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Tridentate C–I $\cdots$ O $^-$ –N $^+$ Halogen Bonds

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The X-ray structures of first co-crystals where the three oxygen lone pairs in *N*-oxides are fully utilized for tridentate C–I $\cdots$ O $^-$ –N $^+$ halogen bonding with 1,2-diiodoperfluoroalkanes are reported, studied computationally, and compared with the corresponding silver(I) *N*-oxide complexes.

Halogen bond (XB), only recently defined by IUPAC,¹ has emerged over the past decade and a half as a strong, specific and highly directional non-covalent interaction producing well-defined structures similar to hydrogen bond (HB).² Halonium ion-based XBs, [N $\cdots$ X $\cdots$ N] $^+X^-$ (X = I, Br), have recently received great interest owing to their exceptionally strong coordinative covalent character. Moreover, the [N $\cdots$ X $\cdots$ N] $^+$ species in halogen bond supramolecular chemistry share remarkable structural and geometrical similarities with [N–Ag–N] $^+$ species in coordination chemistry.³ Inspired by the strength of [N $\cdots$ X $\cdots$ N] $^+X^-$ XBs, evidenced by the solid-state interaction ratio, R_{XB} ,¹ as low as 0.62, we investigated the formation of XB adducts using pyridine *N*-oxides and *N*-haloimides.⁴ The strategy yielded 1:1 XB complexes with strong N $^+$ –I $\cdots$ O $^-$ –N $^+$ halogen bonds with R_{XB} values of 0.66. These XBs are strong, monodentate and tunable both in solution- and solid-state. Despite the apparent weakness of the XBs with R_{XB} values 0.75–0.90, they have witnessed breakthrough applications in materials chemistry, *e.g.* triggering liquid crystallinity⁵ and gelation,⁶ or in crystal engineering.²

Well-known XB acceptors include heterocyclic nitrogen compounds, especially those with sp^2 nitrogen atoms, which have been employed to gain control over formation of structures from simple 1:1 co-crystals to larger aggregates in crystal engineering.² Self-assembly through these monovalent N $\cdots$ X interactions using di- or poly-topic XB donors often requires laborious synthesis of multi-topic nitrogen-containing XB acceptor compounds.² Some oxygen-based acceptors, especially aromatic and aliphatic *N*-oxides could in principle act as multi-dentate HB and XB acceptors, and they have

been shown to form mono, di and tris-Ag(I) complexes.⁷ The isolobal structure of silver and iodine and the existence of μ_3 -O, O,O silver(I) coordination bonds, encouraged us to investigate if indeed that *N*-oxide oxygen could act as a tridentate acceptor for XBs too.

The ability of the halide anions to act as multi-dentate XB acceptors has well been taken advantage of, with the counter cations such as alkali metals and onium cations having a critical role in tuning the properties of the final structures.⁸ However, while the cations can be useful in some situations, their presence can sometimes also introduce unnecessary complexity to the system. This motivated us to use neutral multi-dentate acceptors to construct halogen-bonded structures without the accompanying counter cations. As a result of this search, we report here the C–I $\cdots$ O $^-$ –N $^+$ XB co-crystals where the polar but neutral N $^+$ –O $^-$ group in *N*-oxide acts as a tridentate XB acceptor. The Fig. 1 depicts the chemical structures of the XB acceptors and donors, *viz.* trimethylamine *N*-oxide (**1**), *N,N*-dimethylbenzylamine *N*-oxide (**2**), 4-methylpyridine *N*-oxide (**3**), 3,4-dimethylpyridine *N*-oxide (**4**) as the XB acceptors, and tetrafluoro-1,2-diiodoethane (**DI2**) and octafluoro-1,4-diiodobutane (**DI4**) as the XB donors. Due to the instability of the multiple interactions in solution, the crystallographic and computational studies were used in structural characterizations.

Fig. 1 The chemical structures of acceptors (top) and donors (below): trimethylamine *N*-oxide (**1**), *N,N*-dimethylbenzylamine *N*-oxide (**2**), 4-methylpyridine *N*-oxide (**3**), 3,4-dimethylpyridine *N*-oxide (**4**), 4-methoxypyridine *N*-oxide (**5**), tetrafluoro-1,2-diiodoethane (**DI2**) and octafluoro-1,4-diiodobutane (**DI4**).

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In the co-crystals **1-DI4**, **2-DI4**, **3-DI2** and **4-DI2**, three electron pairs of *N*-oxide oxygen atom point towards the three vertices of tetrahedron to form three C-I...O⁻-N⁺ XBs (Fig. 2a). Co-crystals **1-DI4**, **2-DI4**, **3-DI2** and **4-DI2**, respectively have three, one, three and two symmetrically independent tetrahedra defined in such way. Otherwise, all C-I...O⁻-N⁺ distances are similar, ranging from

(Fig.2c) manifest remarkably short μ_4 -Ag...O contacts of 2.732(3) Å. All of these μ_4 -distances are below the sum of the van der Waals radii of Ag(I) and O-atoms [3.24 Å].⁹ The unusual and diverse *pseudo*- μ_4 -O,O,O,O mode contacts seen in Ag-O skeletons (Fig. 2c-e) could result from either the crystal packing or electrostatic interactions, while similar coordination modes are absent in XB co-crystals due to steric reasons.

Table 1. Average interaction energies, E_{int} [kJ mol⁻¹] of **3** with CF₃I, CH₃COOH and AgCl calculated at PBE0/def2-TZVP level of theory.

	E_{int} [kJ mol ⁻¹]			
	monodentate	μ_2 -O,O	μ_3 -O,O,O	μ_4 -O,O,O,O
CF ₃ I	-33.7	-31.2	-28.2	**
CH ₃ COOH	-68.6	-67.5	-56.6	**
AgCl	-124.9	-115.9	-102.4	-23.6

** Optimized structure did not exhibit μ_4 -O,O,O,O coordination mode.

Fig. 2 General μ_3 -O,O,O mode observed in XB co-crystals **1-DI4**, **2-DI4**, **3-DI2** and **4-DI2** (a), and μ_4 -O,O,O,O silver(I) coordination mode observed in **5-AgClO₄** (WIWXIL)^{7b} (b). The 1-D silver-oxygen coordination environments in **5-AgClO₄** (WIWXIL)^{7b}(c), **5-AgOTf** (WIWXUX)^{7b} (d) and **5-AgBF₄** (WIWXOR)^{7b} (e). Schematic representation of interaction tetrahedra in XB co-crystals (f) and silver(I) complexes (g). Black broken lines in (c)-(e) represent μ_4 -Ag-O contacts shorter than the sum of the van der Waals radii of Ag(I) and O atoms.⁹

2.703(2) to 2.980(15) Å which corresponds to R_{XB} values between 0.77 and 0.85. The tridentate XB interactions are compared with reported silver(I) complexes of **5**.^{7b} The non-coordinated anions in **5-AgClO₄** (WIWXIL)^{7b}, Fig. 2c), **5-AgOTf** (WIWXUX)^{7b} Fig. 2d) and **5-AgBF₄** (WIWXOR)^{7b}, Fig. 2e) minimize the competition between the anions and the *N*-oxide oxygens, and the anions do not coordinate to silver(I) in these complexes. All silver(I) complexes of **5** form 1-D cationic coordination polymers with μ_2 -O,O and μ_3 -O,O,O oxygen coordination modes. Additionally, **5** has μ_4 -O,O,O,O contacts in **5-AgClO₄** (ca. 2.732(3) - 3.224(2) Å; Fig. 2c), **5-AgOTf** (ca. 3.107(3) - 3.357(3) Å; Fig. 2d) and **5-AgBF₄** (ca. 2.872(2) - 3.032(3) Å; Fig. 2e).^{7b}

In the halogen bonded co-crystals, the three vertex iodine atoms bound to the *N*-oxide oxygen are separated by roughly at distances of ca. 4.0 Å (Fig. 2f, A, B and C; Table S2). In contrast, the reported a, b, c (Fig. 2g) and corresponding A, B and C distances in silver(I) complexes deviate more due to ligand-supported d^{10} - d^{10} argentophilic interactions.^{7b} For example, in addition to coordination bonds, *N*-oxide oxygens in **5-AgClO₄** indicated by '*'

Fig. 3 (On top) Electrostatic potential surface of **3** showing the negative charge at the *N*-oxide oxygen. The comparison of 1:4 acceptor:donor complexes obtained from section of X-ray crystal packing (left) **3-DI2** (a), **3** (c) and **5-AgClO₄**^{7b} (e) and, computationally DFT optimized structures (right) **3-4CF₃I** (b), **3-4AcOH** (d) and **3-4AgCl** (f).

To gain more insight into the *N*-oxide oxygen interaction modes, complexes with ratios ranging from 1:1 to 1:4 between **3** and CF₃I and CH₃COOH and AgCl¹⁰ were studied using DFT calculations (see ESI for details). Expectedly, adding additional equivalents of AgCl, AcOH and CF₃I to 1:1 optimised structures decreases the calculated average interaction energies (E_{int}) in the order 1:1 > 1:2 > 1:3 (see Table 1), the effect being more notable for silver(I) than CF₃I. The decrease in average E_{int} is accompanied by an increase in the coordination/hydrogen/halogen bond distances in the same order.

Optimizing the structures with four XB/HB donor molecules resulted in the fourth molecule forming I...I and O-H...O interactions (Fig. 3b,d) with one of the donors at the μ_3 -site, rather than forming μ_4 -XB or μ_4 -HB binding modes. Remarkably, the “passive” (*i.e.* not involved in C-I...O[−]−N⁺ XBs) iodine of the ditopic **DI2** donor in the co-crystals **3-DI2** and **4-DI2** exhibits similar I...I interactions¹¹ with another **DI2** donor (see *e.g.* Fig. 3a). Moreover, a fully “passive” ditopic **DI4** molecule is found in the co-crystal **2-DI4** (Fig. 4b). This further supports the observation that the iodine μ_4 -XB binding mode around the *N*-oxide oxygen is not feasible and cannot even be supported by other weak interactions, unlike *pseudo*- μ_4 -O,O,O,O modes in the silver(I) complexes of **5-AgClO₄**, **5-AgOTf** and **5-AgBF₄** (Figs. 2c-e). The crystal structure of **3** itself (Fig. 3c) shows the *N*-oxide oxygen interactions through complementary μ_4 -C-H...O interactions due to the acidity of the *ortho*-hydrogen,¹² proving that the N-O group can function as a μ_4 -acceptor if supported by other interactions in the crystal structure. However, any attempts to computationally optimize the μ_4 -O,O,O,O HB assembly found in the crystal structure of **3** (Fig. 3c) led to π - π interactions between aromatic rings. On the other hand, the optimized HB model **3-4AcOH** (Fig. 3d) showed an exceptional agreement between Figs 3a and b. The ability of *N*-oxide oxygen to act as a μ_2 - (one XB and one HB), μ_3 - (one XB and two HB) and μ_4 -acceptor (two XB and two HB) has been reported,¹³ but the approach of four iodines around oxygen would evidently manifest steric congestion.

In contrast to the HB and XB structures, the μ_4 -O,O,O,O silver(I) coordination arrangement is observed for the optimized **3-4AgCl** structure (Fig. 3f). This coordination is supported by formation of chloride bridges between Ag(I) atoms. The ring formed by chloride bridges dramatically enhances the stability of **3-4AgCl** complex over **3-3AgCl** [*c.f.* ΔH (adduct formation) **3-3AgCl** −242.3 kJ mol^{−1} vs. **3-4AgCl** −685.5 kJ mol^{−1}, see ESI Table S3 for more details] but results in significantly diminished E_{int} value (see Table 1). This suggests that the *pseudo*- μ_4 -silver(I) coordination found in crystal structure is possible if supported by other *e.g.* ionic or argentophilic interactions.

As expected, the tridentate XB acceptor mode in *N*-oxides enable access to three-dimensional halogen bonded structures with complex topologies. For example, **1** drives the self-assembly of **1-DI4** to a topologically intriguing threaded structure with a 3:5 stoichiometric ratio of **1** and **DI4**. The structure can be rationalized as consisting of a corrugated ladder-like XB polymer with formula (1)₂(DI4)₃ through which a decorated XB chain of formula (1)(DI4)₂ is threaded (Fig. 4a). In **2-DI4**, on the other hand, corrugated (2)₂(DI4)₃ units interpenetrate to form channels filled with “passive” **DI4** molecules (Fig. 4b), effectively giving a host-guest XB

framework. Finally, structures **3-DI2** and **4-DI2** (Fig 4c,d) both consist of decorated XB chains (3)(DI2)₂ and (4)(DI2)₂, respectively, strongly resembling the (1)(DI4)₂ chains in **1-DI4**, once again proving the topological consistency. These chains further pack by means of the C-I...I halogen bonds through the **DI2** “side chains” with the “backbone” **DI2** iodine atoms as the acceptors to give complex interpenetrated 3-D frameworks.

Fig. 4 Supramolecular motifs in the crystal structures of the studied XB co-crystals. In **1-DI4**, decorated XB zig-zag chain (1)(DI4)₂ (shown as CPK model) is threaded through the corrugated XB ladder (1)₂(DI4)₃ (a). In **2-DI4**, corrugated XB layers (2)₂(DI4)₃ interpenetrate to form channels filled with additional molecules of **DI4** (shown as CPK model) (b). Decorated (3)(DI2)₂ and (4)(DI2)₂ XB zig-zag chains, reminiscent of those in **1-DI4**, respectively in **3-DI2** (c) and **4-DI2** (d). Minor disorder components are omitted for clarity.

In conclusion, we have shown that the oxygen lone pairs in aliphatic and aromatic *N*-oxides can manifest rare μ_3 -O,O,O C-I...O[−]−N⁺ halogen bonds in the solid-state. The steric factors prevent the μ_4 arrangements with iodine for XBs, and the fourth donor molecule, if present, is not involved in C-I...O[−]−N⁺ halogen bonds. DFT Calculations support *N*-oxide affinity for halogen, hydrogen and coordination bonds with μ_3 -O,O,O bonding mode, while suggesting that μ_4 -O,O,O,O halogen bonds are highly unlikely. As witnessed by the remarkable similarities in the crystal structures, the described μ_3 -O,O,O C-I...O[−]−N⁺ motif is a reliable design motif

for complex 3-D structures, such as halogen bonded organic frameworks, XBOF's.¹⁴

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- 10 Notes: CF₃I is the simplest XB donor analogue of DI₂ and DI₄, and therefore chosen as the model. Hydrogen bond donor, CH₃COOH, was used as a model, although similar conclusions were drawn with other HB donors e.g. ethanol and water. AgCl was used to model silver(I) coordination instead of Ag⁺ in order to balance the effect of charge repulsion in the discrete optimized structures
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