Robust motifs in 2-phenylethylammonium- and related tetrahalometallates

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Supplementary Information

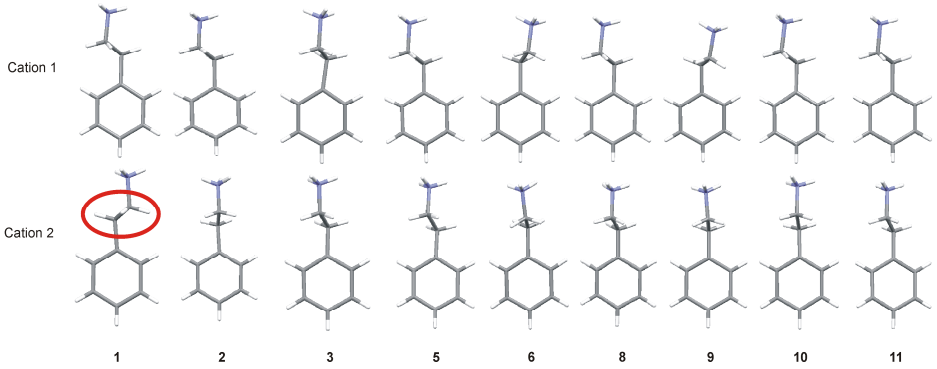

Fig. S1 Comparison of cation geometry in structures **1** to **11**. Cations viewed perpendicular to aromatic plane.

Table S1 Hydrogen bonding parameters involved in formation of the zero-dimensional motifs[a,b]

Motif 1	D…A (Å)	Symmetry operator	Motif 2	D…A (Å)	Symmetry operator
1					
N(1)-H(1C)… Cl(1)	3.438(7)	*-x, -y+1, -z+1*	N(2)-H(2C)…Cl(3)	3.499(9)	*x,y, z+1*
N(1)-H(1D)… Cl(4)	3.314(7)	*x, y, z*	N(2)-H(2D)...Cl(1)	3.378(8)	*x, y, z+1*
			N(2)-H(2E)...Cl(1)	3.310(6)	*-x, -y+1, -z+1*
			C(10)-H(10B)…Cl(4)	3.846	*-x, -y+1, -z+1*
2[12]					
N(2)-H(24)...Br(2)	3.527	*x, y, z*	N(1)-H(20)…Br(3)	3.596	*x, ½ - y, -½+ z*
N(2)-H(22)...Br(1)	3.434	*1-x, -y, -z*	N(1)-H(21)…Br(3)	3.487	*-x, -½+y, ½ - z*
			N(1)-H(20)…Br(2)	3.502	*x, ½-y, -½+z*
3					
N(1)-H(1C)...I(2)	3.640(8)	*x, y, z*	N(2)-H(2C)...I(3)	3.689(11)	*-x+1, -y+1, -z+1*
N(1)-H(1C)...I(1)	3.612(9)	*x, y, z*	N(2)-H(2C)...I(4)	3.860(11)	*x, y, z+1*
N(1)-H(1D)...I(4)	3.627(10)	*-x+1, -y+1, -z+1*	N(2)-H(2E)...I(4)	3.838(9)	*-x+1, -y+1, -z+1*
5					
N(1)-H(1C)...Br(1)	3.510(7)	*-x, -y+1, -z+1*	N(2)-H(2D)...Br(1)	3.493(8)	*x, y, z+1*
N(1)-H(1D)...Br(4)	3.418(7)	*x, y, z*	N(2)-H(2E)...Br(1)	3.603(6)	*-x, -y+1, -z+1*
			C(10)-H(10A)…Br(4)	3.784	*2-x, ½+y, ½-z*
6					
N(1)-H(1D)...I(4)	3.716(12)	*x, y, z*	N(2B)-H(2CB)...I(1)	3.65(3)	*x, y, z* and *x-1, y, z+1*
N(1)-H(1E)...I(1)	3.601(17)	*-x, y-1/2, -z*	N(2B)-H(2CB)...I(3)	3.84(2)	*-x, y+½, -z+1*
			N(2B)-H(2DB)…I(3)	3.68(3)	*x, y, z* and *x-1, y, z+1*
			N(2B)-H(2DB)…I(1)	3.78(2)	*-x, y-½, -z+1*
			C(9B)-H(9B2)…I(4)	4.041	*1-x, ½+y,-z*
			C(10B)-H(1B1)…I(4)	4.001	*1-x,- ½+y,-z*
8					
N(1)-H(1E)...Br(3)	3.474(7)	*-x+1, -y+1, -z+1*	N(2)-H(2D)...Br(1)	3.481(8)	*x, y, z+1*
N(1)-H(1D)...Br(4)	3.438(7)	*x. y. x*	N(2)-H(2E)...Br(1)	3.602(7)	*-x, -y+1, -z+1*
9					
N(1)-H(1D)...I(4)	3.615(8)	*x, y, z*	N(2B)-H(2CB)...I(1)	3.778(13)	*x, y, z* and *x-1, y, z+1*
N(1)-H(1E)...I(1)	3.714(13)	*-x, y-1/2, -z*	N(2B)-H(2CB)...I(3)	3.878(11)	*-x, y+½, -z+1*
			N(2B)-H(2DB)…I(3)	3.737(13)	*x, y, z* and *x-1, y, z+1*
			N(2B)-H(2DB)…I(1)	3.804(11)	*-x, y-½, -z+1*
			C(9B)-H(9B2)…I(4)	4.080	*1-x, ½+y,-z*
			C(10B)-H(1B1)…I(4)	4.096	*1-x,- ½+y,-z*
10					
N(1)-H(1C)...Cl(1)	3.554(11)	*-x, -y+1, -z+1*	N(2)-H(2D)...Cl(1)	3.387(17)	*x, y, z+1*
N(1)-H(1D)...Cl(2)	3.412(11)	*x, y, z*	N(2)-H(2E)...Cl(1)	3.430(12)	*-x, -y+1, -z+1*
N(1)-H(1E)…I(1)	3.598(9)	*-x+1, -y+1, -z+1*			
11[13]					
N(1)-H(1)...Br(2)	3.500	*x, y, z*	N(2)-H(14)…Br(3)	3.487	*-x+1, y- ½ , -z + ½*
N(1)-H(2)...Br(1)	3.434	*1-x, ½+y, ½-z*	N(2)-H(15)…Br(3)	3.606	*x, -y+½ , z+½*

[a] Only the cations with the highest occupancy were considered in structures **6** and **9**.

[b] Hydrogen bonding definition: H…A < radius(A) + 2Å and DHA angle larger than 110°

Table S2 Hydrogen bonding and C-H...Cg interactions in the novel structures **1**, **3**, **5**, **6**, **8**, **9** and **10** involved in formation of the one-dimensional column and three-dimensional structure (Note: Cg(1) refers to the aromatic ring centroid on cation 1 consisting of atoms C(3) to C(8) , and Cg(2) refers to the aromatic ring centroid on cation 2, consisting of atoms C(11) to C(16).

C-H… π^b interactions linking zero-dimensional motifs to form 1-d chains, and one-dimensional motifs to form 2-d sheets			**Hydrogen bonding interactions linking two-dimensional sheets**		
Interaction	H…Cg (Å)	Symmetry transformation of acceptor ring	Interaction	D…A (Å)	Symmetry transformation of acceptor atom
1					
1-d chain interaction C(12)-H(12)…Cg(1)	2.79	*1+x, y, z*	N(1)-H(1E)…Cl(3)	3.381(7)	*-x+1, -y+1, -z+1*
2-d sheet interaction C(8)-H(8)…Cg(2)	2.86	*x, ½-y, ½+z*	N(2)-H(2C)…Cl(3)	3.298(7)	*-x+1, -y+1, -z+1*
C(15)-H(15)…Cg(1)	2.80	*x, ½-y, ½+z*			
3					
1-d chain interaction C(12)-H(12)…Cg(1)	3.07	*-x,y+½ ,-z+½+1*	N(1)-H(1D)…I(3)	3.690(10)	*-x, -y+1, -z+1*
2-d sheet interaction C(15)-H(15)…Cg(1)	2.98	*x, ½-y, ½+z*	N(2)-H(2D)…I(1)	4.166(11)	*-x, -y+1, -z+1*
5					
1-d chain interaction C(12)-H(12)…Cg(1)	2.98	*1+x, y, z*	N(1)-H(1E)...Br(2)	3.864(7)	*-x+1, -y+1, -z+1*
2-d sheet interaction C(15)-H(12)…Cg(1)	2.90	*x, ½-y, ½+z*	N(1)-H(1E)...Br(3)	3.494(6)	*-x+1, -y+1, -z+1*
			N(2)-H(2C)...Br(3)	3.520(7)	*-x+1, -y+1, -z+1*
			N(2)-H(2C)...Br(3)	3.732(8)	*x,y, z+1*
6					
1-d chain interaction (chain 1[a]) C(8)-H(8B)…Cg(1)	3.09	*-x, y-½, -z+1*	N(1)-H(1C)...I(3)	3.62(2)	*-x, y+½ , -z*
1-d chain interaction (chain 2[a]) C(16B)-H(16)…Cg(2)	2.99	*1-x, -½+y,1-z*	N(2B)-H(2EB)…I(2)	4.02(2)	*x, y, z+1*
2-d sheet interaction C(13B)-H(13B)…Cg(1)	2.89	*x, 1+y, z*			
8					
1-d chain interaction C(12)-H(12)…Cg(1)	3.01	*1+x, y, z*	N(1)-H(1C)...Br(1)	3.517(8)	*-x, -y+1, -z+1*
2-d sheet interaction C(15)-H(15)…Cg(1)	2.89	*x, ½-y, ½+z*	N(2)-H(2C)...Br(3)	3.505(7)	*-x+1, -y+1, -z+1*
9					
1-d chain interaction (chain 1[a]) C(8)-H(8)…Cg(1)	3.18	*-x, y-½, -z+1*	N(1)-H(1D)...I(2)	3.571(7)	*x, y, z*
1-d chain interaction (chain 2[a]) C(16B)-H(16B)…Cg(2)	3.05	*1-x, -½+y,1-z*	N(2B)-H(2EB)...I(2)	3.875(8)	*x, y, z+1*
2-d sheet interaction C(13B)-H(13B)...Cg(1)	2.97	*x, 1+y, z*			
10					
1-d chain interaction C(12)-H(12)…Cg(1)	2.89	*1+x, y, z*	N(1)-H(1E)...Br(1)	3.545(10)	*-x+1, -y+1, -z+1*
2-d sheet interaction C(15)-H(15)…Cg(1)	2.88	*x, ½-y, ½+z*	N(2)-H(2C)...Br(1)	3.533(16)	*-x+1, -y+1, -z+1*

[a] In structures **6** and **9** chain 1 consists of motif 1's and chain 2 consists of motif 2's.

[b] Definition: H…Cg < 3.0 Å, and the angle between the X-H…Cg vector and normal to aromatic plane smaller than 30°.

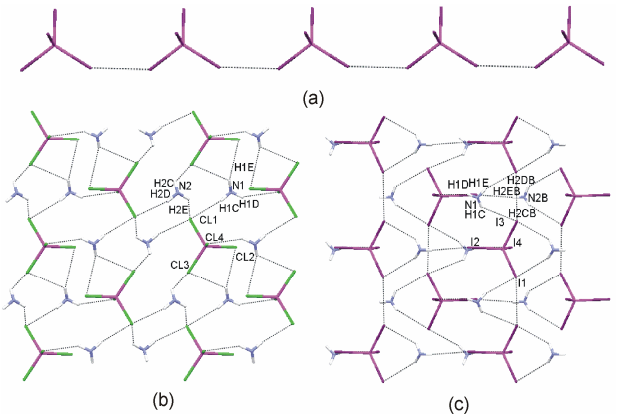

Fig. S2 (a) M-I…I-M close contacts present in structures **6** and **9** (b) hydrogen bonded sheet in structure **1** (c) hydrogen bonded sheet in structure **9**.

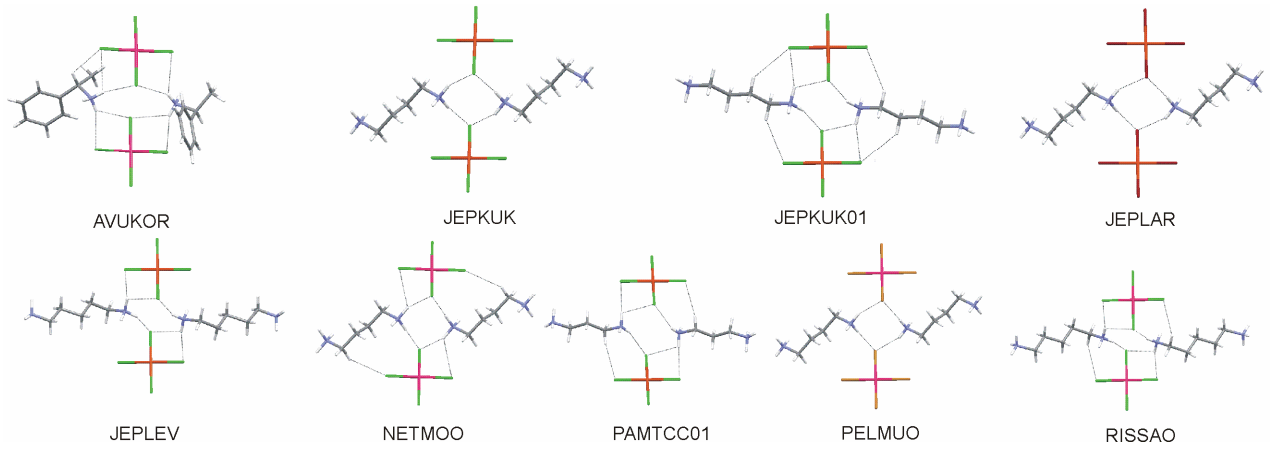

Fig. S3 Zero-dimensional motifs present in structures with square planar anion geometries.

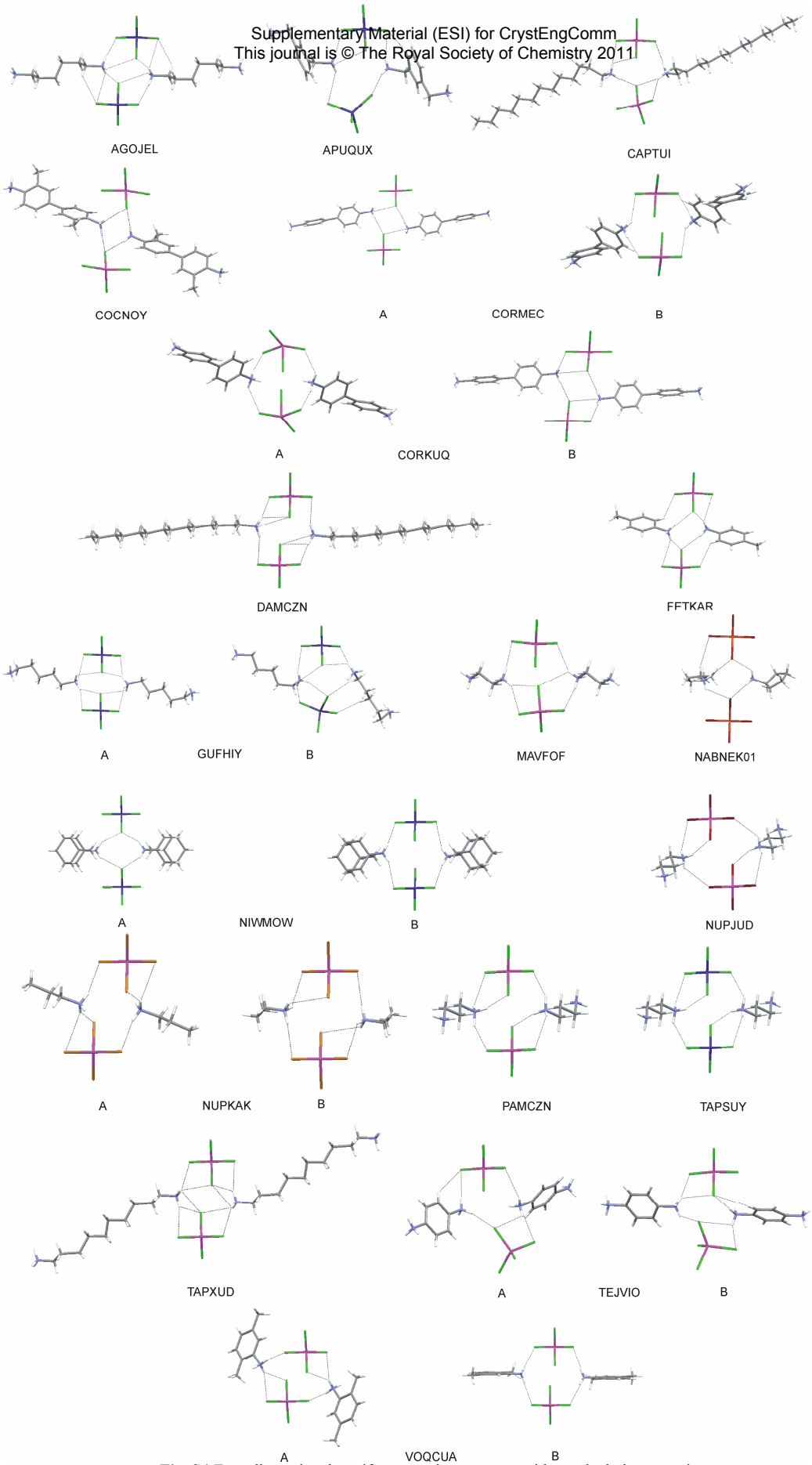

Fig. S4 Zero-dimensional motifs present in structures with tetrahedral geometries.