Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A theoretical study of perovskites related to $CH_3NH_3PbX_3$ (X = F, Cl, Br, I)

Ibon Alkorta and José Elguero

Table S1

The problem of the charge per cubelet in stacked congruent cubes.

Vertices = $\mathbf{n^3 + 3n^2 + 3n + 1 == (n+1)^3}$

Edges = = $\mathbf{3n^3 + 6n^2 + 3n}$

n	cubelets	vertices	edges	edges/vertices	charge*	charge/cubelets
1	----	8	12	1.5	4	4
2	8	27	54	2.00	0.00	0.00
3	27	64	144	2.25	–16	–0.5926
4	64	125	300	2.40	–50	–0.7813
5	125	216	540	2.50	–108	–0.8640
6	216	343	882	2.57	–196	–0.9074
7	343	512	1344	2.62	–320	–0.9329
8	512	729	1944	2.67	–486	–0.9492
9	729	1000	2700	2.70	–700	–0.9602
10	1000	1331	3630	2.73	–968	–0.9680
100	1000000	1030301	3060300	2.97	–999698	–0.9997
1000				3.00		–1

Charge = 2*vertices – edges, since in the vertices are Pb^{2+} and in the edges I^-.

Charge = $2n^3 + 6n^2 + 6n + 2 – 3n^3 – 6n^2 – 6n = – n^3 + 3n + 2$

Charge per cubelet = $–(n^3 + 3n + 2)/n^3$

Table S2

Energetics of the anion and cation monomers.

Cation	Electronic Energy (hartree)
$[NH_4]^+$ (**1**)	-56.905625
$[(CH_3)NH_3]^+$ (**2**)	-96.227237
$[(CF_3)NH_3]^+$ (**12**)	-393.960665
$[(H_2N)NH_3]^+$ (**18**)	-112.230609
$[(HO)NH_3]^+$ (**19**)	-132.065165
$[OH_3]^+$ (**21**)	-76.714731

Anion	Electronic Energy (hartree)
PbI_3^-	-1080.625467
$PbBr_3^-$	-1443.936610
$PbCl_3^-$	-1573.877638

PbF_3^-	-492.711474
PbI_2Br^-	-1201.729203
$PbIBr_2^-$	-1322.832925

Anion	Cation	Electronic Energy (hartree)
PbI_3^-	$[NH_4]^+$ (**1**)	-1137.698630
	$[(CH_3)NH_3]^+$ (**2**)	-1177.011780
	$[(CF_3)NH_3]^+$ (**12**)	-1474.763415
	$[(H_2N)NH_3]^+$ (**18**)	-1193.021266
	$[(HO)NH_3]^+$ (**19**)	-1212.869307
	$[OH_3]^+$ (**21**)	-1157.544137
$PbBr_3^-$	$[NH_4]^+$ (**1**)	-1501.019234
	$[(CH_3)NH_3]^+$ (**2**)	-1540.331870
	$[(CF_3)NH_3]^+$ (**12**)	-1838.084955
	$[(H_2N)NH_3]^+$ (**18**)	-1556.342075
	$[(HO)NH_3]^+$ (**19**)	-1576.190900
	$[OH_3]^+$ (**21**)	-1520.866664
$PbCl_3^-$	$[NH_4]^+$ (**1**)	-1630.967719
	$[(CH_3)NH_3]^+$ (**2**)	-1670.280016
	$[(CF_3)NH_3]^+$ (**12**)	-1968.034253
	$[(H_2N)NH_3]^+$ (**18**)	-1686.290836
	$[(HO)NH_3]^+$ (**19**)	-1706.140340
	$[OH_3]^+$ (**21**)	-1650.816611
PbF_3^-	$[NH_4]^+$ (**1**)	-549.833926
	$[(CH_3)NH_3]^+$ (**2**)	-589.144535
	$[(CF_3)NH_3]^+$ (**12**)	-886.905188
	$[(H_2N)NH_3]^+$ (**18**)	-605.159488
	$[(HO)NH_3]^+$ (**19**)	-625.013042
	$[OH_3]^+$ (**21**)	-569.691238
PbI_2Br^-	$[(CH_3)NH_3]^+$ (**2**)	-1298.118504
	$[(HO)NH_3]^+$ (**19**) (O–H···I)	-1333.976555
	$[(HO)NH_3]^+$ (**19**) (O–H···Br)	-1333.976338
$PbIBr_2^-$	$[(CH_3)NH_3]^+$ (**2**)	-1419.225205
	$[(HO)NH_3]^+$ (**19**) (O–H···I)	-1455.083742
	$[(HO)NH_3]^+$ (**19**) (O–H···Br)	-1455.083657

Table S3
Presence-absence matrix

No	Anion	Cation	E_b	E_{rel}	Br	Cl	F	H	CF_3	NH_2	OH	OH_3^+
1	PbI_3^-	$[NH_4]^+$	–439.9	–22.2	0	0	0	1	0	0	0	0
2		$[(CH_3)NH_3]^+$	–417.7	0.0	0	0	0	0	0	0	0	0
3		$[(CF_3)NH_3]^+$	–465.5	–47.8	0	0	0	0	1	0	0	0
4		$[(H_2N)NH_3]^+$	–433.7	–16.0	0	0	0	0	0	1	0	0
5		$[(HO)NH_3]^+$	–469.1	–51.5	0	0	0	0	0	0	1	0
6		$[OH_3]^+$	–535.4	–117.8	0	0	0	0	0	0	0	1
7	$PbBr_3^-$	$[NH_4]^+$	–464.7	–47.1	1	0	0	1	0	0	0	0
8		$[(CH_3)NH_3]^+$	–441.1	–23.5	1	0	0	0	0	0	0	0
9		$[(CF_3)NH_3]^+$	–492.8	–75.1	1	0	0	0	1	0	0	0
10		$[(H_2N)NH_3]^+$	–459.1	–41.4	1	0	0	0	0	1	0	0
11		$[(HO)NH_3]^+$	–496.5	–78.9	1	0	0	0	0	0	1	0

12		$[OH_3]^+$	–565.3	–147.7	1	0	0	0	0	0	0	1
13	$PbCl_3^-$	$[NH_4]^+$	–484.3	–66.6	0	1	0	1	0	0	0	0
14		$[(CH_3)NH_3]^+$	–459.8	–42.2	0	1	0	0	0	0	0	0
15		$[(CF_3)NH_3]^+$	–514.5	–96.8	0	1	0	0	1	0	0	0
16		$[(H_2N)NH_3]^+$	–479.4	–61.7	0	1	0	0	0	1	0	0
17		$[(HO)NH_3]^+$	–518.6	–101.0	0	1	0	0	0	0	1	0
18		$[OH_3]^+$	–588.7	–171.1	0	1	0	0	0	0	0	1
19	PbF_3^-	$[NH_4]^+$	–569.3	–151.6	0	0	1	1	0	0	0	0
20		$[(CH_3)NH_3]^+$	–540.4	–122.7	0	0	1	0	0	0	0	0
21		$[(CF_3)NH_3]^+$	–611.9	–194.2	0	0	1	0	1	0	0	0
22		$[(H_2N)NH_3]^+$	–570.8	–153.1	0	0	1	0	0	1	0	0
23		$[(HO)NH_3]^+$	–620.7	–203.0	0	0	1	0	0	0	1	0
24		$[OH_3]^+$	–695.8	–278.2	0	0	1	0	0	0	0	1
	Anion	Cation	E_b	E_{rel}	CH_3	OH	No					
1	PbI_3^-	$[(CH_3)NH_3]^+$	–417.7	0.0	1	0	3					
2		$[(HO)NH_3]^+$ (O–H···I)	–469.1	–51.5	0	1	3					
3	PbI_2Br^-	$[(CH3)NH3]^+$	–425.5	–7.8	1	0	2					
4		$[(HO)NH_3]^+$ (O–H···I)	–478.3	–60.7	0	1	2					
5		$[(HO)NH_3]^+$ (O–H···Br)	–477.8	–60.1	0	1	2					
6	$PbIBr_2^-$	$[(CH_3)NH_3]^+$	–433.3	–15.7	1	0	1					
7		$[(HO)NH_3]^+$ (O–H···I)	–487.4	–69.8	0	1	1					
8		$[(HO)NH_3]^+$ O–H···Br)	–487.2	–69.6	0	1	1					
9	$PbBr_3^-$	$[(CH_3)NH_3]^+$	–441.1	–23.5	1	0	0					
10		$[(HO)NH_3]^+$ (O–H···Br)	–496.5	–78.9	0	1	0					

To avoid singular matrices, a compound of reference must be selected. The election being arbitrary we select $[(CH_3)NH_3]^+ \cdot PbI_3^-$ (MAPI) as the most known compound in perovskites. Br, Cl and F stand for the $PbBr_3^-$, $PbCl_3^-$ and PbF_3^- anions. H, CF_3, NH_2, OH and OH_3^+ corresponds to the cations $[NH_4]^+$, $[(CF_3)NH_3]^+$, $[(H_2N)NH_3]^+$, $[(HO)NH_3]^+$ and OH_3^+. Then, 1 and 0 correspond to presence and absence, respectively.