Electronic Supplementary Material (ESI) for ChemComm.

Structure-directing effects in (110)-layered hybrid perovskites containing two distinct organic moieties

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Supplementary Information

Synthesis

Lead (II) bromide ($PbBr_2$, ≥98%), hydrobromic acid (HBr, 48%, w/w aqueous solution), 1,2,4-triazole ($C_2H_3N_3$, 99%) and imidazole ($C_3H_4N_2$, 99%) were purchased from Alfa Aesar. Guanidinium carbonate ($C_2H_{10}N_6H_2CO_3$, 99%) and diethyl ether ($(C_2H_5)_2O$, 99.5%) were purchased from Sigma Aldrich. All chemicals were directly used without further purification.

The title compounds $IGPbBr_4$ and $TGPbBr_4$ were crystallized by a slow evaporation method.
For $IGPbBr_4$ ($C_4H_{11}N_5PbBr_4$), imidazole (204 mg, 3 mmol), guanidinium carbonate (180 mg, 1 mmol) and $PbBr_2$ (734 mg, 2 mmol) were dissolved in conc. HBr (4 mL) with moderate heating. By cooling for a few hours, pale yellow, plate-shaped crystals were obtained. These were filtered and washed with diethyl ether (yield 54% based on $PbBr_2$). Elemental analysis: (Anal. Calc. (%) for $IGPbBr_4$: C, 7.32; H, 1.69; N, 10.67. Found: C, 7.55; H, 1.54; N, 10.59).

For $TGPbBr_4$ ($C_3H_{10}N_6PbBr_4$), stoichiometric amounts of 1,2,4-triazole (138 mg, 2 mmol), guanidinium carbonate (180 mg, 1 mmol) and $PbBr_2$ (734 mg, 2 mmol) were dissolved in conc. HBr (4 mL) with moderate heating. By cooling for a few hours, colourless, needle-shaped crystals were obtained. These were filtered and washed with diethyl ether (yield 43%). Elemental analysis: (Anal. Calc. (%) for $IGPbBr_4$: C, 5.48; H, 1.54; N, 12.79. Found: C, 5.51; H, 1.39; N, 12.75).

Preliminary Characterisation

Powder X-ray diffraction data were collected on a PANalytical EMPYREAN diffractometer using Cu $K_{\alpha 1}$ (λ = 1.5406 Å) radiation to confirm the purity of each sample.

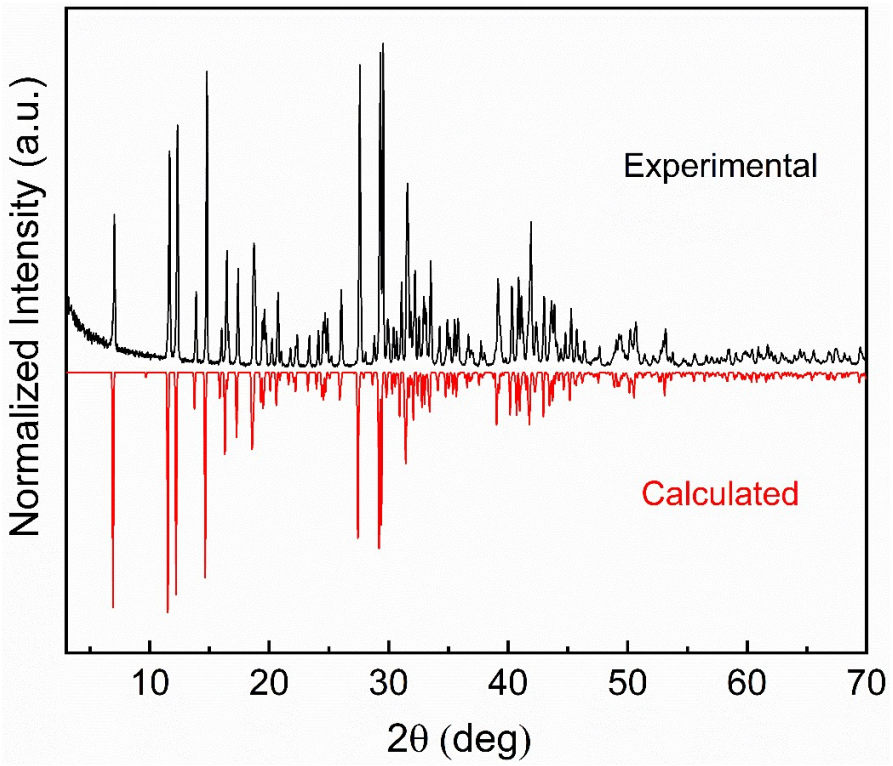

Figure S1 Raw and calculated PXRD data for $IGPbBr_4$

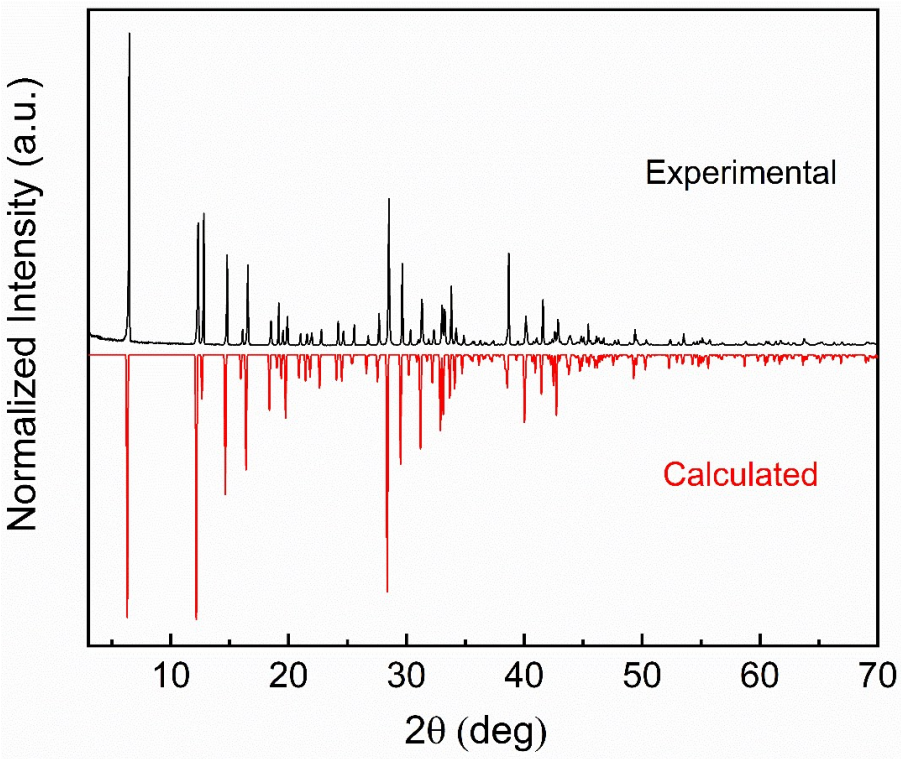

Figure S2 Raw and calculated PXRD data for $TGPbBr_4$

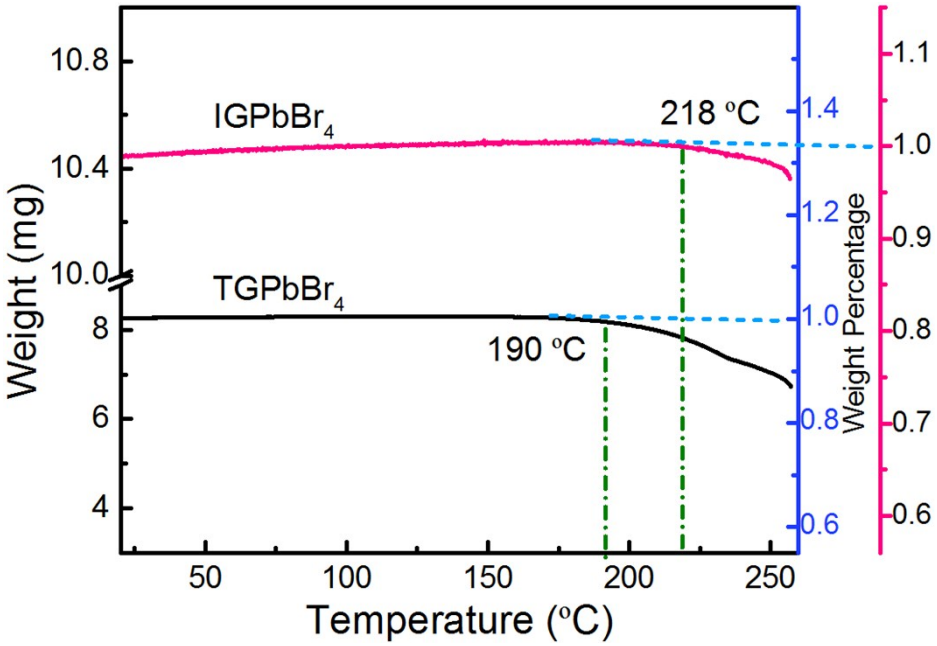

Figure S3 Thermal Gravimetric Analysis (TGA) of $IGPbBr_4$ and $TGPbBr_4$

Single Crystal data were collected at 93 and 298 K on a Rigaku XtaLAB P200 diffractometer and a Rigaku SCX Mini diffractometer using Mo-K_α radiation. Data were collected using CrystalClear (Rigaku)[3]. Structures were solved by direct methods and refined using SHELX-2014[4] incorporated in the WINGX program[5]. Absorption corrections were performed semi-empirically from equivalent reflections on the basis of multi scans. Non-H atoms were refined anisotropically and hydrogen atoms were treated as riding atoms.

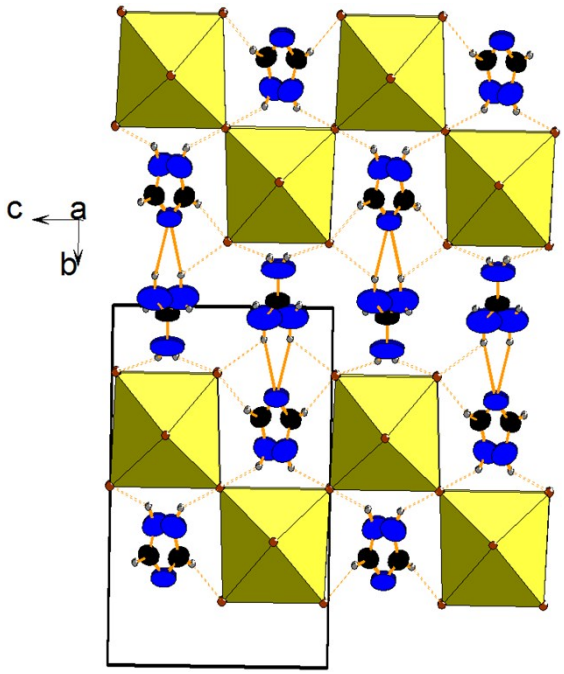

Figure S4 Crystal structure of $TGPbBr_4$ at 298 K, space group *P*2/*c*. Note that the TzH^+ moiety is disordered around the vertical two-fold axis, and there is no octahedral tilting

Solid UV-vis absorbance spectra were collected on a JASCO-V550 ultraviolet-visible spectrophotometer.

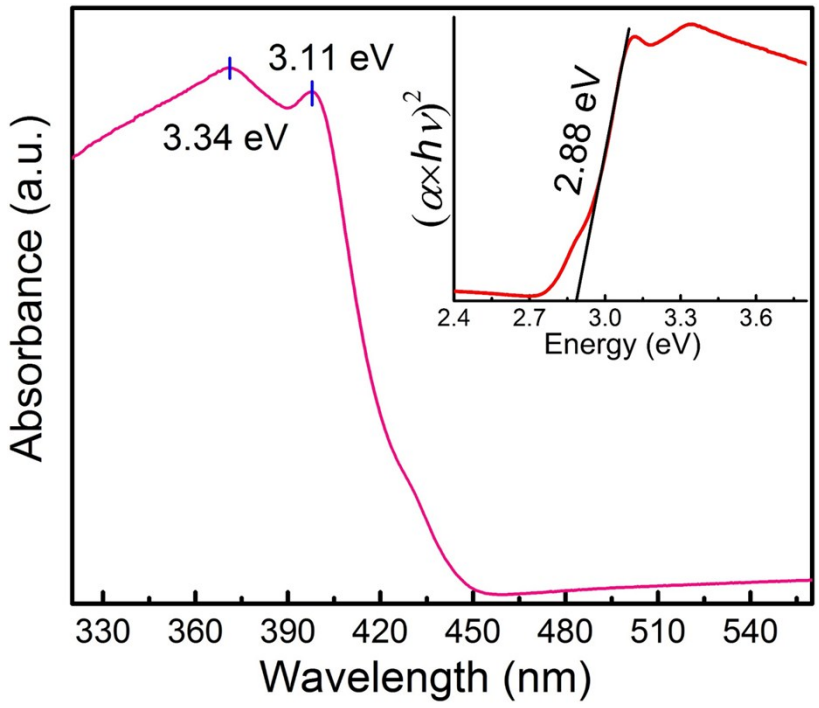

Figure S5 UV absorption spectra and Tauc plot[6] (inset) of $IGPbBr_4$ at room temperature

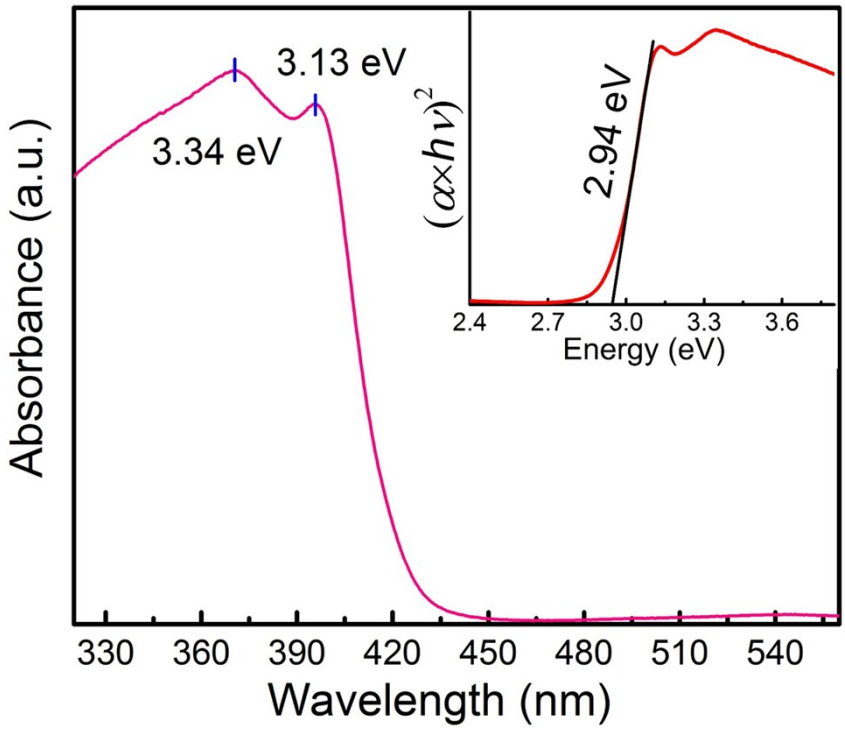

Figure S6 UV absorption spectra and Tauc plot (inset) of $TGPbBr_4$ at room temperature

Photoluminescence spectra were recorded at room temperature using an Edinburgh Instrument FLS980 spectrometer.

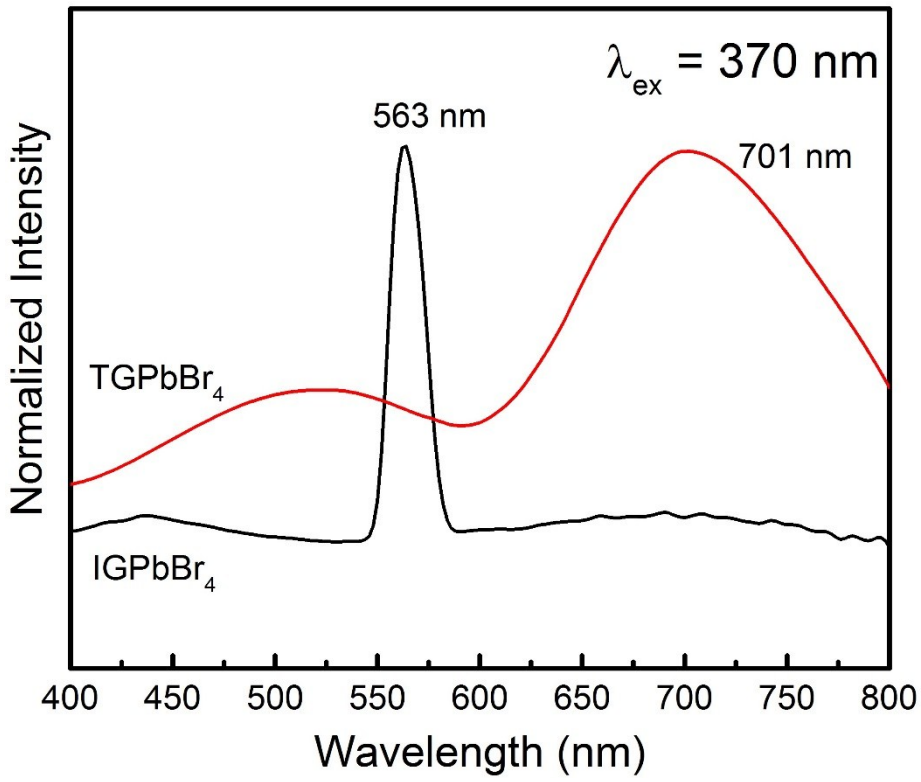

Figure S7 Photoluminescence spectra of $IGPbBr_4$ and $TGPbBr_4$

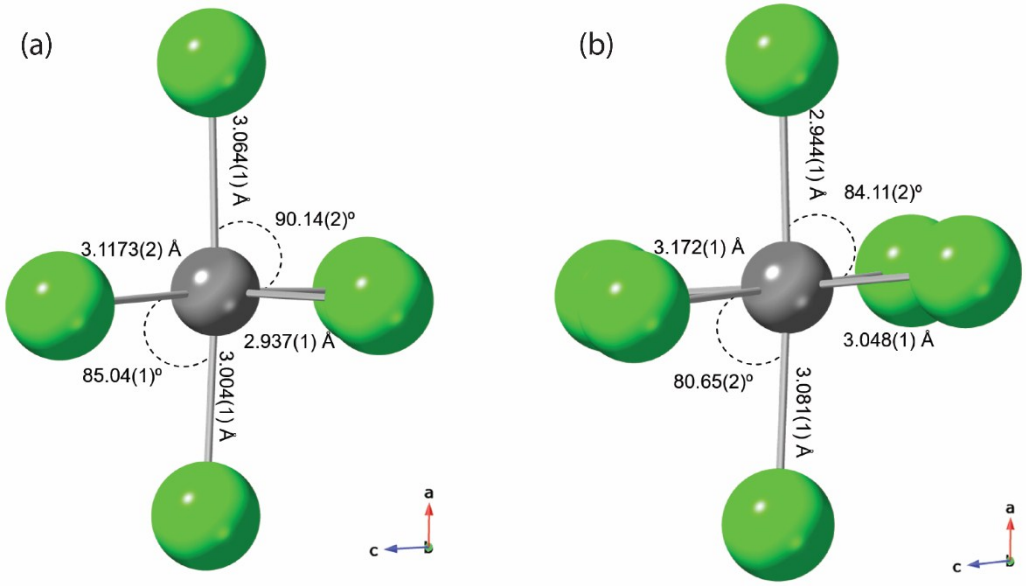

Figure S8 Ball and stick representation of the octahedra present in (a) $IGPbBr_4$ and (b) $TGPbBr_4$ highlighting the greater degree of distortion in both the bond lengths and bond angles of the $TGPbBr_4$ composition

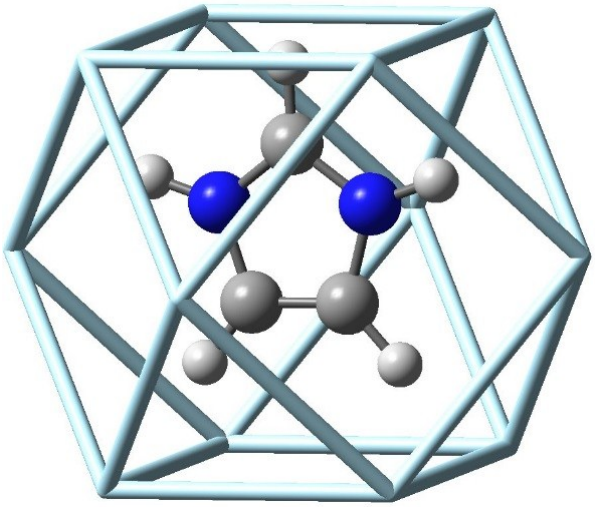

Figure S9 Ion placed inside a cuboctahedron of 12 Ne atoms (at the vertices of the wireframe, atoms omitted for clarity), imidazolium shown as an example (colour code: grey, white and blue for C, H and N, respectively)

Table S1 Crystallographic data and refinement details

	$IGPbBr_4$		**$TGPbBr_4$**	
Temperature	**93 K**	**298 K**	**93 K**	**298 K**
Formula	$(C_3N_2H_5)(CN_3H_6)$ $PbBr_4$	$(C_3N_2H_5)(CN_3H_6)$ $PbBr_4$	$(C_2N_3H_4)(CN_3H_6)$ $PbBr_4$	$(C_2N_3H_4)(CN_3H_6)$ $PbBr_4$
Formula weight	656.01	656.01	657.00	657.00
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/c$	*P*2/c
***a*/Å**	6.0602(16)	6.1106(4)	6.003(2)	6.0734(4)
***b*/Å**	9.3286(2)	9.2753(5)	26.969(9)	14.0000(9)
***c*/Å**	12.8673(3)	13.0429(9)	8.613(3)	8.5374(5)
***α*/°**	95.127(2)	93.474(9)	90	90
***β*/°**	93.490(2)	92.726(9)	96.470(8)	94.866(8)
***γ*/°**	92.402(2)	91.258(8)	90	90
***V*/Å³**	722.35(19)	736.82(8)	1385.5(8)	723.30(8)
Z	2	2	4	2
Measured ref	15685	6225	16723	6554
Independent ref	2539	2580	2411	1428
	[*R*(int) = 0.0362]	[*R*(int) = 0.0831]	[*R*(int) = 0.0671]	[*R*(int)= 0.0471]
GOOF	1.077	0.926	1.089	1.037
Final *R* indices (*I* > 2*σ*(*I*))	R_1 = 0.0256	R_1 = 0.0518	R_1 = 0.0291	R_1 = 0.0261
	wR_2 = 0.0717	wR_2 = 0.1197	wR_2 = 0.0775	wR_2 = 0.0604

Table S2 Selected bond lengths (Å) and bond angles (°) versus temperature for $IGPbBr_4$ and $TGPbBr_4$

	$IGPbBr_4$		**$TGPbBr_4$**	
Temperature	**93 K**	**298 K**	**93 K**	**298 K**
Pb-Br	2.9238(6)	2.9108(19)	2.8613(10)	2.9170(7)
	2.9367(6)	2. 9330(17)	2.9444(11)	2.9171(7)
	3.0035(9)	3.0357(15)	2.9841(11)	3.0451(2)
	3.0635(10)	3.0757(15)	3.0480(10)	3.0451(2)
	3.1358(2)	3.1403(6)	3.0809(12)	3.1191(2)
	3.1173(2)	3.1403(6)	3.1723(11)	3.1191(2)
Br-Pb-Br	84.632(11)	86.01(4)	80.645(19)	83.577(13)
	85.036(12)	86.90(4)	84.11(2)	83.577(13)
	85.327(12)	86.96(4)	84.12(3)	85.00(3)
	87.996(17)	88.22(5)	88.28(3)	86.359(8)
	89.564(12)	89.51(4)	89.09(2)	89.773(19)
	89.625(16)	89.67(5)	89.99(2)	89.773(19)
	89.816(13)	90.33(5)	90.38(2)	90.224(13)
	90.138(16)	90.55(5)	91.33(3)	90.224(13)
	91.482(16)	91.17(4)	92.47(2)	94.322(17)
	93.905(16)	91.55(5)	94.24(2)	94.322(17)
	96.222(11)	93.93(4)	96.26(3)	96.495(19)
	96.478(6)	95.192(16)	99.20(2)	96.495(19)
Pb-Br-Pb	180.0	180.0	169.58(3)	180.0
	174.60(2)	178.08(7)	170.14(3)	171.51(3)

Table S3 Hydrogen bond lengths (Å) and angles (°) for $IGPbBr_4$ at 93 K

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N4-H7...Br4	0.86	2.47	3.315(6)	168.5
N5-H8...Br1#1	0.86	2.85	3.433(6)	126.8
N5-H8...Br1 #5	0.86	2.80	3.442(6)	132.9
C2-H9...Br1 #1	0.93	3.13	3.572(7)	111.4
C2-H9...Br3 #1	0.93	2.85	3.580(7)	136.3
C3-H10...Br4 #6	0.93	2.92	3.819(7)	161.9
N1a-H1a...Br1 #7	0.86	2.64	3.481(7)	167.0
N1a-H2a...Br4 #6	0.86	2.70	3.469(7)	149.1
N2a-H3a...Br3 #7	0.86	2.75	3.527(8)	151.7
N2a-H4a...Br5 #8	0.86	2.74	3.486(7)	146.3
N3a-H5a...Br3 #6	0.86	2.74	3.499(8)	148.5
N3a-H6a...Br2 #8	0.86	2.58	3.410(9)	163.7
N1'b-H1'b...Br1 #7	0.86	2.71	3.46(2)	147.0
N1'b-H2'b...Br3 #7	0.86	2.63	3.307(15)	136.3
N2'b-H4'b...Br2 #8	0.86	2.52	3.192(16)	135.6
N3'b-H5'b...Br4 #6	0.86	2.58	3.232(17)	132.9
N3'b-H6'b...Br3 #6	0.86	2.75	3.535(19)	153.1

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+1,-y,-z #3 x+1,y,z #4 -x+1,-y+1,-z

#5 -x,-y+1,-z+1 #6 -x+1,-y,-z+1 #7 -x+1,-y+1,-z+1

#8 x-1,y,z+1

Table S4 Hydrogen bond lengths (Å) and angles (°) for $IGPbBr_4$ at 298 K

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N4-H7...Br4	0.86	2.54	3.370(16)	161.9
N5-H8...Br1#1	0.86	2.86	3.471(19)	129.2
N5-H8...Br1 #5	0.86	2.97	3.58(2)	130.1
C2-H9...Br3 #1	0.93	2.87	3.61(2)	137.4
C3-H10...Br4 #6	0.93	2.79	3.70(2)	164.3
N1a-H1a...Br1 #7	0.86	2.76	3.59(2)	161.0
N1a-H2a...Br4 #6	0.86	2.79	3.571(19)	151.9
N2a-H3a...Br5 #8	0.86	2.80	3.540(18)	145.2
N2a-H4a...Br3 #7	0.86	2.82	3.61(2)	154.4
N3a-H5a...Br2 #8	0.86	2.71	3.51(2)	154.8
N3a-H6a...Br3 #6	0.86	2.83	3.58(2)	146.8
N1'b-H1'b...Br1 #7	0.86	2.63	3.44(5)	157.5
N1'b-H2'b...Br3 #7	0.86	2.70	3.43(5)	144.4
N2'b-H3'b...Br2 #8	0.86	2.66	3.31(5)	132.8
N2'b-H4'b...Br5 #8	0.86	2.76	3.61(5)	168.7
N3'b-H5'b...Br4 #6	0.86	2.59	3.30(5)	141.4
N3'b-H6'b...Br3 #6	0.86	2.75	3.535(19)	153.1

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+1,-y,-z #3 x+1,y,z #4 -x+1,-y+1,-z

#5 -x,-y+1,-z+1 #6 -x+1,-y,-z+1 #7 -x+1,-y+1,-z+1

#8 x-1,y,z+1

Table S5 Hydrogen bond lengths (Å) and angles (°) for $TGPbBr_4$ at 93 K

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1...Br2 #5	0.86	2.65	3.474(6)	161.0
N1-H2...Br4 #6	0.86	2.91	3.692(6)	152.4
N2-H3...Br4 #6	0.86	2.73	3.548(7)	160.0
N2-H4...Br4 #1	0.86	2.72	3.461(6)	145.0
N3-H5...Br2 #7	0.86	2.92	3.376(6)	114.7
N3-H5...Br2 #5	0.86	3.10	3.829(6)	143.7
N3-H6...N6	0.86	2.21	3.014(9)	155.6
N4-H7...Br1 #8	0.86	2.99	3.509(7)	120.7
N4-H7...Br3 #9	0.86	2.70	3.388(6)	137.9
N5-H8...Br4	0.86	2.39	3.240(6)	169.1
C2-H9...Br1 #8	0.93	3.07	3.551(8)	114.2
C2-H9...Br3 #2	0.93	2.95	3.735(8)	143.5
C3-H10...Br2 #9	0.93	2.77	3.657(8)	159.4

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 x,-y+1/2,z-1/2 #3 x-1,y,z #4 x,-y+1/2,z+1/2

#5 -x+1,-y+1,-z+1 #6 -x+2,-y+1,-z+1 #7 x,y,z-1

#8 x+1,-y+1/2,z-1/2 #9 x+1,y,z-1

Table S6 Hydrogen bond lengths (Å) and angles (°) for $TGPbBr_4$ at 298 K

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1...Br2	0.86	2.80	3.625(3)	160.1
N1-H2...Br2 #3	0.86	2.80	3.625(3)	160.1
N2-H3...Br2	0.86	2.99	3.770(10)	151.0
N2-H4...Br2 #7	0.86	2.91	3.401(8)	118.0
N2-H4...N3 #8	0.86	2.51	3.305(12)	153.5
N4-H5...Br1 #9	0.86	3.06	3.595(7)	122.1
N4-H5...Br3 #1	0.86	2.83	3.553(6)	142.4
C-N4-H5...Br1 #9	0.86	3.06	3.595(7)	122.1
C-N4-H5...Br3 #1	0.86	2.83	3.553(6)	142.4
C2-H8...Br2	0.86	2.58	3.409(7)	161.2
N-C2-H8...Br2	0.86	2.58	3.409(7)	161.2

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2 #2 x+1,y,z #3 -x,y,-z+1/2

#4 -x,y,-z+3/2 #5 x-1,y,z #6 -x+1,-y+1,-z

#7 -x+1,-y+2,-z+1 #8 -x,-y+2,-z+1 #9 -x,-y+1,-z+1

The bond length distortion of the $PbBr_6$ octahedra in each composition at both 93 and 298 K was calculated using eq. 1[7], where *d* is the average Pb-Br bond distance and d_n are the six individual bond distances. The bond angle variance of each octahedron from the ideal 90° of an undistorted structure was calculated using eq. 2[8], where θ_i is the individual Br-Pb-Br angle.

$$\Delta d = \left(\frac{1}{6}\right)\sum\left[\frac{d_n - d}{d}\right]^2 \quad (1)$$

$$\sigma^2 = \sum_{i=1}^{12}\frac{(\theta_i - 90)^2}{11} \quad (2)$$

Table S7 Calculated bond length distortions and bond angle variance for $IGPbBr_4$ and $TGPbBr_4$ at 93 and 298 K

Temperature	**Δd (×10^{-4})**	**σ^2**
$IGPbBr_4$ (93 K)	7.39	16.16
$IGPbBr_4$ (298 K)	8.91	7.71
$TGPbBr_4$ (93 K)	10.97	28.22
$TGPbBr_4$ (298 K)	7.59	22.06

Computational Study

For comparison with the previously estimated empirical effective radii, molecular volumes were first calculated (Method 1) from quantum-chemical calculations (B3LYP-D3 level), obtained from integration over the total electron densities. The resulting radii, given in Table 1, were then calculated for spheres with the same volumes. Arguably for most molecular cations, especially for the "planar" ones considered here, the approximation of the molecule as a sphere may not be very accurate. For an alternative modelling of the coordination environment (Method 2), we chose to optimise the cation within an idealised Ne_{12} cuboctahedron (to mimic the 12-fold coordination of the ideal perovskite A-site by closed-shell anions) with the ions encapsulated (see Figure S11 for an example) and used the resulting optimised Ne-Ne distances (d_{opt}, see Table S8) to calculate the ionic radii in Table 1.

Table S8 Molecular volumes and ionic radii computed at the B3LYP-D3/6-31+G(d,p) level

Cation[i]	***V*** **[Å³]**	r_{calc} **[pm]**[ii]	d_{opt} **[pm]**[iii]	r'_{calc} **[pm]**[iii]
NH_4^+	30.46	193.7	310.4	176.8
MAH^+	54.25	234.8	306.7	227.1
FAH^+	63.13	247.0	379.0	245.4
HAH^+	48.26	225.9	346.4	212.8
AZH^+	88.44	276.4	405.3	271.7
HYH^+	42.63	216.7	335.2	201.6
EAH^+	77.88	264.9	395.2	261.6
DMH^+	77.92	265.0	397.1	263.4
TMH^+	124.1	309.4	440.3	306.7
ImH^+	85.82	273.6	406.4	272.8
GuH^+	79.27	266.4	405.2	271.6
TzH^+	80.41	267.8	402.8	269.2

i. MaH^+ = methylammonium; FAH^+ = formamidinium; HAH^+ = hydrazinium; AZH^+ = azetidinium; HYH^+ = hydroxylammonium; EAH^+ = ethylammonium; DMH^+ = dimethylammonium; TMH^+ = tetramethylammonium.
ii. Calculated for a sphere with volume *V* (Method 1).
iii. From optimisations inside a Ne_{12} cuboctahedron (Method 2).

Geometries for isolated cations were fully optimized at the B3LYP-D3/6-31G+(d,p) level[9,10] of density functional theory (DFT), including Grimme's empirical dispersion[10] correction with Becke-Johnson damping,[11] together with a fine integration grid (75 radial shells with 302 angular points per shell). The

nature of the minima was verified by computations of the harmonic frequencies at the same level of theory. Molecular volumes *V* were computed from a Monte Carlo integration of the volume inside an isodensity surface (ρ = 0.001 electrons/Bohr^3) and a dense grid for evaluating the density (10^6 points per Bohr^3). The ionic radius r_{calc} was then evaluated for a sphere with the same volume, *V*. In addition, B3LYP-D3/6-31G+(d,p) optimisations were performed for the ions placed inside a cuboctahedron of 12 neon atoms, constrained at ideal atomic positions corresponding to O_h symmetry. Besides the single degree of freedom for the constrained Ne_{12} cluster (the Ne-Ne distance), all atomic degrees of freedom of the ions were optimised without constraints. The ionic radius r'_{calc} was then obtained from the optimised Ne-Ne distances d_{opt} *via*

$$r_{calc}^{'} = d_{opt} - \frac{1}{2}d_0 \qquad (\mathbf{3})$$

where d_0 was taken as the Ne-Ne distance from a fully optimised Ne_{12} cluster with a proton at the centre (267.2 pm, O_h symmetry imposed).

To probe for the dependence of the molecular volume on the level of theory, the calculations for dimethylammonium ion, $NH_2Me_2^+$, were repeated with a few other selected method/basis-set combinations (see Table S9). All resulting radii were within 2.5 pm of each other, indicating that the B3LYP-D3/6-31+G(d,p) values used for the other ions should be qualitatively reliable.

Table S9: Computed molecular volume *V* and resulting radius r_{calc} of dimethylammonium, $NH_2Me_2^+$, obtained at different levels of theory

Method / basis set	***V* [Å^3]**	**r_{calc} [pm]^a**
B3LYP/6-31+G(d,p)	77.94	265.0
B3LYP-D3/6-31+G(d,p)	77.92	265.0
B3LYP-D3/aug-cc-pVDZ[12]	77.56	264.5
B3LYP-D3/aug-cc-pVTZ[12]	75.86	262.6
PBE0[13,14] -D3/6-31+G(d,p)	77.51	264.5
PBE[13]-D3/6-31+G(d,p)	78.22	265.3
M06-2X[15]/6-31+G(d,p)	77.50	264.5
MP2/6-31+G(d,p)	78.04	265.1
MP2/cc-pVTZ	77.46	264.4

^{a}Calculated for a sphere with volume *V*.

All computations were performed using the Gaussian09 suite of programs.[16]

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Cartesian coordinates (in Å, B3LYP-D3 optimised)

H+@Ne12

Ne	0.000000	-1.889700	1.889700
Ne	0.000000	1.889700	1.889700
Ne	0.000000	1.889700	-1.889700
Ne	0.000000	-1.889700	-1.889700
Ne	1.889700	0.000000	1.889700
Ne	1.889700	1.889700	0.000000
Ne	1.889700	0.000000	-1.889700
Ne	1.889700	-1.889700	0.000000
Ne	-1.889700	0.000000	1.889700
Ne	-1.889700	1.889700	0.000000
Ne	-1.889700	0.000000	-1.889700
Ne	-1.889700	-1.889700	0.000000
H	0.000000	0.000000	0.000000

NH4+

N	0.000000	0.000000	0.000000
H	0.592773	0.592773	0.592773
H	-0.592773	-0.592773	0.592773
H	-0.592773	0.592773	-0.592773
H	0.592773	-0.592773	-0.592773

NH4+@Ne12

Ne	0.013105	2.265604	2.122293
Ne	0.062067	-2.122149	2.265070
Ne	-0.013079	-2.265751	-2.122286
Ne	-0.062041	2.122002	-2.265063
Ne	-2.157130	0.048485	2.232033
Ne	-2.170222	-2.217193	0.109743
Ne	-2.232276	-0.095117	-2.155323
Ne	-2.219184	2.170560	-0.033033
Ne	2.232302	0.094970	2.155330
Ne	2.219210	-2.170708	0.033040
Ne	2.157156	-0.048632	-2.232026
Ne	2.170248	2.217046	-0.109736
N	-0.000163	0.000752	-0.000085
H	-0.602043	0.830596	-0.034984
H	-0.583828	-0.840504	0.056566
H	0.577958	-0.039192	-0.846161
H	0.607482	0.052671	0.824729

NH3Me+

N	0.000000	0.000000	0.712569
C	0.000000	0.000000	-0.803803
H	0.000000	0.954555	1.089224
H	-0.826669	-0.477278	1.089224
H	0.826669	-0.477278	1.089224
H	0.000000	-1.034670	-1.144279
H	-0.896051	0.517335	-1.144279
H	0.896051	0.517335	-1.144279

NH3Me+@Ne12

Ne	3.607248	0.000000	0.000000
Ne	0.000000	-3.607248	0.000000
Ne	-3.607248	0.000000	0.000000
Ne	0.000000	3.607248	0.000000
Ne	1.803624	-1.803624	2.550709
Ne	-1.803624	-1.803624	2.550709
Ne	-1.803624	1.803624	2.550709
Ne	1.803624	1.803624	2.550709
Ne	1.803624	-1.803624	-2.550709
Ne	-1.803624	-1.803624	-2.550709
Ne	-1.803624	1.803624	-2.550709
Ne	1.803624	1.803624	-2.550709
N	-0.460630	0.457777	0.506152
C	0.267610	-0.268597	-0.598733
H	-0.301598	1.470042	0.458176
H	-1.473051	0.302624	0.453015
H	-0.148552	0.140784	1.429733
H	0.066213	-1.331801	-0.495611
H	-0.102234	0.102355	-1.552104
H	1.330609	-0.067109	-0.493785

CH(NH2)2+

C	0.000000	0.000000	0.429127
H	0.000000	0.000000	1.515793
N	0.000000	1.166785	-0.175772
N	0.000000	-1.166785	-0.175772
H	0.000391	2.019690	0.370337
H	-0.000391	-2.019690	0.370337
H	0.000209	1.268494	-1.185212
H	-0.000209	-1.268494	-1.185212

CH(NH2)2+@Ne12

Ne	3.790043	0.000000	0.000000
Ne	0.000000	-3.790043	0.000000
Ne	-3.790043	0.000000	0.000000
Ne	0.000000	3.790043	0.000000
Ne	1.895022	-1.895022	2.679965
Ne	-1.895022	-1.895022	2.679965
Ne	-1.895022	1.895022	2.679965
Ne	1.895022	1.895022	2.679965
Ne	1.895022	-1.895022	-2.679965
Ne	-1.895022	-1.895022	-2.679965
Ne	-1.895022	1.895022	-2.679965
Ne	1.895022	1.895022	-2.679965
C	-0.426288	0.427795	0.002567
H	-1.193545	1.196267	0.002815
N	0.826154	0.821324	0.004555
N	-0.821801	-0.824027	0.000476
H	1.042011	1.809693	0.005542
H	-1.810511	-1.038157	-0.001962
H	1.610354	0.178822	0.001837
H	-0.180573	-1.609243	0.000659

N2H5+

N	-0.045023	-0.661353	0.000000
N	-0.045023	0.786102	0.000000
H	0.877781	-1.124386	0.000000
H	-0.571319	-0.981919	0.822757
H	-0.571319	-0.981919	-0.822757
H	0.447589	1.107491	0.832811
H	0.447589	1.107491	-0.832811

N2H5+@Ne12

Ne	3.463806	0.000000	0.000000
Ne	0.000000	-3.463806	0.000000
Ne	-3.463806	0.000000	0.000000
Ne	0.000000	3.463806	0.000000
Ne	1.731903	-1.731903	2.449281
Ne	-1.731903	-1.731903	2.449281
Ne	-1.731903	1.731903	2.449281
Ne	1.731903	1.731903	2.449281
Ne	1.731903	-1.731903	-2.449281
Ne	-1.731903	-1.731903	-2.449281
Ne	-1.731903	1.731903	-2.449281
Ne	1.731903	1.731903	-2.449281
N	-0.033173	-0.712046	0.003140
N	-0.104918	0.729270	-0.001517
H	0.912329	-1.122905	0.015118
H	-0.549052	-1.057940	0.821320
H	-0.530516	-1.062317	-0.824585
H	0.365788	1.072610	0.833628
H	0.387464	1.068368	-0.825858

cyclo-(CH2)3(NH2)+

C	-0.095567	-0.024387	1.078847
C	-0.095567	-0.024387	-1.078847
C	-0.095567	-1.129548	0.000000
N	0.252297	1.017777	0.000000
H	-1.076997	0.213429	1.488919
H	-1.076997	0.213429	-1.488919
H	0.818152	-1.725993	0.000000
H	1.242842	1.274518	0.000000
H	0.651144	-0.059473	1.871085
H	0.651144	-0.059473	-1.871085

```
 H   -0.959461   -1.793105    0.000000
 H   -0.295701    1.882167    0.000000

cyclo-(CH2)3(NH2)+@Ne12
Ne    4.053149    0.000000    0.000000
Ne    0.000000   -4.053149    0.000000
Ne   -4.053149    0.000000    0.000000
Ne    0.000000    4.053149    0.000000
Ne    2.026574   -2.026574    2.866009
Ne   -2.026574   -2.026574    2.866009
Ne   -2.026574    2.026574    2.866009
Ne    2.026574    2.026574    2.866009
Ne    2.026574   -2.026574   -2.866009
Ne   -2.026574   -2.026574   -2.866009
Ne   -2.026574    2.026574   -2.866009
Ne    2.026574    2.026574   -2.866009
 C    0.124765    0.224626    1.076920
 C    0.122007    0.223461   -1.078055
 C   -0.510415   -0.680136    0.000726
 N    0.995089    0.890387   -0.002040
 H   -0.542693    0.974556    1.495504
 H   -0.546515    0.972944   -1.495623
 H   -0.104452   -1.691070    0.000766
 H    1.960311    0.552943   -0.003087
 H    0.724043   -0.232824    1.861093
 H    0.719218   -0.234793   -1.863347
 H   -1.598236   -0.727321    0.002114
 H    1.017684    1.913023   -0.002637

NH3OH+
 N    0.042868   -0.628089    0.000000
 O    0.042868    0.780217    0.000000
 H    1.040013   -0.885953    0.000000
 H   -0.396723   -1.017599    0.848253
 H   -0.396723   -1.017599   -0.848253
 H   -0.889596    1.076042    0.000000

NH3OH+@Ne12
Ne    3.352029    0.000000    0.000000
Ne    0.000000   -3.352029    0.000000
Ne   -3.352029    0.000000    0.000000
Ne    0.000000    3.352029    0.000000
Ne    1.676015   -1.676015    2.370242
Ne   -1.676015   -1.676015    2.370242
Ne   -1.676015    1.676015    2.370242
Ne    1.676015    1.676015    2.370242
Ne    1.676015   -1.676015   -2.370242
Ne   -1.676015   -1.676015   -2.370242
Ne   -1.676015    1.676015   -2.370242
Ne    1.676015    1.676015   -2.370242
 N   -0.064506   -0.625666   -0.005170
 O    0.003000    0.774570    0.073092
 H    0.464813   -0.959261    0.812223
 H   -1.033605   -0.967805    0.068328
 H    0.385871   -0.988208   -0.858233
 H   -0.474941    1.134148   -0.699720

NH3Et+
 C    1.315237   -0.141972    0.000000
 C    0.000000    0.614640    0.000000
 N   -1.177659   -0.363150    0.000000
 H    2.132763    0.583771    0.000000
 H    1.429540   -0.764697    0.892820
 H    1.429540   -0.764697   -0.892820
 H   -1.150840   -0.971414    0.826062
 H   -2.080454    0.124006    0.000000
 H   -1.150840   -0.971414   -0.826062
 H   -0.128757    1.235242    0.888845
 H   -0.128757    1.235242   -0.888845

NH3Et+@Ne12
Ne    3.951751    0.000000    0.000000
Ne    0.000000   -3.951751    0.000000
Ne   -3.951751    0.000000    0.000000
Ne    0.000000    3.951751    0.000000
Ne    1.975876   -1.975876    2.794310
Ne   -1.975876   -1.975876    2.794310
Ne   -1.975876    1.975876    2.794310
Ne    1.975876    1.975876    2.794310
Ne    1.975876   -1.975876   -2.794310
Ne   -1.975876   -1.975876   -2.794310
Ne   -1.975876    1.975876   -2.794310
Ne    1.975876    1.975876   -2.794310
 C   -0.087442    0.079917    0.662921
 N   -1.055626    1.048631   -0.011142
 H   -1.597650    1.582606    0.675682
 H   -0.552898    1.718173   -0.602542
 H   -1.717972    0.547247   -0.611792
 C    0.691030   -0.687601   -0.387337
 H    1.289467   -0.021026   -1.014963
 H    1.378023   -1.373805    0.112725
 H    0.031698   -1.285846   -1.022763
 H    0.552892    0.690642    1.300510
 H   -0.700032   -0.567843    1.291053

NH2Me2+
 N    0.000000    0.000000    0.542423
 C    0.000000    1.266413   -0.276762
 H    0.000000    2.121725    0.399124
 H    0.894660    1.271572   -0.899018
 H   -0.894660    1.271572   -0.899018
 C    0.000000   -1.266413   -0.276762
 H    0.894660   -1.271572   -0.899018
 H    0.000000   -2.121725    0.399124
 H   -0.894660   -1.271572   -0.899018
 H    0.817811    0.000000    1.161006
 H   -0.817811    0.000000    1.161006

NH2Me2+@Ne12
Ne    3.971468    0.000000    0.000000
Ne    0.000000   -3.971468    0.000000
Ne   -3.971468    0.000000    0.000000
Ne    0.000000    3.971468    0.000000
Ne    1.985734   -1.985734    2.808252
Ne   -1.985734   -1.985734    2.808252
Ne   -1.985734    1.985734    2.808252
Ne    1.985734    1.985734    2.808252
Ne    1.985734   -1.985734   -2.808252
Ne   -1.985734   -1.985734   -2.808252
Ne   -1.985734    1.985734   -2.808252
Ne    1.985734    1.985734   -2.808252
 N    0.049129    0.040422    0.626239
 C   -0.844077    0.915810   -0.212149
 H   -1.429911    1.560199    0.440706
 H   -0.212442    1.510608   -0.869744
 H   -1.495949    0.269873   -0.797970
 C    0.898698   -0.887883   -0.200312
 H    1.522061   -0.281470   -0.855037
 H    1.515029   -1.494143    0.460832
 H    0.234757   -1.518516   -0.789097
 H    0.653515    0.628151    1.210526
 H   -0.523424   -0.508224    1.276779

NMe4+
 N    0.000000    0.000000    0.000000
 C    0.870441    0.870441    0.870441
 H    0.231575    1.494862    1.494862
 H    1.494862    0.231575    1.494862
 H    1.494862    1.494862    0.231575
 C   -0.870441   -0.870441    0.870441
 H   -1.494862   -0.231575    1.494862
 H   -1.494862   -1.494862    0.231575
 H   -0.231575   -1.494862    1.494862
 C    0.870441   -0.870441   -0.870441
 H    0.231575   -1.494862   -1.494862
 H    1.494862   -0.231575   -1.494862
 H    1.494862   -1.494862   -0.231575
 C   -0.870441    0.870441   -0.870441
 H   -0.231575    1.494862   -1.494862
 H   -1.494862    0.231575   -1.494862
 H   -1.494862    1.494862   -0.231575

NMe4+@Ne12
Ne    4.402983    0.000000    0.000000
```

```
Ne     0.000000   -4.402983    0.000000
Ne    -4.402983    0.000000    0.000000
Ne     0.000000    4.402983    0.000000
Ne     2.201491   -2.201491    3.113379
Ne    -2.201491   -2.201491    3.113379
Ne    -2.201491    2.201491    3.113379
Ne     2.201491    2.201491    3.113379
Ne     2.201491   -2.201491   -3.113379
Ne    -2.201491   -2.201491   -3.113379
Ne    -2.201491    2.201491   -3.113379
Ne     2.201491    2.201491   -3.113379
 N     0.000036   -0.000508    0.000270
 C     0.867434    0.866333    0.872218
 H     0.226097    1.488280    1.495723
 H     1.489252    0.224539    1.495409
 H     1.493976    1.492723    0.237368
 C    -0.868386   -0.868922    0.869611
 H    -1.491385   -0.228276    1.492770
 H    -1.493708   -1.494638    0.232918
 H    -0.227765   -1.491524    1.493189
 C     0.868191   -0.867663   -0.870601
 H     0.227364   -1.489422   -1.494817
 H     1.490984   -0.226154   -1.493091
 H     1.493731   -1.494239   -0.234971
 C    -0.867086    0.868152   -0.870115
 H    -0.225541    1.490627   -1.492877
 H    -1.489479    0.227691   -1.494081
 H    -1.493071    1.493995   -0.234189

ImH+
 C     0.000000    0.000000    1.143576
 H     0.000000    0.000000    2.223237
 N     0.000000    1.074578    0.348605
 N     0.000000   -1.074578    0.348605
 C     0.000000    0.681873   -0.978521
 C     0.000000   -0.681873   -0.978521
 H     0.000000    2.033122    0.680122
 H     0.000000   -2.033122    0.680122
 H     0.000000    1.390839   -1.791575
 H     0.000000   -1.390839   -1.791575

ImH+@Ne12
Ne     4.063937    0.000000    0.000000
Ne     0.000000   -4.063937    0.000000
Ne    -4.063937    0.000000    0.000000
Ne     0.000000    4.063937    0.000000
Ne     2.031968   -2.031968    2.873637
Ne    -2.031968   -2.031968    2.873637
Ne    -2.031968    2.031968    2.873637
Ne     2.031968    2.031968    2.873637
Ne     2.031968   -2.031968   -2.873637
Ne    -2.031968   -2.031968   -2.873637
Ne    -2.031968    2.031968   -2.873637
Ne     2.031968    2.031968   -2.873637
 C    -0.000042    0.000711    1.459124
 H    -0.000282    0.000490    2.537474
 N     0.000077    1.074437    0.664549
 N     0.000204   -1.072733    0.664121
 C     0.000394    0.682943   -0.662601
 C     0.000478   -0.680714   -0.662861
 H    -0.000037    2.032849    0.993578
 H     0.000195   -2.031261    0.992808
 H     0.000568    1.392068   -1.473297
 H     0.000681   -1.389506   -1.473859

C(NH2)3+
 C     0.000000    0.000000    0.000000
 N     0.000000    1.336715    0.000000
 N     1.157629   -0.668358    0.000000
 N    -1.157629   -0.668358    0.000000
 H     0.839925    1.862743    0.195204
 H     1.193221   -1.658768    0.195204
 H    -2.033145   -0.203976    0.195204
 H    -0.839925    1.862743   -0.195204
 H     2.033145   -0.203976   -0.195204
 H    -1.193221   -1.658768   -0.195204

C(NH2)3+@Ne12
Ne     4.052186    0.000000    0.000000
Ne     0.000000   -4.052186    0.000000
Ne    -4.052186    0.000000    0.000000
Ne     0.000000    4.052186    0.000000
Ne     2.026093   -2.026093    2.865328
Ne    -2.026093   -2.026093    2.865328
Ne    -2.026093    2.026093    2.865328
Ne     2.026093    2.026093    2.865328
Ne     2.026093   -2.026093   -2.865328
Ne    -2.026093   -2.026093   -2.865328
Ne    -2.026093    2.026093   -2.865328
Ne     2.026093    2.026093   -2.865328
 C     0.025676   -0.326983    0.057648
 N     0.065167    1.005610    0.160089
 N     1.161023   -1.028231    0.022569
 N    -1.149475   -0.956902   -0.011108
 H     0.916875    1.488813    0.406405
 H     1.157645   -2.032965    0.117478
 H    -2.015252   -0.480012    0.191487
 H    -0.758425    1.569597    0.008995
 H     2.053838   -0.577404   -0.110409
 H    -1.205577   -1.933383   -0.260086

TzH+
 C     1.079126    0.331603    0.000000
 H     2.112004    0.650347    0.000000
 N     0.000000    1.101013    0.000000
 N     0.617538   -0.927637    0.000000
 C    -0.759447   -0.861305    0.000000
 H    -0.040684    2.116263    0.000000
 H     1.187204   -1.768547    0.000000
 H    -1.411198   -1.722792    0.000000
 N    -1.155452    0.384187    0.000000

TzH+@Ne12
Ne     4.027922    0.000000    0.000000
Ne     0.000000   -4.027922    0.000000
Ne    -4.027922    0.000000    0.000000
Ne     0.000000    4.027922    0.000000
Ne     2.013961   -2.013961    2.848171
Ne    -2.013961   -2.013961    2.848171
Ne    -2.013961    2.013961    2.848171
Ne     2.013961    2.013961    2.848171
Ne     2.013961   -2.013961   -2.848171
Ne    -2.013961   -2.013961   -2.848171
Ne    -2.013961    2.013961   -2.848171
Ne     2.013961    2.013961   -2.848171
 C    -0.908905   -0.042791    0.691265
 H    -1.906215   -0.130199    1.093636
 N    -0.123674   -1.021756    0.268706
 N    -0.203905    1.082664    0.512220
 C     1.013323    0.724201   -0.022707
 H    -0.320510   -2.018283    0.252628
 H    -0.516048    2.022103    0.735654
 H     1.796686    1.423565   -0.271219
 N     1.078684   -0.571808   -0.179513
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