are involved in similar type of halogen bonding between the iodines and triflates. However, the iodine-triflate distances are different. The I···O distances are 2.848 Å and 2.802 Å for the first dimer and 2.832 Å and 2.850 Å for the second. The halogen bond distances for the structure (a) are clearly shorter compared to the distances of the (b) structure as one might expect based on the electron withdrawing substituents. The third compound (c) in Fig. 21 contains two $–CF_3$ substituents on the aromatic ring, making it the most electron deficient of the three. Again there are two crystallographically independent dimers (only one is shown if Fig. 21) that have slightly different geometries. Despite of this the basic halogen bonding geometry involving the iodine atoms is similar with slightly different I···O distances (2.767Å and 2.985Å for the first dimer and 2.881Å and 2.893Å for the second). Now the message obtained from the halogen bond distances is not so obvious. Although the shortest distance in (c) is clearly the shortest of them all, the variation of the distances is large. This is a useful reminder that the final solid state structure is a result of several competing interactions and conclusions based only on distances is often an oversimplification and may be misleading.[67]

In most cases metal bound halogens act as halogen bond acceptors.[44,68] There are some examples where the interaction seems to be more amphoteric, but these are relatively rare cases.[69–71] In general, using metal centers to form synthons for halogen bonding networks can be beneficial, because they readily permit the formation of well defined geometries. In addition, by changing the oxidation state of the metal, the geometry and chemical properties of the system can also be changed.[72] Metal compounds can also possess interesting magnetic and luminescent properties.[46,73]

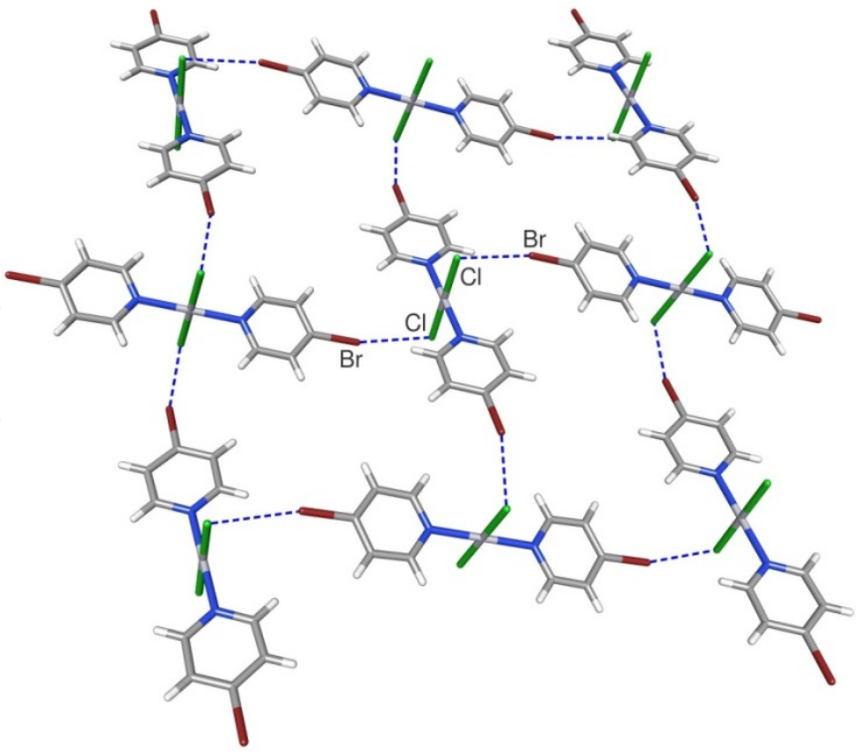

Figure 22. The halogen bonding network of $PtCl_2(C_5NBrH_4)_2$.[70]

In Fig. 22 there is an example of a network consisting of $PtCl_2(NC_5H_4Br)_2$ linked together via halogen bonds. In addition to the halogen bonds, the two dimensional layers consist of weak hydrogen bonds and π-π stacking interactions. The structure shown is a good example of a network structure of a metal complex formed by halogen bonding.[70]

13. Future perspectives

Even if the very essence of crystal engineering is to produce functional materials, a large number of studies and papers in this field are still devoted solely to the structural aspects of the molecular assemblies and frameworks. The same is true with halogen bonding. The latter is understandable since establishing the whole concept of halogen bonding has required (and still requires) a considerable amount of work. Nevertheless, examples already exist of the utilization of halogen bonding in the production of functional materials. The role of halogen bonding has been investigated in the context of the inhibition of the human protein kinase CK2α.[74]It has also been used for selective recognition of halide anions and employed in host-guest systems.[23] There are examples of the use of halogen bonding for controlling the luminescent properties of Au_2-Ag_2 clusters and the birefringence properties of chains of square planar Au complexes[45,75]. There are also examples of the utilization of halogen bonding in catalysis.[76] In the future the number of these types of applications is expected to grow rapidly. All of this means that halogen bonding is in the process of being transformed from a strange solid-state phenomenon to a versatile tool in the hands of crystal engineers.

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Acknowledgement

Financial support provided by the Academy of Finland (project no.139571) is gratefully acknowledged. Molecular graphics was created with the UCSF Chimera package. Chimera is developed by the Resource for Biocomputing, Visualization, and Informatics at the University of California, San Francisco, with support from the National Institutes of Health (National Center for Research Resources grant 2P41RR001081, National Institute of General Medical Sciences grant 9P41GM103311).

14. Footnotes

†Crystal data for 1,2-TFIB: $C_6F_4I_2$, M = 401.86, brown block, 0.43 × 0.32 × 0.20 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 10.606(4), b = 5.770(2), c = 14.548(5) Å, β = 110.344(4)°, V = 834.7(5) $Å^3$, Z = 4, D_c = 3.198 g/cm^3, F_{000} = 712, Bruker SMART APEX II CCD, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 70.0º, 18326 reflections collected, 3673 unique (R_{int} = 0.0353). Final *GooF* = 1.105, *R1* = 0.0184, *wR2* = 0.0375, *R* indices based on 3154

reflections with I >2sigma(I) (refinement on F^2), 109 parameters, 0 restraints. Lp and absorption corrections applied, μ = 7.540 mm^{-1}. The crystal was obtained in methanol by slow evaporation. CCDC-875313 contain the supplementary crystallographic data for this structure. It can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

‡ Crystal data for co-crystals of 1,2-diiodoimidazole and 1,3,4.-diidoimidazole: $C_9H_5I_7N_6$, M = 1085.49, colourless plate, 0.19 × 0.15 × 0.08 mm^3, monoclinic, space group $P2_1/m$ (No. 11), a = 4.27080(10), b = 27.9241(6), c = 8.8926(2) Å, β = 101.6110(10)°, V = 1038.81(4) $Å^3$, Z = 2, D_c = 3.470 g/cm^3, F_{000} = 944, Bruker SMART APEX II CCD, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 71.2º, 17788 reflections collected, 4803 unique (R_{int} = 0.0353). Final *GooF* = 1.124, *R1* = 0.0433, *wR2* = 0.0785, *R* indices based on 3855 reflections with I >2sigma(I). (refinement on F^2), 103 parameters, 0 restraints. Lp and absorption corrections applied, μ = 10.461 mm^{-1}. The crystal was obtained in methanol by slow evaporation. CCDC-875314 contain the supplementary crystallographic data for this structure. It can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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