Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information Available for

Halogen bonding of electrophilic bromocarbons with pseudohalide anions

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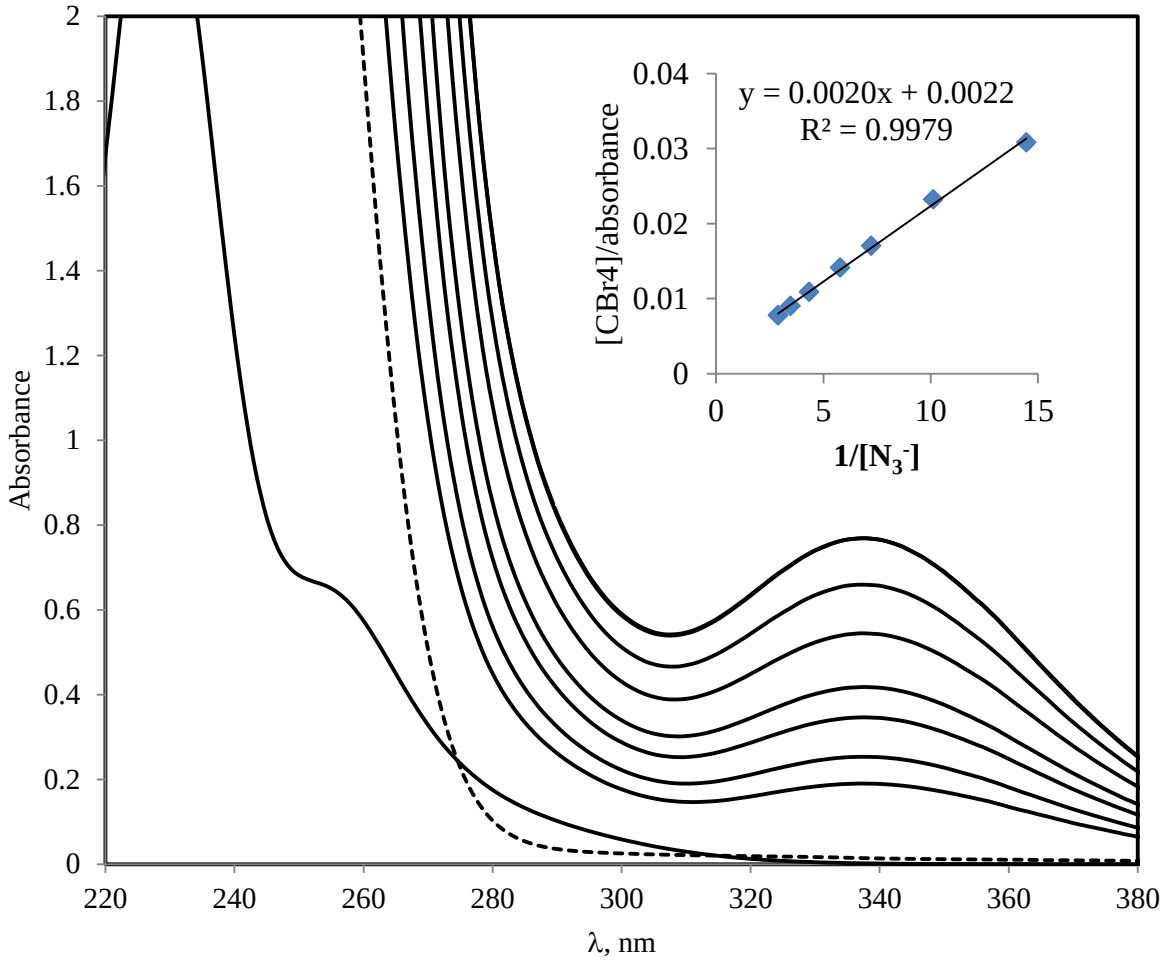


Figure S1. Spectral changes resulting from the addition of $(Bu_4N)N_3$ to 5.2 mM solution of CBr_4 in dichloromethane (20 ^oC). Concentration of $(Bu_4N)N_3$ (solid lines, from bottom to top at 300 nm): 0 mM , 69 mM , 99 mM , 138 mM , 173 mM, and 230 mM, 288 mM, 345 mM . Dashed line corresponds to the separate 345 mM solution of $(Bu_4N)N_3$.
Insert: Benesi-Hildebrandt treatment of the spectral data.

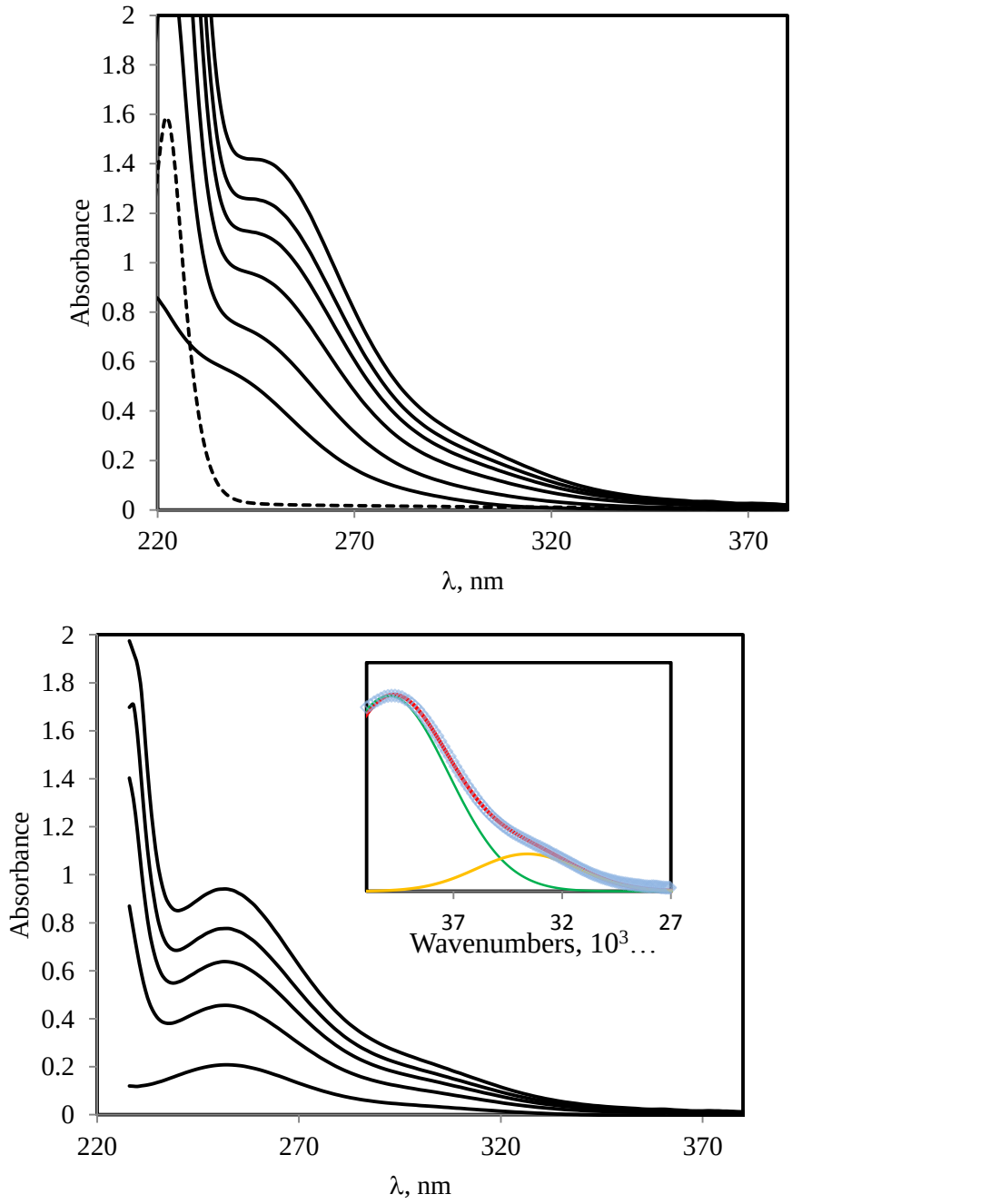


Figure S2. (Top) Spectral changes resulting from the addition of $(Bu_4N)NCO$ to 3.0 mM solution of CBr_3NO_2 in dichloromethane (19 ^oC). Concentration of $(Bu_4N)NCO$ (solid lines, from bottom to top at 270 nm): 0 mM , 55 mM , 110 mM , 164 mM , 219 mM, and 274 mM . Dashed line corresponds to the separate 55 mM solution of $(Bu_4N)NCO$. (Bottom): Spectra of the solutions containing $(Bu_4N)NCO$ and CBr_3NO_2 after subtracting absorption of the reagents. Insert: Illustration of the deconvolution of the spectrum of the$[CBr_3NO_2, NCO^-]$ complex into Gaussian components.

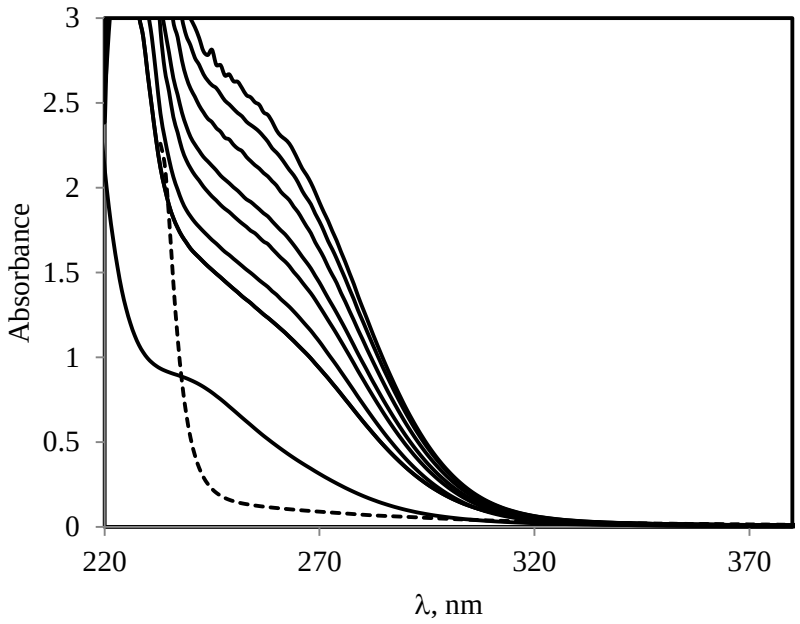


Figure S3. Spectral changes resulting from the addition of $(Bu_4N)NCO$ to 5.3 mM solution of CBr_3CN in dichloromethane (20 ^oC). Concentration of $(Bu_4N)NCO$ (solid lines, from bottom to top at 300 nm): 0 mM , 67 mM , 96 mM , 135 mM , 168 mM, and 225 mM, 281 mM, 337 mM . Dashed line corresponds to the separate 337 mM solution of $(Bu_4N)NCO$.

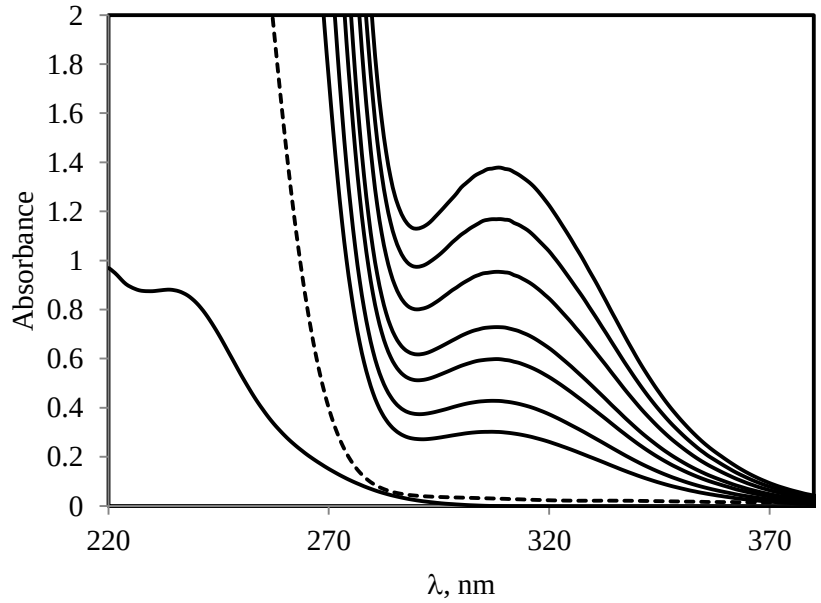


Figure S4. Spectral changes resulting from the addition of $(Bu_4N)N_3$ to 5.9 mM solution of CBr_3F in dichloromethane (20 ^oC). Concentration of $(Bu_4N)N_3$ (solid lines, from bottom to top at 310 nm): 0 mM , 25 mM , 50 mM , 86 mM , 131 mM, and 176 mM, 266 mM, 345mM . Dashed line corresponds to the separate 40 mM solution of $(Bu_4N)N_3$.

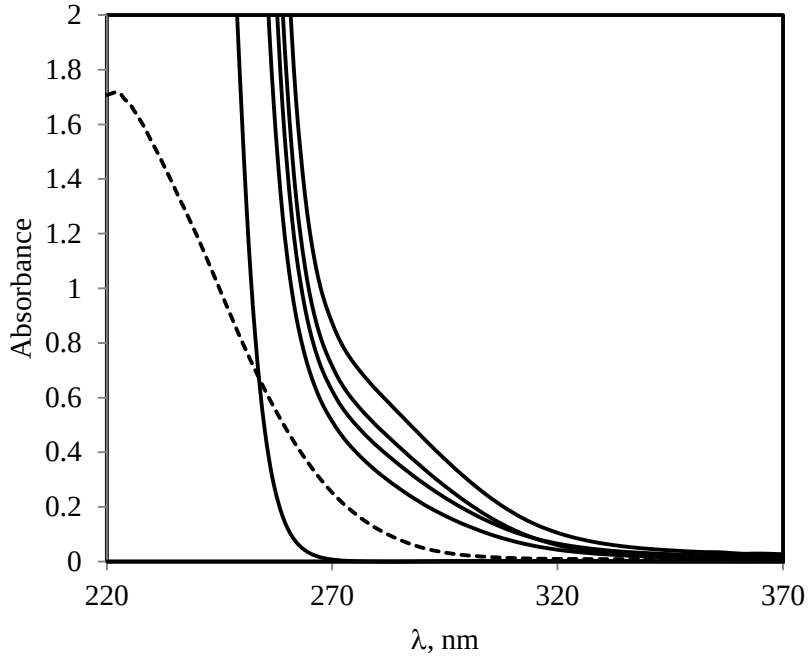


Figure S5. Spectral changes resulting from the addition of $(Bu_4N)NCS$ to 5.3 mM solution of CBr_3CONH_2 in dichloromethane (20 ^oC). Concentration of $(Bu_4N)NCS$ (solid lines, from bottom to top at 310 nm): 0 mM , 76 mM , 126 mM , 191 mM , 274 mM, and 421 mM. . Dashed line corresponds to the separate 140 mM solution of $(Bu_4N)NCS$.

Table S1. Details of the Mulliken correlation between the energies of the electronic transition in the [R-Br,A^-] complex, hν, and difference of the E(LUMO) of R-Br and E(HOMO) of anions.

	E(LUMO),[a]	hν, 10^3 cm^{-1}			
	hartree	N_3^-	NCO^-	NCS^-	Br^-
CBr4	0.0465	3.662	4.500	3.929	4.249
CHBr3	0.0756	4.210	5.052	4.500	4.790
CBr3NO2	0.0473	3.438	4.167	3.750	3.877
CBr3CN	0.0559	3.929	4.670	4.125	4.338
CFBr3	0.0613	4.031	4.816	4.282	4.612
CBr3CONH2	0.0726	4.125	4.797	4.468	4.963
C3Br2F6	0.1004	4.452		4.911	5.371
CBr3COCBr3	0.0465	3.705	4.268		3.794

a) Energies of LUMO of R-Br molecules. Note that energies of the HOMOs of anions are (in hartrees): N_3^- : -0.254, NCO^-: -0.311, NCS^-: -0.278 and Br^-: - 0.291. Energies of the frontier orbitals were calculated at MP2/6-311G** level in CH_2Cl_2 using SCIPCM solvation model.

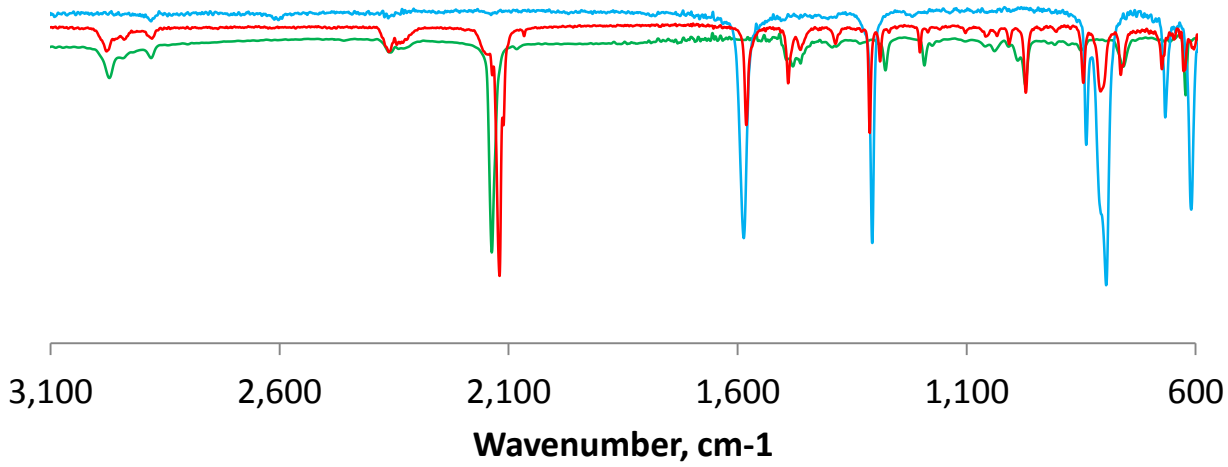


Figure S6. FT-IR spectra of CBr_3NO_2 (blue), Pr_4N NCO (green) and Pr_4N NCO·CBr_3NO_2 co-crystals (red).

Table S2. Selected vibration frequencies for R-Br molecules , Pr_4NA salts and their co-crystals.[a]

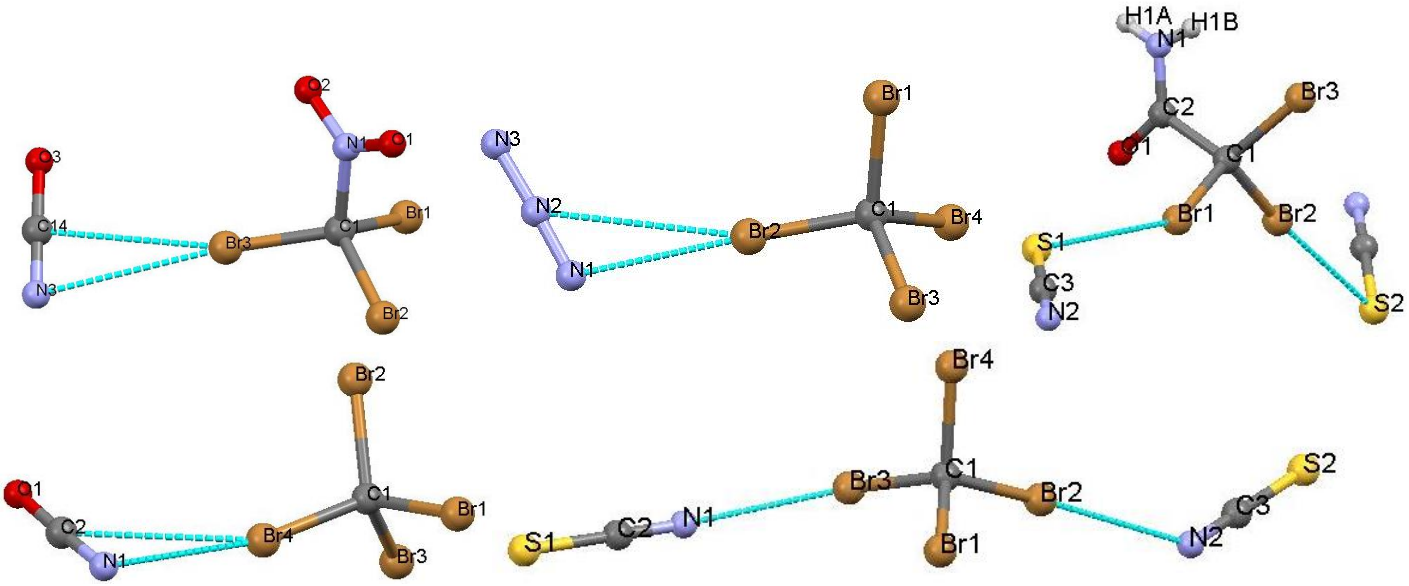
	ν, cm^{-1}
CBr_4	659
CBr_3NO_2	1589 839 806 795 666 610
CBr_3CONH_2	1678 1607 1343 1097 767 708 608 591 585
Pr_4N NCO	2972 2136 1479 1277 1192 972 757
Pr_4N NCS	2972 2054 1475 976 752
Pr_4N N_3	2970 1998 1477 971 760
Pr_4N NCO·CBr_3NO_2	2978 2120 1581 1489 1311 1202 971 845 807 763 674 626
Pr_4N NCO· CBr_4	2975 2120 1489 1285 1199 970 763 677 648
Pr_4N N_3 · CBr_4	2972 1991 1486 971 762 670 645
Pr_4N NCS· CBr_4	2972 2054 1485 970 681 672 661

a) Measured as neat liquids or crystalline salts.

Table S3. Characteristics of short (halogen- and hydrogen-bonding) contacts in the [R-Br, A^-] co-crystals

Co-crystals	Contact	D(Z-X…Y), Å	∠(Z-X…Y), deg	∠X-X…Br), deg	R
$(Pr_4N)NCO\cdot CBr_4$	Br3N1	2.875(3)	167.66(12)	99.3(2)	0.85
	Br3N2	3.251(2)	155.08(10)		0.96
	Br2 N1	2.806 (3)	176.90(11)	108.2(2)	0.83
	Br3N2	3.331(3)			0.98
	Br4N1	3.216(4)	160.48(18)	79.0 (2)	0.95
	Br3N2	3.198(2)	175.69(11)	136.5(2)	0.94
$(Pr_4N)NCO\cdot CBr_4$	Br2 N1	2.823(3)	176.39(12)	109.7(3)	0.83
	Br2 C2	3.384(3)	164.07(11)		0.95
	Br4N1	2.937(3)	167.40(12)	96.5(2)	0.86
	Br4 C2	3.270(3)	154.65(11)		0.92
	Br3N1	3.188(3)	173.74(12)	79.8(2)	0.94
	Br3 C2	3.190(3)	163.03(12)		0.90
$(Pr_4N)NCO\cdot CBr_3NO_2$	Br2N3	3.004(3)	167.74(9)	94.4(2)	0.88
	Br2C14	3.291(2)	153.96(9)		0.93
	Br1N3	2.763(3)	176.06(9)	112.9(2)	0.81
	Br1C14	3.369(3)	165.37(9)		0.95
	Br3N3	3.212(3)	173.50(9)	80.3(2)	0.94
	Br3C14	3.221(3)	166.09(9)		0.91
$2((Pr_4N)NCS)\cdot CBr_4$	Br4S1	3.2309(11)	171.76(11)	93.23(13)	0.92
	Br1S1	3.2147(11)	170.15(11)	108.83(13)	0.91
	Br3N1	3.013(3)	167.07(13)	139.2(3)	0.89
	Br2N2	2.897(4)	172.74(13)	136.5(3)	0.85
$2((Pr_4N)NCS)\cdot CBr_3CONH_2$	Br2S2	3.2294(6)	174.50(6)	96.21(8)	0.88
	Br3S1	3.3377(6)	178.02(6)	79.13(8)	0.91
	Br3C3	3.434(2)	150.47(8)		0.97
	Br1S1	3.5286(6)	151.85(7)	123.56(8)	0.95
	H1a N2	2.101(3)			

Table S4. Intramolecular bond lengths (in Å) of bromocarbon and pseudohalides in the [R-Br, A^-] co-crystals



Co-crystal	Bond		d, Å	Co-crystal	Bond		d, Å
	Atom 1	Atom 2			Atom 1	Atom 2	
$(Pr_4N)N_3{\cdot}CBr_4$	Br1	C1	1.939(3)	2($(Pr_4N)NCS$)	Br1	C1	1.945(4)
	Br2	C1	1.945(3)	$\cdot CBr_4$	Br2	C1	1.938(4)
	Br3	C1	1.943(3)		Br3	C1	1.932(4)
	Br4	C1	1.967(4)		Br4	C1	1.948(4)
	N1	N2	1.121(4)		S1	C2	1.653(4)
	N2	N3	1.209(4)		N1	C2	1.166(5)
					S2	C3	1.647(4)
					N2	C3	1.149(5)
$(Pr_4N)NCO{\cdot}CBr_4$	Br1	C1	1.955(3)	2($(Pr_4N)NCS$)	Br1	C1	1.956(2)
	Br2	C1	1.936(3)	$\cdot CBr_3CONH_2$	Br2	C1	1.943(2)
	Br3	C1	1.939(4)		Br3	C1	1.950(2)
	Br4	C1	1.938(4)		O1	C2	1.231(3)
	O1	C2	1.245(4)		N1	H1A	0.79(3)
	N1	C2	1.145(4)		N1	H1B	0.79(3)
$(Pr_4N)NCO$	Br1	C1	1.934(1)		N1	C2	1.251(3)
$\cdot CBr_3NO_2$	Br2	C1	1.917(2)		C1	C2	1.601(3)
	Br3	C1	1.919(2)		S1	C3	1.650(3)
	O1	N1	1.206(2)		N2	C3	1.156(4)
	O2	N1	1.210(2)		S2	C4	1.648(3)
	N1	C1	1.562(2)		N3	C4	1.167(4)
	O3	C14	1.240(2)		S1	C3	1.650(3)
	N3	C14	1.133(3)		N2	C3	1.156(4)

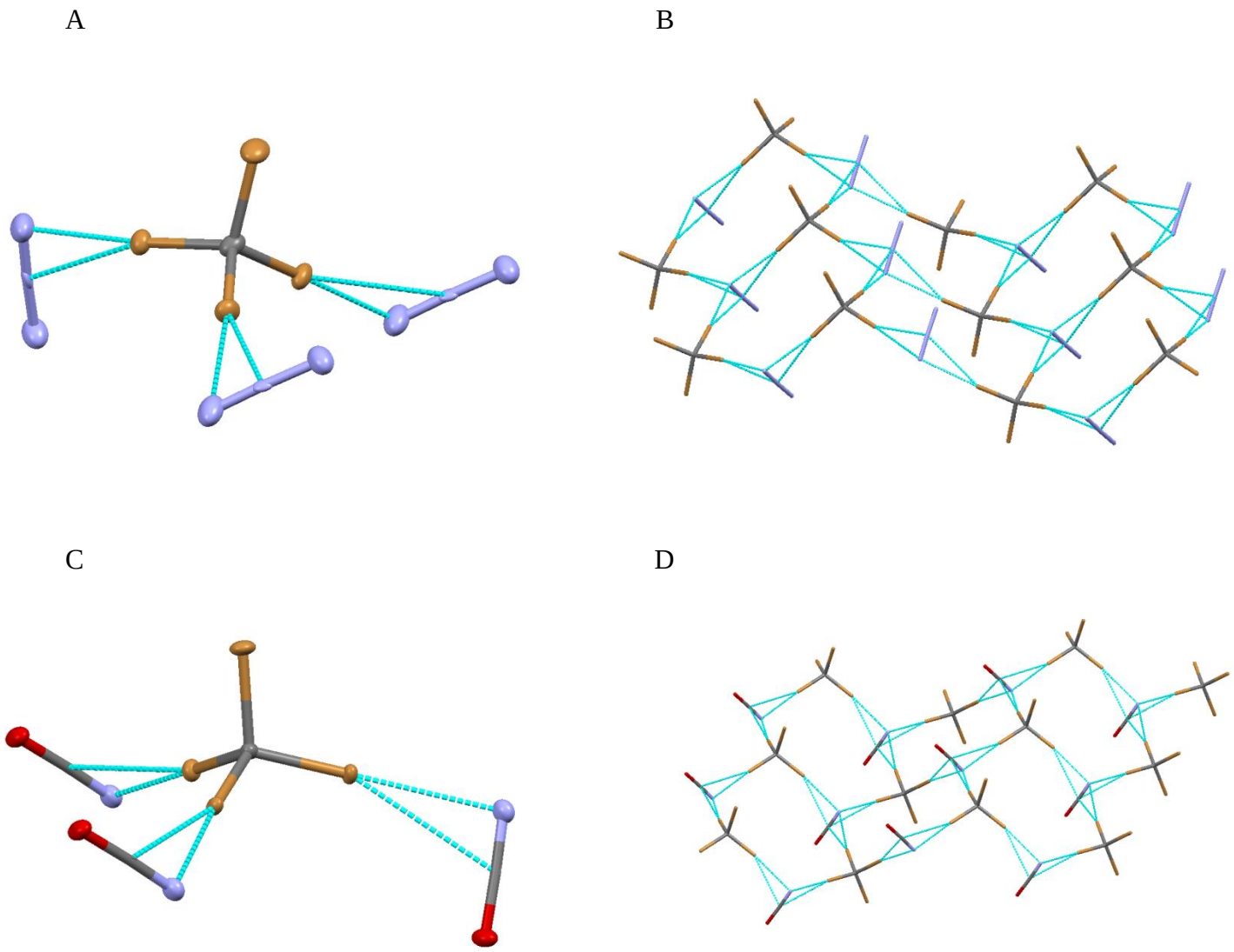


Figure S7. Fragments of the X-ray structure of the $(Pr_4N)N_3 \cdot CBr_4$(A and B) and $(Pr_4N)NCO \cdot CBr_4$ (C and D) co-crystals illustrating short contacts (blue lines) between carbon tetrabromide and azide or cyanate anions (A and C) and zigzag layer formed by (3:3) coordination of carbon tetrabromide and azide or cyanate anions (B and D, for clarity, Pr_4N^+ cations are not shown).

Table S5. Energies (in hartrees) of the halogen bonded complexes [R-Br, A^-] and separate anions resulted from the M06-2X/6-311+G(dp) calculations in the gas phase and in CH_2Cl_2. [a]

Anion	R-Br	Gas-phase	CH_2Cl_2
N_3^-	CBr_4	-10498.98559110	-10499.05548890
N_3^-	CBr_3NO_2	-8129.90314952	-8129.96970886
N_3^-	CBr_3CONH_2	-8094.11818333	-8094.19519474
N_3^-	CBr_3F	-8024.66287964	-8024.73451545
N_3^-	CBr_3H	-7925.42429751	-7925.50157568
N_3^-	CBr_3CN	-8017.65480388	-8017.72179079
N_3^-	$C_3Br_2F_6$	-6025.93326282	-6026.00428654
NCO^-	CBr_4	-10502.88976080	-10502.96274580
NCO^-	CBr_3NO_2	-8133.80659367	-8133.87685476
NCO^-	CBr_3CONH_2	-8098.02439943	-8098.10289668
NCO^-	CBr_3F	-8028.56866567	-8028.64230714
NCO^-	CBr_3H	-7929.33101440	-7929.40943115
NCO^-	CBr_3CN	-8021.55854610	-8021.62888330
NCO^-	$C_3Br_2F_6$	-6029.83979854	-6029.91217884
NCS^-	CBr_4	-10825.86056390	-10825.93047600
NCS^-	CBr_3NO_2	-8456.77682680	-8456.84387781
NCS^-	CBr_3CONH_2		-8421.06902024
NCS^-	CBr_3CONH_2 [b]	-8421.00915366	-8421.07676758
NCS^-	CBr_3CONH_2 [c]	-8421.00623032	-8421.07564690
NCS^-	CBr_3F	-8351.53928018	-8351.60979068
NCS^-	CBr_3H	-8252.30341054	-8252.37777285
NCS^-	CBr_3CN	-8344.52894764	-8344.59617800
NCS^-	$C_3Br_2F_6$	-6352.81043855	-6352.87964628
N_3^-	-	-164.21257800	-164.30248827
NCO^-	-	-168.11985138	-168.21112349
NCS^-	-	-491.09806424	-491.17992038

a) See ref. 10 for the energies of the separate bromocarbons. For clarity, only characteristics of the lowest-energy halogen-bonded complexes are listed, if not mentioned otherwise. b) Adduct bonded via combination of Br…S/H….N bonds. c) Adduct bonded via combination of Br…N/H….S bonds.

Table S6. Amount of A^- →R-Br charge transfer, Δq (in e) determined via NBO analysis of the [R-Br, A^-] complexes in the gas phase and in CH_2Cl_2[a] and corresponding intermolecular separation, $D_{Br\cdots X}$ (in Å) and $R_{XY} = D_{X\cdots Y}/(r_X + r_Y)$ (where r_X and r_Y are van der Waals radii). [a]

		Gas-phase			CH_2Cl_2		
Anion	R-Br	Δq, e	$D_{Br\cdots X}$, Å	R_{XY}	Δq, e	$D_{Br\cdots X}$, Å	R_{XY}
N_3^-	CBr_4	0.254	2.371	0.697	0.083	2.708	0.796
N_3^-	CBr_3NO_2	0.316	2.293	0.674	0.126	2.584	0.760
N_3^-	CBr_3CONH_2	0.188	2.465	0.725	0.063	2.778	0.817
N_3^-	CBr_3F	0.195	2.453	0.722	0.064	2.774	0.816
N_3^-	CBr_3H	0.150	2.538	0.746	0.046	2.864	0.842
N_3^-	CBr_3CN	0.291	2.318	0.682	0.112	2.617	0.770
N_3^-	$C_3Br_2F_6$	0.170	2.480	0.729	0.061	2.771	0.815
NCO^-	CBr_4	0.160	2.426	0.713	0.048	2.752	0.809
NCO^-	CBr_3NO_2	0.215	2.341	0.689	0.066	2.677	0.787
NCO^-	CBr_3CONH_2	0.097	2.553	0.751	0.039	2.809	0.826
NCO^-	CBr_3F	0.110	2.514	0.739	0.042	2.773	0.816
NCO^-	CBr_3H	0.080	2.592	0.762	0.028	2.895	0.852
NCO^-	CBr_3CN	0.198	2.363	0.695	0.065	2.697	0.793
NCO^-	$C_3Br_2F_6$	0.097	2.538	0.746	0.037	2.780	0.818
NCS^-	CBr_4	0.215	2.861	0.784	0.064	3.187	0.873
NCS^-	CBr_3NO_2	0.301	2.746	0.752	0.084	3.117	0.854
NCS^-	CBr_3CONH_2	b			0.042	3.295	0.903
NCS^-	CBr_3F	0.156	2.957	0.810	0.049	3.250	0.890
NCS^-	CBr_3H	0.105	3.083	0.845	0.035	3.322	0.910
NCS^-	CBr_3CN	0.271	2.778	0.761	0.080	3.131	0.858
NCS^-	$C_3Br_2F_6$	0.112	3.046	0.834	0.046	3.253	0.891

a) For clarity, only characteristics of the lowest-energy halogen-bonded complexes, e.g. adducts bonded via nitrogen end of NCO^-, and sulfur end of NCS^- are listed. b) Only adduct formed via combination of halogen and hydrogen bonds was found.

Table S7. Elongation of the C-Br bond lengths (Δd, in Å) established as a sum of the differences between the corresponding bond length in the separate and halogen-bonded bromocarbons (C-Br_S and C-Br_C, respectively, in Å). [a]

A^-	R-Br	Δd	C-Br_S [a]	C-Br_C [b]			
			Gas-phase				
N_3^-	CBr_4	0.14522	1.942388	2.02383	1.96096	1.96443	1.96555
N_3^-	CBr_3NO_2	0.1763	1.922593	2.08165	1.93167	1.93076	
N_3^-	CBr_3CONH_2	0.08634	1.94333	2.00714	1.93899	1.9702	
N_3^-	CBr_3F	0.10601	1.937457	1.97971	1.96933	1.96934	
N_3^-	CBr_3H	0.07802	1.930933	1.95803	1.95635	1.95644	
N_3^-	CBr_3CN	0.15083	1.94379	2.06903	1.9578	1.95537	
N_3^-	$C_3Br_2F_6$	0.07198	1.927795	1.98457	1.943		
NCO^-	CBr_4	0.09922	1.942388	1.97743	1.96268	1.96252	1.96614
NCO^-	CBr_3NO_2	0.12075	1.922593	2.01807	1.93524	1.93522	
NCO^-	CBr_3CONH_2	0.04616	1.94333	1.95936	1.97219	1.9446	
NCO^-	CBr_3F	0.06538	1.937457	1.9422	1.96565	1.9699	
NCO^-	CBr_3H	0.05261	1.930933	1.92873	1.9579	1.95878	
NCO^-	CBr_3CN	0.10602	1.94379	2.01286	1.96169	1.96284	
NCO^-	$C_3Br_2F_6$	0.03272	1.927795	1.94801	1.9403		
NCS^-	CBr_4	0.09897	1.942388	1.99297	1.9608	1.95805	1.9567
NCS^-	CBr_3NO_2	0.13092	1.922593	2.04198	1.92651	1.93021	
NCS^-	CBr_3F	0.07035	1.937457	1.95819	1.96055	1.96398	
NCS^-	CBr_3H	0.04623	1.930933	1.93815	1.95045	1.95043	
NCS^-	CBr_3CN	0.11048	1.94379	2.03397	1.95687	1.95101	
NCS^-	$C_3Br_2F_6$	0.02404	1.927795	1.94903	1.9306		
N_3^-	CBr_4	0.03307	1.943008	1.95739	1.94842	1.94902	1.95027
N_3^-	CBr_3NO_2	0.05451	1.921727	1.97365	1.92235	1.92369	
N_3^-	CBr_3CONH_2	0.01987	1.944407	1.95682	1.95994	1.93633	
N_3^-	CBr_3F	0.02544	1.937003	1.94136	1.94713	1.94796	
N_3^-	CBr_3H	0.01682	1.93238	1.93397	1.93969	1.9403	
N_3^-	CBr_3CN	0.04532	1.942843	1.97519	1.94989	1.94877	

Table S7.(cont.) Elongation of the C-Br bond lengths (Δd, in Å)

A^-	R-Br	Dd	$C\text{-}Br_S$[a]	$C\text{-}Br_C$[b]			
N_3^-	$C_3Br_2F_6$	0.01999	1.925765	1.93794	1.93358		
NCO^-	CBr_4	0.02398	1.943008	1.9435	1.94993	1.95173	1.95085
NCO^-	CBr_3NO_2	0.03005	1.921727	1.94733	1.92634	1.92156	
NCO^-	CBr_3CONH_2	0.01575	1.944407	1.94741	1.96354	1.93802	
NCO^-	CBr_3F	0.01638	1.937003	1.93345	1.94831	1.94563	
NCO^-	CBr_3H	0.01338	1.93238	1.92795	1.94128	1.94129	
NCO^-	CBr_3CN	0.02934	1.942843	1.95504	1.95155	1.95128	
NCO^-	$C_3Br_2F_6$	0.00909	1.925765	1.92881	1.93181		
NCS^-	CBr_4	0.02105	1.943008	1.95274	1.94607	1.94628	1.94799
NCS^-	CBr_3NO_2	0.03059	1.921727	1.95294	1.92414	1.91869	
NCS^-	CBr_3CONH_2	0.01437	1.944407	1.94003	1.95646	1.9511	
NCS^-	CBr_3F	0.01601	1.937003	1.93993	1.94344	1.94365	
NCS^-	CBr_3H	0.01185	1.93238	1.93399	1.9375	1.9375	
NCS^-	CBr_3CN	0.02693	1.942843	1.9611	1.94555	1.94881	
NCS^-	$C_3Br_2F_6$	0.01225	1.925765	1.93322	1.93056		

a) Average C-Br bond length in the separate R-Br molecule (from ref. 10). b) C-Br bond length in the halogen-bonded R-Br molecules As in Table S6, only characteristics of the lowest-energy halogen-bonded complexes are listed. Note that Figure 10 demonstrates correlation between values of Δd from Table S7 and Δq from Table S6.

Table S8. Atomic coordinate resulted from M06-2X/6-311+G(dp) computations of the [R-Br,A^-] complexes in gas-phase and in dichloromethane (the coordinates of the lowest-energy halogen-bonded adducts are presented, i.e. C-Br….N≡C bonding in complexes with NCO^- and C-Br….S-C bonding in complexes with NCS, if not stated otherwise}.

Anion	R-Br	Gas-phase calculations			
N_3^-	CBr_4	Br	-1.26279000	-0.26503400	1.83233400
		Br	1.36132600	0.47035000	0.00275600
		Br	-1.66427700	1.42719900	-0.83150100
		Br	-0.92068500	-1.66047300	-1.00433500
		C	-0.60576100	-0.00552200	-0.00068800
		N	4.32011800	0.03604300	0.00138600
		N	3.66543000	1.03031400	0.01001600
		N	4.96581100	-0.92183000	-0.00708400
N_3^-	CBr_3NO_2	Br	-1.29796400	-0.14242800	0.44727700
		Br	1.40689600	-1.45477400	-0.95256000
		Br	1.24742900	1.69250400	-0.63103700
		C	0.75731400	-0.00533200	0.14676900
		N	-4.12243800	0.00864800	-0.24930700
		N	-3.56414000	-0.29890300	0.76102200
		N	-4.67508400	0.30191400	-1.21588200
		N	1.37927800	-0.11612900	1.54047900
		O	1.50014000	0.90606900	2.17342000
		O	1.60738200	-1.22760700	1.95613400
N_3^-	CBr_3CONH_2	Br	1.24931700	-0.16940600	0.33800400
		Br	-1.29043400	1.81560100	-0.05102300
		Br	-1.36605900	-1.07354500	-1.38944100
		C	-0.74560300	-0.03278700	0.16412400
		N	4.30333800	0.10949300	-0.13294100
		N	3.67053600	-0.47037300	0.68798400
		N	4.92943000	0.67089900	-0.92918900
		C	-1.48351700	-0.64650300	1.38444700
		O	-2.49915200	-0.17586800	1.83677100
		N	-0.91600100	-1.78830500	1.84834800
		H	-1.32680100	-2.18919500	2.67538000
		H	0.03479200	-2.02284800	1.60568300
N_3^-	CBr_3F	Br	1.15573700	-0.00013100	0.52030700
		Br	-1.55915900	1.60199900	-0.40056100
		Br	-1.55931700	-1.60186400	-0.40071000
		C	-0.82350700	-0.00001400	0.47731400
		N	4.06989000	0.00001800	-0.41968500
		N	3.60428200	-0.00018100	0.67275300
		N	4.53112400	0.00022500	-1.48224900
		F	-1.31112600	-0.00005100	1.73045900

N_3^-	CBr_3H	Br	1.07329500	-0.00110600	-0.55148200
		Br	-1.66932500	-1.60251900	0.22644700
		Br	-1.66767200	1.60366300	0.22521500
		C	-0.88457800	-0.00008800	-0.57607600
		N	4.08480400	-0.00001900	0.41546400
		N	3.60863100	-0.00256500	-0.66930900
		N	4.55910100	0.00251000	1.47557300
		H	-1.23068900	-0.00031300	-1.60191300
N_3^-	CBr_3CN	Br	1.22437900	-0.24943200	0.47538000
		Br	-1.28429600	1.73917400	-0.37827500
		Br	-1.60543900	-1.41990800	-0.80087900
		C	-0.82734700	-0.02479300	0.33102400
		N	4.04156500	0.01830300	-0.30447600
		N	3.52350700	-0.49976200	0.63727400
		N	4.55445600	0.51512700	-1.20938700
		C	-1.42619500	-0.14091800	1.64249000
		N	-1.86113700	-0.24080000	2.70387600
N_3^-	$C_3Br_2F_6$	C	1.68526200	-1.61621100	0.06505800
		C	0.82383100	-0.41260900	-0.35235100
		C	1.18833700	0.85315900	0.44291900
		F	1.33596400	-2.70246400	-0.62144200
		F	1.56603200	-1.88291800	1.36492000
		F	2.98790700	-1.40915000	-0.18579600
		F	1.15071200	-0.16988100	-1.65837500
		F	2.50967500	1.10624400	0.36099100
		F	0.90233400	0.69856300	1.73649600
		Br	-1.10061700	-0.86019400	-0.16612500
		Br	0.25557100	2.41792500	-0.23289000
		N	-3.51759700	-1.38371600	0.01891500
		N	-4.13112300	-0.38346500	0.19480600
		N	-4.73436400	0.59144300	0.36636600
NCO^-	CBr_4	Br	-1.58895300	-1.20517800	-1.22032900
		Br	-0.98965600	1.84695900	-0.57851500
		Br	-1.40139300	-0.22167100	1.79400600
		Br	1.30405600	-0.37662500	0.00463100
		C	-0.63610600	0.00547400	0.00118300
		N	3.67843100	-0.87296500	0.00906500
		C	4.58635400	-0.10483700	0.00034700
		O	5.52594800	0.64812100	-0.00817200

NCO^{-} [a]	CBr_4	Br	-1.60755900	-1.41689900	-0.91539100
		Br	-0.99110400	1.69632400	-0.91792900
		Br	-1.30331900	0.14290500	1.83099600
		Br	1.28908700	-0.37024900	0.00149400
		C	-0.61590100	0.00807400	-0.00031500
		O	3.73244400	-0.92482200	0.00389600
		C	4.58327200	-0.03125100	0.00129300
		N	5.39822100	0.81639700	-0.00114400

a) C-Br…O-C mode of bonding

NCO^{-}	CBr_3NO_2	Br	1.63958300	-1.58361900	-0.48349700
		Br	1.63977000	1.58354100	-0.48338400
		Br	-1.23190900	0.00011300	-0.33599000
		C	0.72585300	-0.00000900	0.15627900
		N	-3.48455600	0.00029000	-0.95287200
		C	-4.39440300	0.00004600	-0.18250600
		O	-5.33432100	-0.00019500	0.56140300
		N	0.77735200	-0.00006800	1.70261200
		O	0.74845900	-1.07326500	2.25111800
		O	0.74850600	1.07308800	2.25118900

NCO^{-}[a]	CBr_3NO_2	Br	1.84344200	-1.34982600	-0.61467600
		Br	1.18524700	1.74478000	-0.59753800
		Br	-1.19027500	-0.37390700	-0.06651700
		C	0.70842300	0.02367300	0.14546300
		C	-4.43319600	-0.06262100	-0.15344800
		N	0.97736800	0.06601700	1.68680000
		O	1.21151900	-0.98640600	2.22087800
		O	0.85434700	1.13076900	2.23118200
		O	-3.56606000	-0.91434000	-0.37796700
		N	-5.26227300	0.74210500	0.05759600

a) C-Br…O-C mode of bonding

NCO^{-}	CBr_3F	Br	-1.07059700	0.28980100	0.05866500
		Br	1.45585700	-1.73788000	-0.23894800
		Br	1.96320900	1.41878900	-0.25315300
		C	0.80768800	-0.01412100	0.44830000
		N	-3.51565900	0.70259400	-0.35503700
		F	1.01386400	-0.04176700	1.77725800
		C	-4.51989000	0.09634200	-0.17351600
		O	-5.55479500	-0.50130900	0.00144000

NCO^-	CBr_3H	Br	-1.00828400	0.04080400	-0.02032300
		Br	1.78515600	-1.62434700	-0.04287800
		Br	1.85372000	1.57681600	-0.02648700
		C	0.84093300	-0.00514100	0.52582900
		N	-3.53440000	0.13990800	-0.59358600
		H	0.90350700	-0.01223900	1.60617500
		C	-4.60491500	0.01891300	-0.09926200
		O	-5.70619300	-0.10179200	0.39107400
NCO^-	CBr_3CN	Br	1.15372900	-0.30118900	0.36703200
		Br	-1.28839800	1.76276300	-0.37083400
		Br	-1.73099900	-1.38637300	-0.75578500
		C	-0.83818700	-0.01434300	0.32733400
		C	-1.38980900	-0.10196700	1.66506600
		N	-1.79963300	-0.17833400	2.73737800
		C	4.29511900	-0.05614800	-0.18953700
		O	5.13537000	0.54252800	-0.80392600
		N	3.48716500	-0.66988200	0.43402100
NCO^-	$C_3Br_2F_6$	C	1.48675900	-1.80506600	0.02264200
		C	0.79639100	-0.47765200	-0.35621100
		C	1.38052400	0.70659200	0.44490700
		F	0.95702200	-2.81769600	-0.65766400
		F	1.37555300	-2.06373400	1.32427100
		F	2.79383000	-1.78345000	-0.27559600
		F	1.12562400	-0.26759200	-1.66732300
		F	2.72133700	0.73410300	0.33670200
		F	1.09708500	0.58417500	1.74181900
		Br	-1.13113300	-0.62660800	-0.11700400
		Br	0.71099700	2.41083000	-0.19702400
		C	-4.60511200	-0.14900900	0.14706200
		N	-3.64422800	-0.84465500	0.16267600
		O	-5.59638400	0.54292200	0.13524500
NCS^-	CBr_4	Br	1.38304700	-0.74416500	1.73237000
		Br	1.87682200	1.60948300	-0.34434600
		Br	1.25880300	-1.32809500	-1.38810000
		Br	-1.11474200	0.39859000	-0.00053900
		C	0.83474200	-0.01546900	-0.00035200
		S	-3.90322000	1.04085700	0.00083900
		N	-4.94558100	-1.59953600	0.00080900
		C	-4.51256900	-0.51960200	0.00075500

NCS^{-b}	CBr_4	Br	1.51583000	1.69233700	-0.86094300
		Br	1.68248200	0.03170400	1.83859900
		Br	-0.91496400	-0.22438000	-0.01882800
		Br	1.89552300	-1.45595800	-0.95492700
		C	1.00636500	0.00618100	-0.00121100
		S	-6.24074200	0.21179900	0.00851100
		N	-3.51389400	-0.52379100	-0.02756300
		C	-4.64158600	-0.21482300	-0.01208000

b) C-Br…N≡C mode of bonding

NCS^-	CBr_3NO_2	Br	-1.03737700	-0.38428000	0.24455200
		Br	1.80731000	-1.04250900	-1.27251900
		Br	1.33243800	1.85238800	-0.08370300
		C	0.97026500	-0.02659100	0.13921600
		N	1.53932100	-0.49662000	1.49254100
		O	1.56842700	0.31099600	2.38769000
		O	1.82621700	-1.66473500	1.58637500
		C	-4.23340100	0.50850100	-0.47054100
		S	-3.73969600	-0.85064600	0.37912600
		N	-4.58591500	1.44702800	-1.05856200
NCS^{-c}	CBr_3CONH_2	Br	1.48244800	1.18243700	-1.33178400
		Br	2.11864400	-1.37444500	0.45820200
		Br	-0.88576800	-0.72284000	-0.36276100
		C	0.82331400	0.04002700	0.12468000
		S	-4.32208500	-0.73178300	-0.39840200
		N	-3.25145600	1.47643500	1.00140900
		C	-3.72699900	0.57457500	0.42781400
		C	0.76915000	0.97615300	1.38234000
		O	1.78207400	1.15789200	2.02123200
		N	-0.40547600	1.57072600	1.61325000
		H	-0.42310100	2.20707300	2.39525500
		H	-1.31075000	1.38333600	1.16967800

c) Combined C-Br…S-C and N-H…N-C mode of bonding

NCS^{-d}	$CBr_3CONH_2{}^c$	Br	1.48244800	1.18243700	-1.33178400
		Br	2.11864400	-1.37444500	0.45820200
		Br	-0.88576800	-0.72284000	-0.36276100
		C	0.82331400	0.04002700	0.12468000
		S	-4.32208500	-0.73178300	-0.39840200
		N	-3.25145600	1.47643500	1.00140900
		C	-3.72699900	0.57457500	0.42781400
		C	0.76915000	0.97615300	1.38234000
		O	1.78207400	1.15789200	2.02123200
		N	-0.40547600	1.57072600	1.61325000
		H	-0.42310100	2.20707300	2.39525500
		H	-1.31075000	1.38333600	1.16967800

d) Combined C-Br…N-C and N-H…S-C mode of bonding

NCS^-	CBr_3F	Br	-0.87216200	-0.29510100	-0.02292500
		Br	2.17784100	-1.42288900	-0.04396800
		Br	1.66166200	1.71879200	-0.37564200
		C	0.99484300	0.06710600	0.44354100
		F	1.10781000	0.22355000	1.77060600
		C	-4.39075600	0.40822100	0.21470500
		S	-3.70985900	-0.87299300	-0.62237600
		N	-4.87056800	1.29656300	0.79454400
NCS^-	CBr_3H	Br	-0.81555300	0.00001100	-0.17346300
		Br	2.00042800	-1.59915600	0.01833900
		Br	2.00042500	1.59915100	0.01838600
		C	0.99796900	-0.00002100	0.51031300
		N	-4.59779700	-0.00011100	1.73730900
		H	0.96094600	-0.00003000	1.59181300
		S	-3.78975500	0.00006100	-0.98404100
		C	-4.26893700	-0.00004200	0.61927400
NCS^-	CBr_3CN	Br	0.95395200	-0.37784200	0.34057600
		Br	-1.45997600	1.80577600	-0.06359100
		Br	-1.92621500	-1.22306200	-0.99568800
		C	-1.05556100	-0.06413400	0.31892300
		N	4.46586700	1.43902200	-1.15276000
		C	-1.61030900	-0.38245200	1.61831500
		N	-2.02114900	-0.64442000	2.66059100
		C	4.14541700	0.51467800	-0.52457600
		S	3.69613100	-0.82133100	0.38273900
NCS^-	$C_3Br_2F_6$	C	1.97557400	-1.53753000	0.03544500
		C	1.03601200	-0.38286200	-0.37260200
		C	1.36190500	0.92585500	0.38323000
		F	1.72399000	-2.61483600	-0.70486100
		F	1.83848800	-1.86446800	1.31682100
		F	3.26080100	-1.21772800	-0.16630800
		F	1.29247500	-0.15190400	-1.69065600
		F	2.63571300	1.28562900	0.13900600
		F	1.25699000	0.72759500	1.70088500
		Br	-0.81895200	-0.91834000	-0.10597100
		Br	0.21637800	2.38715400	-0.14554900
		S	-3.80979400	-1.39911000	0.20953500
		C	-3.97068400	0.25966700	0.04758700
		N	-4.06373900	1.41541100	-0.06647200
N_3^-	-	N	0.00000000	0.00000000	1.17435200
		N	0.00000000	0.00000000	0.00000000
		N	0.00000000	0.00000000	-1.17435200

NCO^-	-	N	0.00000000	0.00000000	-1.25491400
		C	0.00000000	0.00000000	-0.07123100
		O	0.00000000	0.00000000	1.15147300
NCS^-	-	N	0.00000000	0.00000000	-1.80722400
		C	0.00000000	0.00000000	-0.63917700
		S	0.00000000	0.00000000	1.03035200

Anion	R-Br		Calculations in CH_2Cl_2		
N_3^-	CBr_4	Br	1.14745300	0.64551700	1.76716000
		Br	-1.25877100	-0.51693600	0.00508700
		Br	1.74013900	-1.52206100	-0.47399200
		Br	0.91710000	1.42944400	-1.29946000
		C	0.62735000	0.00639700	-0.00048500
		N	-4.42711900	-0.05930700	0.00214800
		N	-3.90031100	-1.11307300	0.00682200
		N	-4.93990600	0.98707700	-0.00252400
N_3^-	CBr_3NO_2	Br	-1.19515300	-0.26032700	0.42147500
		Br	1.46090300	-1.33260500	-1.06327800
		Br	1.14474500	1.76505400	-0.49508200
		C	0.74055900	-0.00876400	0.13005800
		N	-4.21364900	-0.00393600	-0.22515700
		N	-3.74625300	-0.54974900	0.71264800
		N	-4.66218400	0.53546500	-1.15141800
		N	1.37532200	-0.20254400	1.54485100
		O	1.45949000	0.77502800	2.24101600
		O	1.65509200	-1.32831900	1.86450600
N_3^-	CBr_3CONH_2	Br	0.91025003	-0.12725865	0.28899288
		Br	-1.62950097	1.85774835	-0.10003412
		Br	-1.70512597	-1.03139765	-1.43845212
		C	-1.08466997	0.00936035	0.11511288
		N	4.30333800	0.10949300	-0.13294100
		N	3.67053600	-0.47037300	0.68798400
		N	4.92943000	0.67089900	-0.92918900
		C	-1.82258397	-0.60435565	1.33543588
		O	-2.83821897	-0.13372065	1.78775988
		N	-1.25506797	-1.74615765	1.79933688
		H	-1.66586797	-2.14704765	2.62636888
		H	-0.30427497	-1.98070065	1.55667188

N_3^-	CBr_3F	Br	1.15573700	-0.00013100	0.52030700
		Br	-1.55915900	1.60199900	-0.40056100
		Br	-1.55931700	-1.60186400	-0.40071000
		C	-0.82350700	-0.00001400	0.47731400
		N	4.39597257	0.00001134	-0.39938315
		N	3.93036457	-0.00018766	0.69305485
		N	4.85720657	0.00021834	-1.46194715
		F	-1.31112600	-0.00005100	1.73045900
N_3^-	CBr_3H	Br	1.0733	-0.00111	-0.55148
		Br	-1.66933	-1.60252	0.22645
		Br	-1.66767	1.60366	0.22522
		C	-0.88458	-0.00009	-0.57608
		N	4.43635	-0.00022	0.39913
		N	3.96018	-0.00277	-0.68565
		N	4.91065	0.00231	1.45924
		H	-1.23069	-0.00031	-1.60191
N_3^-	CBr_3CN	Br	1.22437900	-0.24943200	0.47538000
		Br	-1.17617881	1.72733649	-0.37066806
		Br	-1.49732181	-1.43174551	-0.79327206
		C	-0.71922981	-0.03663051	0.33863094
		N	4.41010437	-0.02182372	-0.27852516
		N	3.89204637	-0.53988872	0.66322484
		N	4.92299537	0.47500028	-1.18343616
		C	-1.31807781	-0.15275551	1.65009694
		N	-1.75301981	-0.25263751	2.71148294
N_3^-	$C_3Br_2F_6$	C	1.68526200	-1.61621100	0.06505800
		C	0.82383100	-0.41260900	-0.35235100
		C	1.18833700	0.85315900	0.44291900
		F	1.33596400	-2.70246400	-0.62144200
		F	1.56603200	-1.88291800	1.36492000
		F	2.98790700	-1.40915000	-0.18579600
		F	1.15071200	-0.16988100	-1.65837500
		F	2.50967500	1.10624400	0.36099100
		F	0.90233400	0.69856300	1.73649600
		Br	-1.10061700	-0.86019400	-0.16612500
		Br	0.25557100	2.41792500	-0.23289000
		N	-3.97572208	-1.48294668	0.05398830
		N	-4.58924808	-0.48269568	0.22987930
		N	-5.19248908	0.49221232	0.40143930

NCO^-	CBr_4	Br	-1.56119600	-1.21262300	-1.24782500
		Br	-1.05392100	1.84395900	-0.55621600
		Br	-1.44062700	-0.26507100	1.77976600
		Br	1.22377000	-0.32012100	0.02103800
		C	-0.69142900	0.00973500	0.00060600
		N	3.92545300	-0.84225300	0.03460700
		C	4.86262900	-0.11864500	0.00663900
		O	5.82671500	0.61677400	-0.02155400
NCO^- [a]	CBr_4	Br	-1.64583500	-1.31335700	-1.02620600
		Br	-0.92727100	1.77038500	-0.78983900
		Br	-1.31052100	0.02305300	1.83206900
		Br	1.24078400	-0.42779900	-0.01472100
		C	-0.64905400	0.01249100	-0.00273300
		O	3.91882200	-1.02424300	-0.00587200
		C	4.63304900	-0.03253900	-0.00104700
		N	5.32070600	0.92633900	0.00343800

a) C-Br…O-C mode of bonding

NCO^-	CBr_3NO_2	Br	-1.40777300	1.66790400	-0.63029000
		Br	-1.83827000	-1.46403200	-0.42247000
		Br	1.13044700	-0.27063200	-0.23782100
		C	-0.75796400	0.02399600	0.13528400
		N	3.72371600	-0.69564500	-0.74928100
		C	4.60382100	-0.13290200	-0.18892200
		O	5.50856000	0.43726100	0.37858100
		N	-0.83876600	0.15933800	1.69858400
		O	-0.52795400	1.22856000	2.15268700
		O	-1.13359600	-0.82280000	2.32461200
NCO^{-a}	CBr_3NO_2	Br	1.81041600	-1.47486800	-0.39354800
		Br	1.38858300	1.65365000	-0.66179000
		Br	-1.14088200	-0.27016800	-0.23194200
		C	0.73640300	0.02543800	0.13448200
		C	-4.58331400	-0.07739100	-0.12466500
		N	0.81794900	0.19749500	1.69888800
		O	0.46953500	1.26522800	2.12601400
		O	1.15821700	-0.75597600	2.34411000
		O	-3.74240600	-0.70518400	-0.75298700
		N	-5.39443600	0.52789200	0.48093900

a) C-Br…O-C mode of bonding

NCO^-	CBr_3CONH_2	Br	1.13064800	-0.22134700	0.27109100
		Br	-1.26688800	1.84096500	-0.05734300
		Br	-1.49606800	-1.05437200	-1.35898600
		C	-0.80422600	-0.02781700	0.16515800
		N	3.90109800	-0.60828800	0.52230100
		C	-1.54827100	-0.60177000	1.41311700
		O	-2.57528400	-0.09286200	1.80110200
		N	-0.99917500	-1.70509700	1.94214100
		H	-1.47695400	-2.15061300	2.71087700
		H	-0.11587700	-2.08050600	1.63531100
		O	5.59053700	0.63850000	-0.63587500
		C	4.73385300	0.00893700	-0.05090100
NCO^-	CBr_3F	Br	1.01867000	-0.29916400	0.02863500
		Br	-1.45313800	1.73781900	-0.24623500
		Br	-1.98225400	-1.41110000	-0.22211400
		C	-0.84255200	0.02314200	0.44117200
		N	3.70409400	-0.77608700	-0.47319500
		F	-0.98988400	0.05914800	1.77625800
		C	4.63836400	-0.11433800	-0.17061200
		O	5.59883700	0.56037900	0.13658900
NCO^-	CBr_3H	Br	-0.96643600	-0.00005400	-0.05710300
		Br	1.81996900	-1.59829100	-0.01966200
		Br	1.81989200	1.59833000	-0.02016900
		C	0.86823700	0.00007800	0.53531300
		N	-3.75537800	-0.00014100	-0.83477900
		H	0.87687000	0.00025600	1.61698000
		C	-4.69123900	0.00000200	-0.10979400
		O	-5.65263300	0.00009400	0.63325700
NCO^-	CBr_3CN	Br	1.07465800	-0.26790300	0.40677100
		Br	-1.31338900	1.75256600	-0.36989200
		Br	-1.69368000	-1.39815500	-0.78812600
		C	-0.86221400	-0.01885100	0.31354600
		C	-1.41989400	-0.12949100	1.65101700
		N	-1.84835600	-0.22040800	2.71311200
		C	4.44767100	-0.06013200	-0.17298600
		O	5.17577800	0.53821000	-0.93303500
		N	3.73904000	-0.64853600	0.57381200

NCO^-	$C_3Br_2F_6$	C	1.51989500	-1.80852600	0.03248600
		C	0.83423700	-0.47482100	-0.35757900
		C	1.39013000	0.72243300	0.45628500
		F	0.98747600	-2.81383600	-0.65503700
		F	1.38513300	-2.05938400	1.33072900
		F	2.82058400	-1.77534400	-0.25593700
		F	1.15645600	-0.26635800	-1.66080700
		F	2.72801600	0.73580600	0.37226600
		F	1.07186700	0.58573900	1.74458200
		Br	-1.07543100	-0.63511900	-0.13902400
		Br	0.72821500	2.41440900	-0.20020300
		C	-4.78500400	-0.16071600	0.15271100
		N	-3.83013000	-0.86035700	0.16071900
		O	-5.76723200	0.55219100	0.14529000
NCS^-	CBr_4	Br	-1.32606500	-1.04541700	-1.58470200
		Br	-1.89451300	1.64386700	-0.00066300
		Br	-1.32555200	-1.04384200	1.58588600
		Br	1.04004200	0.39879000	-0.00050400
		C	-0.86894200	-0.01229300	-0.00012000
		S	4.15826800	1.05602600	0.00002100
		N	4.85443500	-1.69041900	-0.00007900
		C	4.56890300	-0.55977400	0.00005600
NCS^-	CBr_4	Br	1.51237900	1.72356600	-0.81325800
		Br	1.71161800	-0.01193600	1.83686900
		Br	-0.85962100	-0.24720700	-0.02198600
		Br	1.93876500	-1.41626300	-0.99818200
		C	1.06083300	0.00887300	-0.00145400
		S	-6.39789400	0.22815500	0.00924000
		N	-3.68363600	-0.56676000	-0.02707800
		C	-4.80386200	-0.23700500	-0.01167600
NCS^-	CBr_3NO_2	Br	-0.94148200	-0.43761900	0.21198200
		Br	1.86292500	-1.02653800	-1.24396600
		Br	1.26958700	1.85805300	-0.08451800
		C	0.96546000	-0.02402900	0.13148200
		N	1.53206900	-0.48958500	1.51967000
		O	1.67099300	0.34800300	2.36891600
		O	1.72098700	-1.67085700	1.64202400
		C	-4.23255700	0.59255900	-0.40766500
		S	-4.02062700	-0.92163100	0.25832900
		N	-4.37339500	1.65121100	-0.87482700

NCS^-	CBr_3CONH_2	Br	1.37304900	-1.74745900	-0.52982900
		Br	1.51538000	0.53030300	1.69403900
		Br	-0.93621200	0.41705400	-0.35080700
		C	0.96944900	0.12113400	-0.13961700
		S	-4.21221800	0.72346900	-0.52304600
		N	-4.26795400	-1.58837900	1.11294500
		C	-4.24832100	-0.63626000	0.43917600
		C	1.76541900	1.12453600	-1.03364600
		O	1.31107400	2.22909200	-1.22471600
		N	2.95730500	0.70352800	-1.48098000
		H	3.52538500	1.35991800	-1.99515200
		H	3.30917600	-0.22706700	-1.32672900
NCS^{-b}	CBr_3CONH_2	Br	1.53090600	-0.57234700	1.69348900
		Br	1.28244200	1.82802500	-0.39063700
		Br	-0.81912600	-0.54532900	-0.45925500
		C	1.03018200	-0.09328700	-0.13584500
		N	-3.66553100	-1.29460000	-0.86388500
		S	-4.94540700	0.78947400	0.55807200
		C	-4.19924900	-0.43585200	-0.27748000
		C	1.96353400	-0.94184200	-1.05898200
		O	1.59309600	-2.02713400	-1.44095900
		N	3.17154500	-0.41676400	-1.31315600
		H	3.82397100	-0.97284400	-1.84506700
		H	3.45112500	0.50155400	-1.00917000

b) C-Br…N≡C mode of bonding

NCS^{-c}	CBr_3CONH_2	Br	1.62787200	1.12194000	-1.32238100
		Br	2.01579500	-1.44153700	0.54002500
		Br	-0.88044200	-0.62622200	-0.44665300
		C	0.84755800	0.05079800	0.11720200
		S	-4.42383900	-0.68713800	-0.42758600
		N	-3.33151700	1.44439800	1.07204700
		C	-3.80497300	0.57074200	0.45665100
		C	0.79892000	1.00385600	1.35834600
		O	1.83804000	1.23866700	1.93892100
		N	-0.38419200	1.54247300	1.65740200
		H	-0.39686200	2.19561700	2.42781300
		H	-1.27797500	1.33245000	1.21816300

c) Combined C-Br…S-C/N-H….N-C mode of bonding

NCS^{-d}	CBr_3CONH_2 [c]	Br	0.57678800	1.58593600	-0.99087700
		Br	2.59451900	-0.69668500	-0.09270000
		Br	-0.50554300	-1.33756400	-0.29464800
		C	0.81463600	0.01802700	0.15331000
		N	-3.99816200	-1.73428300	-0.32528500
		S	-3.56083200	1.01089000	0.21844700
		C	-3.82271200	-0.60323300	-0.10248200
		C	0.62279900	0.49093700	1.63574700
		O	1.57132300	0.53351400	2.38707900
		N	-0.62709300	0.84966600	1.94565700
		H	-0.79082600	1.19424800	2.88011400
		H	-1.41975400	0.81228000	1.30389800

d) Combined C-Br…N-C/N-H….S-C mode of bonding

NCS^-	CBr_3F	Br	-0.75093977	-0.27041431	0.00268266
		Br	2.29906323	-1.39820231	-0.01836034
		Br	1.78288423	1.74347869	-0.35003434
		C	1.11606523	0.09179269	0.46914866
		F	1.22903223	0.24823669	1.79621366
		C	-4.51197823	0.38353431	0.18909734
		S	-3.83108123	-0.89767969	-0.64798366
		N	-4.99179023	1.27187631	0.76893634

NCS^-	CBr_3H	Br	-0.720146	-0.000069	-0.127855
		Br	2.058585	-1.597437	0.058417
		Br	2.058121	1.598031	0.059813
		C	1.085745	-0.000064	0.564287
		N	-4.547435	0.000947	1.703862
		H	1.026194	-0.000576	1.644370
		S	-3.909487	-0.001100	-1.056031
		C	-4.286641	0.000126	0.566615

NCS^-	CBr_3CN	Br	0.95395200	-0.37784200	0.34057600
		Br	-1.36713821	1.79128296	-0.06259065
		Br	-1.83337721	-1.23755504	-0.99468765
		C	-0.96272321	-0.07862704	0.31992335
		N	4.72434829	1.39721816	-1.14878566
		C	-1.51747121	-0.39694504	1.61931535
		N	-1.92831121	-0.65891304	2.66159135
		C	4.40389829	0.47287416	-0.52060166
		S	3.95461229	-0.86313484	0.38671334

NCS^-	$C_3Br_2F_6$	C	1.97557400	-1.53753000	0.03544500
		C	1.03601200	-0.38286200	-0.37260200
		C	1.36190500	0.92585500	0.38323000
		F	1.72399000	-2.61483600	-0.70486100
		F	1.83848800	-1.86446800	1.31682100
		F	3.26080100	-1.21772800	-0.16630800
		F	1.29247500	-0.15190400	-1.69065600
		F	2.63571300	1.28562900	0.13900600
		F	1.25699000	0.72759500	1.70088500
		Br	-0.81895200	-0.91834000	-0.10597100
		Br	0.21637800	2.38715400	-0.14554900
		S	-4.24617804	-1.46925759	0.25556946
		C	-4.40706804	0.18951941	0.09362146
		N	-4.50012304	1.34526341	-0.02043754
N_3^-	-	N	0.00000000	0.00000000	1.17221000
		N	0.00000000	0.00000000	0.00000000
		N	0.00000000	0.00000000	-1.17221000
NCO^-	-	N	0.00000000	0.00000000	-1.25230900
		C	0.00000000	0.00000000	-0.06965400
		O	0.00000000	0.00000000	1.14801100
NCS^-	-	N	0.00000000	0.00000000	-1.80408300
		C	0.00000000	0.00000000	-0.63663200
		S	0.00000000	0.00000000	1.02802300

Table S9. Results of the CSD (version 5.35, Nov. 2013) search for the structures containing non-covalent intermolecular contacts shorter than sum of the corresponding van der Waals radii and involving covalently-bonded chlorine, bromine or iodine atom and azide anions R-X…N_3 (where X= Cl, Br, or I and R = Cl, Br, I or C).[a]

Refcode	Contact	X…N, Å	Compound name
RIHQAC	Br…N	3.187	bis((μ-azido)-(N-(5-bromo-2-(hydroxy)benzylidene)pyridine-4-carbohydrazonato)-methanol-manganese)
CAPVOF	Cl…N	3.150	bis(μ–Azido-N,N')-bis(azido-(4,5-dichloro-1,2-bis(2-pyridinecarboxamido)benzene))-(meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane)-copper(ii)-di-iron(iii) dihydrate
CESTAW	Cl…N	3.277	bis(μ–acetato)-tetrakis(μ–azido)-bis(μ–4-chloro-2-((2-dimethylaminoethylimino)methyl)phenolato-N,N',O,O)-tetra-copper(ii)
EFISAO	Br…N	3.035	catena-(bis(μ-Azido-N,N)-bis(μ–azido-N,N')-bis(4-bromopyridine-N)-di-copper(ii))
	Br…N	3.221	
EHEWOE	Cl…N	3.230	catena-((μ–Azido-N,N)-(μ–2-chloropyridine-3-carboxylato)-(μ–methanol)-copper(ii) methanol solvate)
EPAKAI	Cl…N	3.129	azido-(4-chloro-2-(((2-(morpholin-4-yl)ethyl)imino)methyl)phenolato-N,N',O)-(4-chloro-2-(((2-(morpholin-4-yl)ethyl)imino)methyl)phenolato-N,O)-cobalt(iii) methanol solvate
FOXTUI	Br…N	3.269	bis(μ–Azido-N,N)-bis(2,4-dibromo-6-((3-(cyclohexylamino)propylimino)-methyl)phenolato-N,N',O)-di-copper(ii)
GITLIE	Cl…N	3.037	catena-(pentakis(μ–Azido-N,N)-(μ–azido-N,N')-hexakis(3-chloropyridyl)-tri-copper)
	Cl…N	3.268	catena-(pentakis(μ–Azido-N,N)-(μ–azido-N,N')-hexakis(3-chloropyridyl)-tri-copper)
JUVZEF	Br…N	3.226	catena(bis(μ–Azido-N,N)-(2-bromopyridinato)-copper(ii))
MILROP	Cl…N	3.274	catena-(bis(μ–Azido-N,N'')-(μ–3,5-bis(bis(2-(ethylthio)ethyl)aminomethyl)-pyrazolato)-di-nickel(ii) perchlorate dichloromethane solvate)
NEHJAL	Cl…N	3.284	trans-Diazido-bis(2-chloropyridyl)-palladium(ii)
NODCOZ	Br…N	3.076	catena-(bis(μ–azido-N,N)-(3-bromopyridine)-zinc(ii))
PUCWUF	Cl…N	3.287	bis((μ–Azido)-(azido)-(cyclohexylimido))-tetrapyridyl-di-titanium(iv) dichloromethane solvate
RETCAV	Br…N	3.348	catena-((μ–azido)-(4,4'-bromo-N,N'-ethylene-bis(salicylideneaminato))-manganese(iii))
RIXSOG	Cl…N	3.06	(μ–Oxo)-(μ–bis(1,3,5-trimethyl-1,3-cyclohexanedicarboximide-5-carboxylato)-N,N'-4,6-dimethyl-m-phenylene)-bis(azido-(2,2'-bipyridyl)-iron) 1,3,5-trimethylbenzene dichloromethane solvate
SILKOO	Cl…N	3.099	azido(N,N'-bis(3-(2-nitrophenyl)prop-2-enylidene)ethylenediamine)-(triphenylphosphine)copper(i) chloroform solvate
TEKKUR	Br…N	3.381	tris(tetramethylammonium) (μ–oxo)-tris(μ–2,4-dibromo-6-[(oxidoimino)-methyl]phenolato)-hexakis(μ–azido)-dichloro-tri-manganese(iii)-di-zinc(ii)
	Br…N	3.055	
	Br…N	3.159	
	Br…N	3.058	

a) Note that the sum of the van der Waals radii are 3.30Å for Cl…N contact and 3.40Å for Br…N contact (A. Bondi, *J. Phys. Chem.* 1964, **68**, 441).

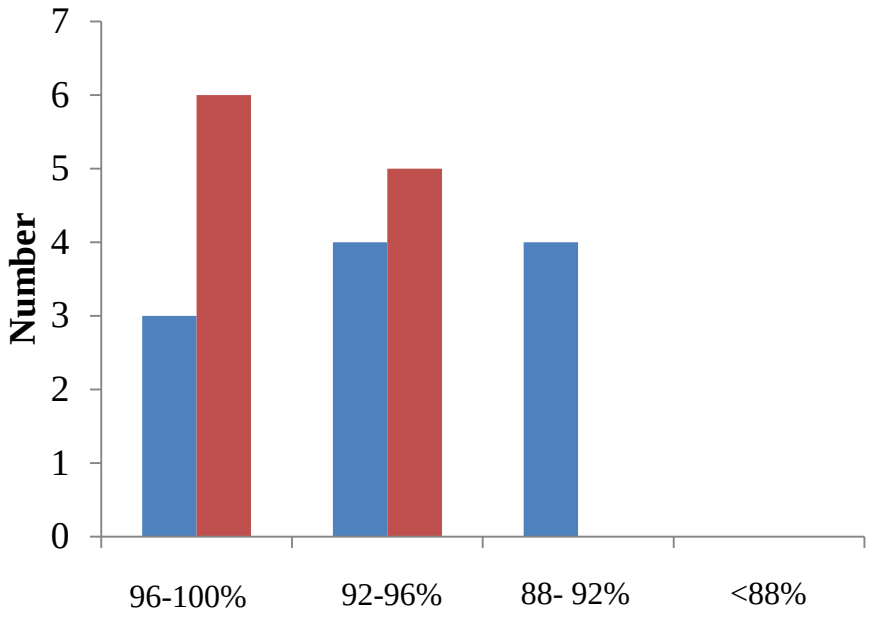


Figure S8. Numbers of crystallographically independent intermolecular contacts involving covalently-bonded chlorine or bromine atoms and azide anions R-X…N_3 (X= Br, blue and X= Cl, red) which are in the 96 -100% , 92 -96% , 88-92% and less than 88% range of the corresponding sums of the van der Waals radii (CSD version 5.35). Note that all these contacts involve coordinated azide anions, see Table S9 above for the details.