Electronic Supplementary Material (ESI) for CrystEngComm.

Tridentate C–I···O^{-}–N^{+} Halogen Bonds

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SUPPLEMENTARY INFORMATION

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I General information

All the solvents used for syntheses and crystal growth were of reagent grade and were used as received. Trimethylamine-*N*-oxide (**1**), N,N-dimethylbenzylamine, 4-methylpyridine-*N*-oxide (**3**) and 3,4-dimethylpyridine were purchased from Sigma Aldrich, while the tetrafluoro-1,2-diiodoethane (**DI2**) and octafluoro-1,4-diiodobutane (**DI4**) were purchased from Apollo Scientific Chemicals Ltd. *N*,*N*-Dimethylbenzylamine-*N*-oxide (**2**) and 3,4-dimethylpyridine-*N*-oxide (**4**) were synthesized according to a reported procedure.[1]

II Preparation of halogen bond co-crystals

1) **1·DI4** Solid trimethylamine-*N*-oxide dihydrate (**1**, 11.91 mg, 0.11 mmol) and liquid octafluoro-1,4-diiodobutane (**DI4**, 55.1 µL, 0.30 mmol) were dissolved in 0.250 ml of acetonitrile with heating. The sample was left to slowly evaporate at room temperature for two days, yielding colourless crystals suitable for X-ray crystallography.

2) **2·DI4** Solid *N*,*N*-dimethylbenzylamine-*N*-oxide (**2**, 8.68 mg, 0.0574 mmol) was suspended in liquid octafluoro-1,4-diiodobutane (**DI4**, 50.0 µL, 0.273 mmol) and briefly sonicated. The closed sample was left at room temperature for two days, yielding colourless crystals suitable for X-ray crystallography.

3) **3·DI2** Solid 4-methylpyridine-*N*-oxide (**3**, 7.54 mg, 0.0691 mmol) was suspended in liquid tetrafluoro-1,2-diiodoethane (**DI2**, 27.2 µL, 0.202 mmol) and briefly sonicated. The closed sample was left at room temperature for four days, yielding colourless crystals suitable for X-ray crystallography.

3) **4·DI2** Solid 3,4-dimethylpyridine-*N*-oxide (**4**, 6.37 mg, 0.0517 mmol) was suspended in liquid tetrafluoro-1,2-diiodoethane (**DI2**, 27.2 µL, 0.202 mmol) and briefly sonicated. The closed sample was left at room temperature for four days, yielding colourless crystals suitable for X-ray crystallography.

III X-Ray Experimental details

Single crystal X-ray data for **2·DI4** and **3** were measured on a Bruker-Nonius Kappa CCD diffractometer with an APEX-II CCD detector using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. The data for **3·DI2** and **4·DI2**, were measured on a Rigaku Oxford diffractometer equipped with an Eos CCD detector using mirror-monochromated Mo-*K*α (λ = 0.71073 Å) radiation. Single crystal X-ray data for **1·DI4** were collected on a dual source Rigaku Oxford diffractometer with an Atlas detector using mirror-monochromated Mo-*K*α (λ = 0.71073 Å). The crystal data and experimental details for the data collections are given in Table S1. Data collection and reduction for Rigaku Oxford diffractometers were performed using the program *CrysAlisPro*,[2] while for Bruker-Nonius Kappa CCD diffractometer using the program *COLLECT*[3] and *HKL DENZO AND SCALEPACK*[4]. Gaussian face indexing-based absorption correction method through *CrysAlisPro*[2] was used for **1·DI4**, **3·DI2** and **4·DI2**, while the multi-scan absorption correction through *SADABS*[5] was used for **2·DI4** and **3**. The structures were solved by direct methods with SHELXS[6], and refined by full-matrix least squares on F^2 using the *OLEX2*[7] and/or WinGX[8] which utilize the *SHELXL*-2016[6] module. No attempt was made to locate the hydrogens from difference electron density Fourier maps, and appropriate constraints and restraints were used when necessary for disordered molecules.

Table S1. Crystal data and X-Ray experimental details for **1·DI4** - **4·DI2** and **3**

Complex	**1·DI4**	**2·DI4**	**3·DI2**	**4·DI2**	**3**
CCDC Number	1557841	1557842	1557843	1557848	1557847
Empirical formula	$C_{29}H_{27}F_{40}I_{10}N_3O_3$	$C_{32.4}H_{26}F_{28.8}I_{7.2}N_2O_2$	$C_{10}H_7F_8I_4NO$	$C_{11}H_9F_8I_4NO$	C_6H_7NO
Formula weight	2494.53	1936.23	816.77	830.79	109.13
Temperature (K)	123.0(1)	170.0(1)	123.0(1)	123.0(1)	170.0(1)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Tetragonal
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$I4_1/amd$
Unit cell dimensions: a (Å)	20.8752(5)	12.6238(3)	16.0396(5)	15.8260(10)	7.920(3)
b (Å)	11.2667(2)	11.3737(3)	18.4264(4)	19.3955(8)	7.920(3)
c (Å)	28.8275(7)	21.9526(4)	20.1968(6)	13.3936(6)	19.588(4)
α (°)	90	90	90	90	90
β (°)	108.327(3)	105.4035(15)	90	90.345(5)	90
γ (°)	90	90	90	90	90
Volume (Å^3)	6436.2(3)	3038.72(12)	5969.2(3)	4111.1(4)	1228.7(10)
Z	4	2	12	8	8
Density (calculated) (mg m^{-3})	2.574	2.116	2.727	2.685	1.180
Absorption coefficient (mm^{-1})	4.964	3.793	6.332	6.108	0.082
F(000)	4544	1782	4392	2992	464
Crystal size (mm^3)	0.376×0.342×0.229	0.350×0.279×0.047	0.183×0.157×0.093	0.272×0.157×0.133	0.13×0.09×0.05
ϑ range for data collection (°)	2.873 to 29.363	2.033 to 26.851	2.948 to 28.931	2.998 to 28.946	2.774 to 25.245
Reflections collected [R(int)]	26621 [0.0165]	22249 [0.0453]	38462 [0.0381]	26758 [0.0460]	4574 [0.1126]
Reflections [$I > 2\sigma(I)$]	13227	5185	10898	8589	189
Data completeness (%)	99.3 to ϑ = 25.25°	99.4 to ϑ = 25.25°	99.7 to ϑ = 25.25°	99.8 to ϑ = 25.25°	99.7 to ϑ = 25.24°
Data/restraints/ parameters	14844/3920/1014	6428/2839/643	13577/4425/927	9592/2355/657	454/0/29
Goodness-of-fit on F^2	1.123	1.045	1.168	1.085	1.007
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0274, wR_2 = 0.0503	R_1 = 0.0581, wR_2 = 0.1622	R_1 = 0.0576, wR_2 = 0.1068	R_1 = 0.0394, wR_2 = 0.0925	R_1 = 0.0571, wR_2 = 0.1579
Final R indices [all data]	R_1 = 0.0336, wR_2 = 0.0522	R_1 = 0.0711, wR_2 = 0.1726	R_1 = 0.0795, wR_2 = 0.1187	R_1 = 0.0478, wR_2 = 0.1025	R_1 = 0.1212, wR_2 = 0.1644
Largest diff. peak/hole (e Å^{-3})	1.082/−1.195	1.679/−0.988	1.738/−1.431	0.952/−1.499	0.166/−0.147

IV Solid-state analysis

Table S2. Bond parameters in halogen bonded co-crystals

Code	*ca.,* Å		*ca.,* Å		*ca.,* Å	
	a	**A**	b	**B**	c	**C**
1·DI4	2.745(2)	4.1081(16), 4.340(8)*	2.874(3), 2.872(8)*	4.0175(16), 3.998(8)*	2.810(3)	4.5207(6)
	2.836(3)	4.165(2), 4.029(11)*	2.885(3), 2.860(11)*	4.054(3), 4.326(12),* 3.938(15),* 4.194**	2.786(3), 2.741(10)*	4.6755(7), 4.374(11)*
	2.805(2)	4.1585(6)	2.825(2)	3.9946(7)	2.703(2)	4.1366(6)
2·DI4	2.808(5)	4.387(3), 4.312(6)*	2.788(5), 2.835(6)*	4.256(3), 3.967(6)*	2.832(5)	3.8839(8)
3·DI2	2.892(12)	4.030(2)	2.875(11)	4.008(6), 4.164(16)*	2.775(13), 2.864(19)*	4.224(5), 4.555(15)*
	2.856(11)	3.937(12), 4.056(14)*	2.875(16), 2.843(17)*	4.453(15), 4.234(15),* 4.273(16),* 4.045(16)*	2.777(15), 2.790(15)*	3.998(11), 3.978(11)*
	2.769(12)	4.351(8), 4.45(2)*	2.980(15), 2.90(3)*	3.971(9), 3.97(3)*	2.944(11)	4.023(2)
4·DI2	2.804(6)	4.371(3), 4.316(10)*	2.853(7), 2.926(11)*	4.208(4), 4.090(10)*	2.879(4)	4.4694(7)
	2.862(6)	4.162(4), 4.385(5)*	2.768(7), 2.816(7)*	4.368(5), 4.111(5),* 4.250(9),* 4.006(9)*	2.833(7), 2.763(10)*	4.544(3), 4.291(8)*

*Corresponding to minor disorder components.

**Could not be measured reliably because of a very low occupancy of the minor disorder component.

V Computational Studies

Adduct formation enthalpies of halogen (CF_3I), hydrogen (CH_3COOH) and coordination (AgCl) bonded ligand **3** adducts were calculated to show stability trends of optimized structures. The reaction enthalpies in Table S5 show there is energy gain in adding more molecules around *N*-oxide oxygen of **3**, although the gain diminishes with each added donor molecule except for structures with four added molecules. In **3**•4AgCl the Ag(I) bonding changes from two-coordinate found in **3**•3AgCl to chlorine-bridged three-coordinate bonding. In **3**•4CF_3I and **3**•4CH_3COOH the added fourth CF_3I and CH_3COOH molecules form halogen-halogen and hydrogen bond interactions, respectively, with donor molecules actively participated in μ₃-*O,O,O* coordination around *N*-oxide oxygen. These halogen-halogen and hydrogen bond interactions between donor molecules are stronger than the alternative interactions with the *N*-oxide oxygen giving added stability to the overall optimized structures.

Table S3. Reaction enthalpies for adduct formation of **3** with one to four model halogen (CF_3I), hydrogen (CH_3COOH) and coordination (AgCl) bond donors.

	Number of donors			
	monodentate	μ_2-*O,O*	μ_3-*O,O,O*	μ_4-*O,O,O*
CF_3I	–26.7	–52.6	–68.0	–95.9
CH_3COOH	–52.2	–100.9	–131.2	–192.2
AgCl	–113.3	–191.5	–242.3	–685.5

COMPUTATIONAL DETAILS

Gaussian 09 program package was used for all theoretical calculations.[9] Optimized geometries and harmonic vibrational frequencies of all structures were obtained from DFT calculations performed with PBE0 hybrid functional[10] and def2-TZVP basis[11] set employing Grimme's empirical correction D3 with Becke-Johnson dampening[12] for treating dispersion interactions. Basis set superposition error corrections were treated by counterpoise method.[13]

VI References

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