Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Chlorotellurate(IV) supramolecular associates with "trapped" Br_2: features of non-covalent halogen···halogen interactions in crystalline phases

Andrey N. Usoltsev, Sergey A. Adonin, Alexander S. Novikov, Pavel A. Abramov, Maxim N. Sokolov and Vladimir P. Fedin

Table 1. Selected geometric parameters in 1-4 (Å).

1			
Cl1—Te1	2.511 (2)	Cl5—Te1	2.4246 (18)
Cl2—Te1	2.6857 (18)	Cl6—Te1	2.6578 (19)
Cl3—Te1	2.4316 (19)	Br1—Br2	2.3137 (8)
Cl4—Te1	2.5277 (19)		
2			
Cl1—Te1	2.6277 (8)	Cl3—Te1	2.4571 (7)
Cl2—Te1	2.5272 (7)	Br1—Br1^{i}	2.3096 (6)
3			
Cl1—Te1	2.8178 (11)	Br1—Br1^{ii}	2.3235 (9)
Cl2—Te1	2.5786 (12)	Br2—Br2^{iii}	2.317 (3)
Cl3—Te1	2.3787 (11)	Br2—Br3	1.0297 (19)

Cl4—Te1	2.4877 (12)	Br2—Br3^{iii}	2.0721 (19)
Cl5—Te1	2.5140 (11)	Br3—Br3^{iii}	2.3109 (15)
Cl6—Te1	2.5236 (11)		
4			
Te1—Cl1	2.5656 (16)	Te1—Cl4	2.5506 (11)
Te1—Cl2^{iv}	2.5306 (9)	Te1—Cl4^{iv}	2.5506 (11)
Te1—Cl2	2.5306 (9)	Br1—Br1^{v}	2.3110 (9)
Te1—Cl3	2.4755 (16)		

Symmetry code(s): (i) -*x*+3/2, -*y*+3/2, -*z*+1; (ii) -*x*+1, -*y*+1, -*z*+1; (iii) -*x*+2, -*y*+1, -*z*; (iv) -*y*+1, -*x*+1, -*z*+1/2; (v) -*y*, -*x*, -*z*+1/2.

Table S2. Cartesian atomic coordinates for model structures.

Atom	X	Y	Z
1			
Cl	4.797105	2.310847	7.888313
Cl	5.939216	3.978663	4.781517
Cl	5.491234	0.417889	5.017113
Cl	8.732249	1.665803	4.807820
Cl	7.530333	0.174440	7.800594
Cl	8.133776	3.631030	7.946457

Te	6.771023	1.980178	6.371160
Br	4.463912	6.256156	3.680181
Br	3.523838	8.105984	2.656748
Cl	-0.810931	12.066053	1.595685
Cl	0.331180	10.398237	-1.511112
Cl	-0.116801	13.959011	-1.275516
Cl	3.124213	12.711097	-1.484809
Cl	1.922298	14.202460	1.507965
Cl	2.525740	10.745870	1.653829
Te	1.162987	12.396722	0.078532
2			
Cl	8.419886	3.737476	4.594898
Cl	9.362832	1.855806	1.626473
Cl	6.291282	0.111292	1.735836
Te	7.325099	1.857599	3.121110
Cl	6.230311	3.737476	1.647322
Cl	5.287365	1.855806	4.615747
Cl	8.358915	0.111292	4.506383

Br	9.921498	6.202979	5.700145
Br	10.963246	7.956271	6.784294
Cl	12.464858	10.421774	7.889541
Cl	11.521912	12.303444	10.857966
Cl	14.593462	14.047958	10.748602
Te	13.559646	12.301651	9.363329
Cl	14.654433	10.421774	10.837117
Cl	15.597379	12.303444	7.868692
Cl	12.525829	14.047958	7.978056
4			
Te	3.307846	5.905954	6.273675
Cl	5.122044	4.091756	6.273675
Cl	3.916418	6.460072	8.666706
Cl	1.599608	4.227199	7.150735
Cl	1.557409	7.656391	6.273675
Cl	2.753728	5.297382	3.880644
Cl	4.986601	7.614192	5.396615
Br	-0.726785	2.301054	6.583595

Br	-2.301054	0.726785	5.963755
Te	-5.905954	-3.307846	6.273675
Cl	-4.091756	-5.122044	6.273675
Cl	-5.297382	-2.753728	8.666706
Cl	-7.614192	-4.986601	7.150735
Cl	-7.656391	-1.557409	6.273675
Cl	-6.460072	-3.916418	3.880644
Cl	-4.227199	-1.599608	5.396615
Optimized equilibrium structure of $[TeCl_6]^{2-}$			
Cl	1.429940	-1.508489	1.599563
Cl	-0.918103	-2.144213	-1.200015
Cl	-1.999484	-0.094464	1.694828
Cl	-1.430027	1.508675	-1.599292
Cl	0.918019	2.144414	1.199585
Cl	1.999579	0.094218	-1.694610
Te	0.000025	-0.000046	-0.000019
Optimized equilibrium structure of $[TeBr_6]^{2-}$			

Br	-1.390395	-1.360964	-2.016386
Br	-2.291990	1.513175	0.558470
Br	-0.817905	-1.926522	1.863182
Br	1.390621	1.360904	2.016680
Br	2.291734	-1.513259	-0.558536
Br	0.817932	1.926414	-1.863331
Te	0.000002	0.000170	-0.000053
1_big			
C	5.582217	3.569305	1.203151
H	5.688210	4.513292	1.444360
H	4.696515	3.257882	1.483600
H	5.671124	3.468887	0.231934
C	7.989525	3.221384	1.496387
H	8.101315	3.129295	0.526731
H	8.660452	2.675014	1.955736
H	8.101964	4.160608	1.750433
C	6.454341	1.317883	1.648669

H	5.596875	1.027891	2.024112
H	7.183414	0.826432	2.082457
H	6.467278	1.138497	0.685733
N	6.628794	2.763240	1.882754
H	6.532462	2.919076	2.865373
C	8.018884	1.848869	11.212205
H	8.057610	1.795982	12.189589
H	8.857639	2.223713	10.871245
H	7.887286	0.951492	10.840927
C	5.596251	2.148867	11.265063
H	5.488997	1.249573	10.891180
H	4.858138	2.718547	10.963344
H	5.590944	2.098625	12.243882
C	7.059217	4.111793	11.312887
H	6.346241	4.681972	10.956309
H	7.929289	4.457280	11.023552
H	7.017261	4.110212	12.291932

N	6.883288	2.723943	10.806960
H	6.865353	2.761505	9.807904
Cl	4.797105	2.310847	7.888313
Cl	5.939216	3.978663	4.781517
Cl	5.491234	0.417889	5.017113
Cl	8.732249	1.665803	4.807820
Cl	7.530333	0.174440	7.800594
Cl	8.133776	3.631030	7.946457
Te	6.771023	1.980178	6.371160
Br	4.463912	6.256156	3.680181
Br	3.523838	8.105984	2.656748
Cl	-0.810931	12.066053	1.595685
Cl	0.331180	10.398237	-1.511112
Cl	-0.116801	13.959011	-1.275516
Cl	3.124213	12.711097	-1.484809
Cl	1.922298	14.202460	1.507965
Cl	2.525740	10.745870	1.653829

Te	1.162987	12.396722	0.078532
C	2.410848	12.528031	4.919577
H	2.449574	12.580918	5.896960
H	3.249603	12.153187	4.578617
H	2.279250	13.425408	4.548299
C	-0.011785	12.228033	4.972435
H	-0.119039	13.127327	4.598552
H	-0.749897	11.658353	4.670716
H	-0.017092	12.278275	5.951253
C	1.451181	10.265107	5.020259
H	0.738205	9.694928	4.663681
H	2.321253	9.919620	4.730924
H	1.409225	10.266688	5.999304
N	1.275253	11.652957	4.514332
H	1.257317	11.615395	3.515276
C	-0.025819	10.807595	-5.089478
H	0.080174	9.863608	-4.848269

H	-0.911521	11.119018	-4.809028
H	0.063088	10.908013	-6.060695
C	2.381489	11.155516	-4.796241
H	2.493279	11.247605	-5.765898
H	3.052416	11.701886	-4.336892
H	2.493928	10.216292	-4.542195
C	0.846306	13.059018	-4.643960
H	-0.011161	13.349009	-4.268516
H	1.575378	13.550468	-4.210171
H	0.859243	13.238403	-5.606895
N	1.020758	11.613660	-4.409874
H	0.924426	11.457824	-3.427255
2_big			
Cl	8.419886	3.737476	4.594898
Cl	9.362832	1.855806	1.626473
Cl	6.291282	0.111292	1.735836
Te	7.325099	1.857599	3.121110

Cl	6.230311	3.737476	1.647322
Cl	5.287365	1.855806	4.615747
Cl	8.358915	0.111292	4.506383
Br	9.921498	6.202979	5.700145
Br	10.963246	7.956271	6.784294
C	3.995384	-3.974030	4.317119
H	3.573332	-4.804422	4.130913
C	3.257876	-2.829962	4.443212
H	2.311923	-2.849898	4.355109
C	3.901485	-1.675511	4.696646
H	3.403013	-0.871681	4.783825
C	5.208980	-1.639641	4.822739
H	5.640924	-0.811410	4.998507
C	5.918937	-2.720464	4.712876
H	6.862134	-2.674663	4.811852
N	5.335484	-3.902289	4.460690
H	5.826791	-4.629036	4.388767

C	3.995384	5.465471	4.317119
H	3.573332	4.635078	4.130913
C	3.257876	6.609538	4.443212
H	2.311923	6.589602	4.355109
C	3.901485	7.763989	4.696646
H	3.403013	8.567819	4.783825
C	5.208980	7.799859	4.822739
H	5.640924	8.628090	4.998507
C	5.918937	6.719036	4.712876
H	6.862134	6.764837	4.811852
N	5.335484	5.537211	4.460690
H	5.826791	4.810464	4.388767
Cl	12.464858	10.421774	7.889541
Cl	11.521912	12.303444	10.857966
Cl	14.593462	14.047958	10.748602
Te	13.559646	12.301651	9.363329
Cl	14.654433	10.421774	10.837117

Cl	15.597379	12.303444	7.868692
Cl	12.525829	14.047958	7.978056
C	16.889360	8.693780	8.167320
H	17.311412	9.524172	8.353525
C	17.626868	7.549712	8.041227
H	18.572821	7.569648	8.129330
C	16.983259	6.395261	7.787793
H	17.481731	5.591431	7.700614
C	15.675764	6.359391	7.661700
H	15.243820	5.531160	7.485931
C	14.965807	7.440214	7.771563
H	14.022610	7.394413	7.672586
N	15.549260	8.622039	8.023749
H	15.057953	9.348786	8.095671
C	16.889360	18.133280	8.167320
H	17.311412	18.963672	8.353525
C	17.626868	16.989212	8.041227

H	18.572821	17.009148	8.129330
C	16.983259	15.834761	7.787793
H	17.481731	15.030931	7.700614
C	15.675764	15.798891	7.661700
H	15.243820	14.970660	7.485931
C	14.965807	16.879714	7.771563
H	14.022610	16.833913	7.672586
N	15.549260	18.061539	8.023749
H	15.057953	18.788286	8.095671
4_big			
Te	3.307846	5.905954	6.273675
Cl	5.122044	4.091756	6.273675
Cl	3.916418	6.460072	8.666706
Cl	1.599608	4.227199	7.150735
Cl	1.557409	7.656391	6.273675
Cl	2.753728	5.297382	3.880644
Cl	4.986601	7.614192	5.396615

C	1.242020	5.543022	10.898126
H	2.119460	5.913463	10.668836
H	1.277254	4.564535	10.848188
H	0.999780	5.814691	11.807985
N	0.233109	6.046096	9.950299
C	-0.698406	5.198426	9.469485
H	-0.682079	4.286149	9.735012
C	-1.672305	6.949969	8.219267
H	-2.337569	7.266731	7.618876
C	-1.664012	5.630553	8.606227
H	-2.321177	5.027731	8.277688
C	0.244166	7.326814	9.583917
H	0.910766	7.912037	9.924552
C	-0.718676	7.807774	8.702340
H	-0.715433	8.720373	8.438545
Br	-0.726785	2.301054	6.583595
Br	-2.301054	0.726785	5.963755

C	3.364880	10.149922	7.922899
H	2.487440	10.520363	8.152189
H	3.329646	9.171435	7.972837
H	3.607120	10.421591	7.013040
N	4.373791	10.652996	8.870726
C	5.305306	9.805326	9.351540
H	5.288979	8.893049	9.086013
C	6.279205	11.556869	10.601758
H	6.944469	11.873631	11.202149
C	6.270912	10.237453	10.214798
H	6.928077	9.634631	10.543337
C	4.362734	11.933714	9.237108
H	3.696134	12.518937	8.896473
C	5.325576	12.414674	10.118685
H	5.322333	13.327273	10.382480
Te	-5.905954	-3.307846	6.273675
Cl	-4.091756	-5.122044	6.273675

Cl	-5.297382	-2.753728	8.666706
Cl	-7.614192	-4.986601	7.150735
Cl	-7.656391	-1.557409	6.273675
Cl	-6.460072	-3.916418	3.880644
Cl	-4.227199	-1.599608	5.396615
C	-10.149922	-3.364880	4.624451
H	-10.520363	-2.487440	4.395161
H	-9.171435	-3.329646	4.574513
H	-10.421591	-3.607120	5.534310
N	-10.652996	-4.373791	3.676624
C	-9.805326	-5.305306	3.195810
H	-8.893049	-5.288979	3.461337
C	-11.556869	-6.279205	1.945592
H	-11.873631	-6.944469	1.345201
C	-10.237453	-6.270912	2.332552
H	-9.634631	-6.928077	2.004013
C	-11.933714	-4.362734	3.310242

H	-12.518937	-3.696134	3.650877
C	-12.414674	-5.325576	2.428665
H	-13.327273	-5.322333	2.164870
C	-5.543022	-1.242020	1.649224
H	-5.913463	-2.119460	1.878514
H	-4.564535	-1.277254	1.699162
H	-5.814691	-0.999780	0.739365
N	-6.046096	-0.233109	2.597051
C	-5.198426	0.698406	3.077865
H	-4.286149	0.682079	2.812338
C	-6.949969	1.672305	4.328083
H	-7.266731	2.337569	4.928474
C	-5.630553	1.664012	3.941123
H	-5.027731	2.321177	4.269662
C	-7.326814	-0.244166	2.963433
H	-7.912037	-0.910766	2.622798
C	-7.807774	0.718676	3.845010

H	-8.720373	0.715433	4.108805

Table S3. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$ and appropriate λ_2 eigenvalues (with promolecular approximation), energy density – H_b, potential energy density – V(**r**), and Lagrangian kinetic energy – G(**r**) (a.u.) at the bond critical points (3, –1), corresponding to Te–Cl and Br–Br bonds in **1**, **2**, and **4**.

Bond	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	λ_2	H_b	V(**r**)	G(**r**)
1						
Te–Cl	0.051	0.069	-0.055	-0.010	-0.037	0.027
Br–Br	0.078	0.112	-0.097	-0.013	-0.054	0.041
2						
Te–Cl	0.054	0.071	-0.058	-0.011	-0.040	0.029
Br–Br	0.078	0.109	-0.098	-0.013	-0.054	0.041
4						
Te–Cl	0.061	0.077	-0.066	-0.015	-0.049	0.034
Br–Br	0.078	0.109	-0.098	-0.013	-0.053	0.040

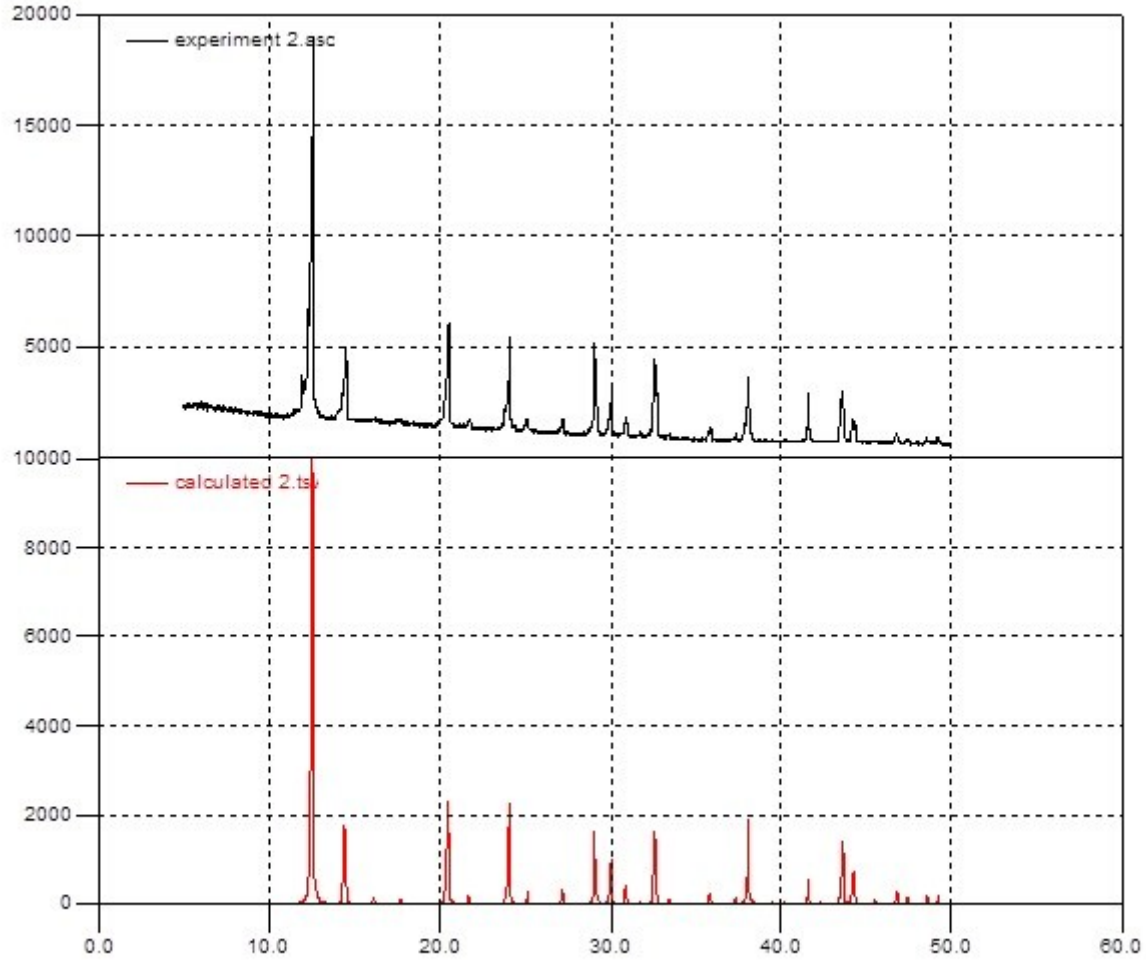

Figure S1. PXRD data for decomposition product of **1** (top) and calculated pattern for $(Me_3NH)_2[TeCl_6]$ (bottom)

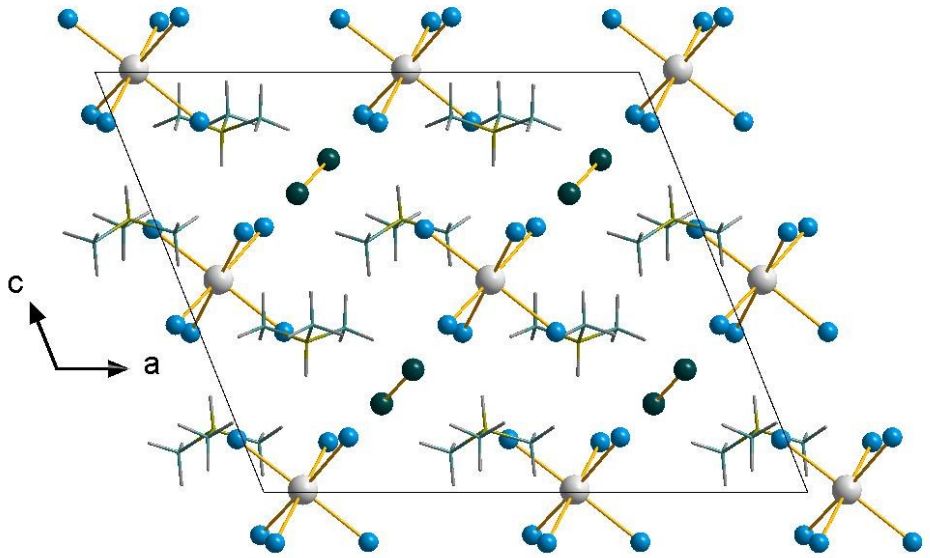

Figure S2. Crystal packing is the structure of **1.** Cations are shown in wire-and-stick representation

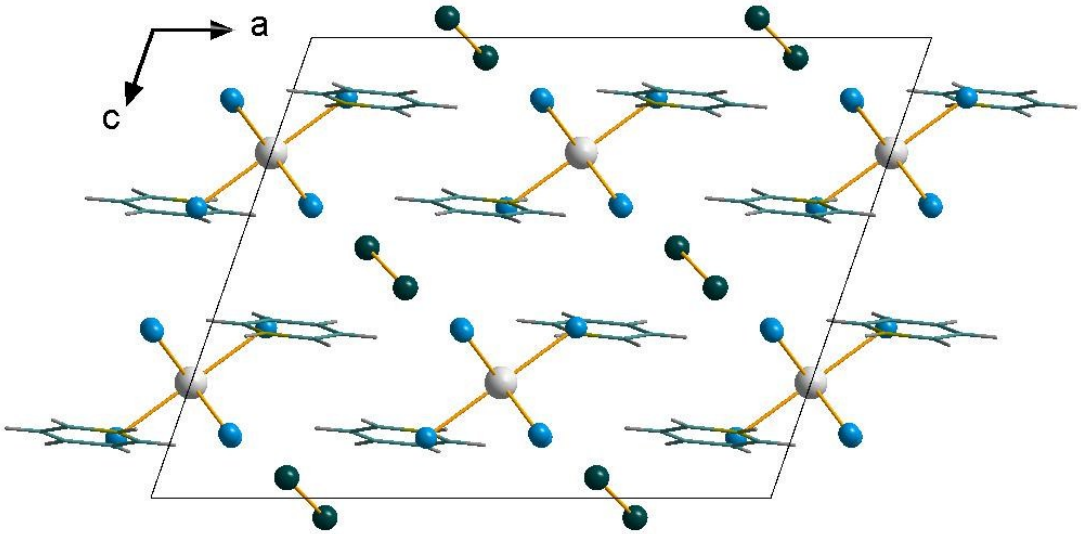

Figure S3. Crystal packing is the structure of **2.** Cations are shown in wire-and-stick representation

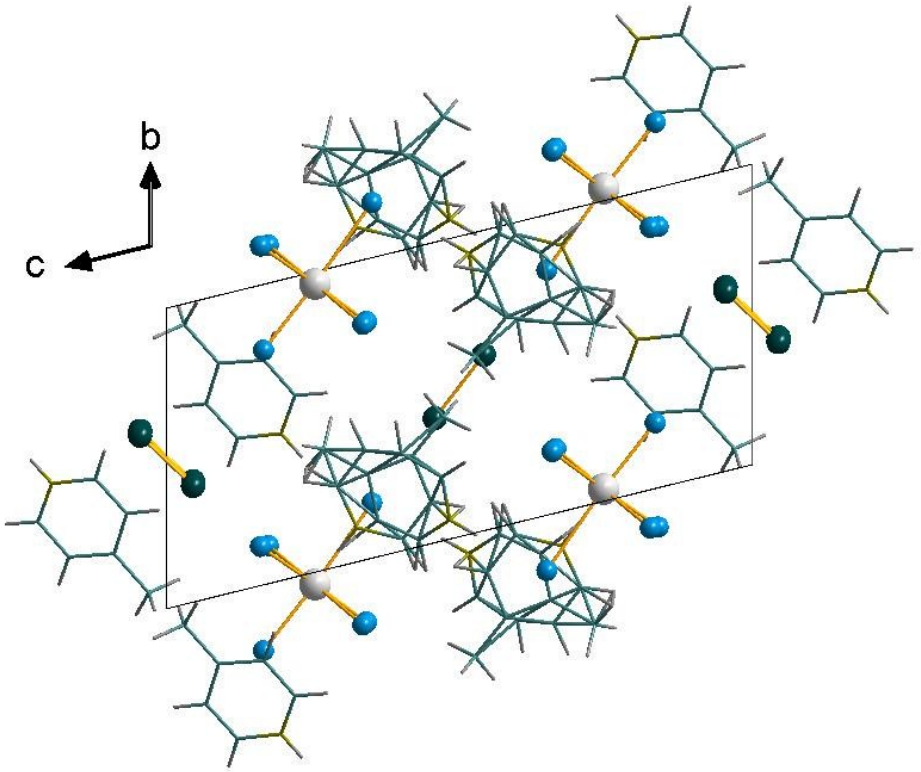

Figure S4. Crystal packing is the structure of **3.** Cations are shown in wire-and-stick representation

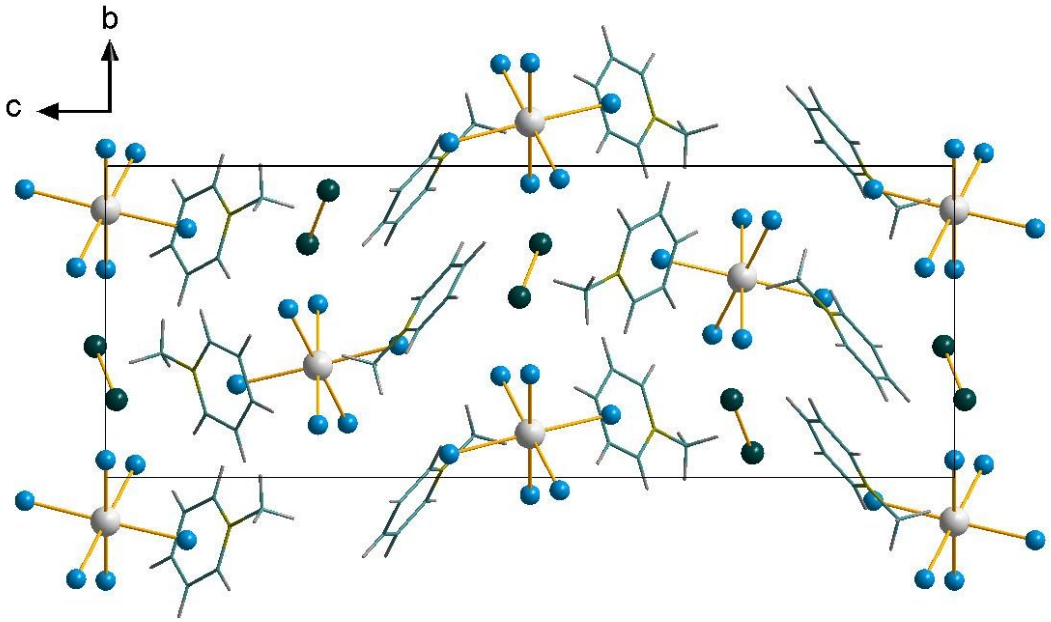

Figure S5. Crystal packing is the structure of **4.** Cations are shown in wire-and-stick representation

Table S4. Values of the density of all electrons – $\rho(\mathbf{r})$, Laplacian of electron density – $\nabla^2\rho(\mathbf{r})$ and appropriate λ_2 eigenvalues (with promolecular approximation), energy density – H_b, potential energy density – $V(\mathbf{r})$, and Lagrangian kinetic energy – $G(\mathbf{r})$ (a.u.) at the bond critical points (3, –1), corresponding to different intermolecular non-covalent interactions in model structures **1_big**, **2_big**, and **4_big**, bond lengths – *l* (Å), as well as energies for these contacts E_{int} (kcal/mol), defined by different approaches.*

Contact	$\rho(\mathbf{r})$	$\nabla^2\rho(r)$	λ_2	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E_{int}[a]	E_{int}[b]	E_{int}[c]	E_{int}[d]	*l*
1_big											
Br···Cl	0.022	0.073	-0.029	0.002	-0.015	0.017	4.7	4.6	5.5	6.1	2.929
Br···Cl	0.019	0.065	-0.025	0.002	-0.013	0.014	4.1	3.8	4.7	5.0	2.995
N–H···Cl	0.018	0.047	-0.026	0.001	-0.010	0.011	3.1	3.0	--	--	2.269
2_big											
Br···Cl	0.016	0.052	-0.021	0.002	-0.010	0.011	3.1	3.0	3.6	3.9	3.091
N–H···Cl	0.008	0.023	-0.014	0.001	-0.004	0.005	1.3	1.3	--	--	2.814
4_big											
Br···Cl	0.017	0.055	-0.022	0.002	-0.010	0.012	3.1	3.2	3.6	4.3	3.073

* Values of the density of all electrons, Laplacian of electron density and appropriate λ_2 eigenvalues (with promolecular approximation), energy density, potential energy density, and Lagrangian kinetic energy at the bond critical points (3, –1), corresponding to intermolecular non-covalent interactions Br···Cl in model structures **1_big**, **2_big**, and **4_big** changes very slightly compare with these in initial "small" model systems **1**, **2** and **4** (see **Table 1** in the main text).

[a] $E_{int} = -V(\mathbf{r})/2$[62] [b] $E_{int} = 0.429G(\mathbf{r})$[63] [c] $E_{int} = 0.58(-V(\mathbf{r}))$[64] [d] $E_{int} = 0.57G(\mathbf{r})$[64] [appropriate references are given in the main text]