

Bis(1-phenylethylammonium) tetraiodoplumbate(II)

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Key indicators

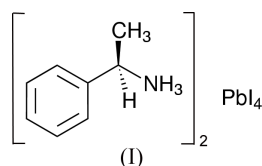
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$
 R factor = 0.024
 wR factor = 0.057
Data-to-parameter ratio = 27.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2[\text{PbI}_4]$, crystallizes as an organic–inorganic hybrid-perovskite, with Pb located on a centre of inversion. As such, it consists of layers of tilted corner-sharing iodoplumbate octahedra, parallel to the bc plane. Adjacent inorganic layers are separated by organic 1-phenylethylammonium layers. The individual organic cations are linked to the inorganic layer by hydrogen bonds, and to adjacent cations by π – π interactions.

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Comment

Self-assembling organic–inorganic hybrid perovskites have been the focus of a number of investigations in recent years. The fascination with these materials is generated by their interesting structural, magnetic, electrical, optical and chemical properties. A few hybrid perovskites have even been used for the construction of novel opto-electric devices. Moreover, the property of interest can easily be modified by replacement of the metal, halide or amine. For recent reviews, see Mitzi (1999, 2001).



The room-temperature structure of the title compound, (I), to the best of my knowledge, represents the first report of a hybrid perovskite that contains a chiral amine, albeit as the racemic mixture.

Fig. 1 shows the asymmetric unit of (I), with the atomic numbering scheme. The alternating perovskite sheets and ammonium cation layers of (I) are clearly visible in the packing diagram (Fig. 2). The perovskite sheets consist of tilted corner-sharing PbI_6 octahedra. Adjacent sheets have the octahedra eclipsed, when viewed down the c axis. The Pb–I bond length (Table 1) for the axial bond is 3.1896 (5) Å, while the equatorial bonds are either 3.2609 (4) or 3.3227 (9) Å in length. These, although marginally longer, compare favourably with those reported for $[\text{H}_3\text{N}(\text{CH}_2)_6\text{NH}_3]\text{PbI}_4$ by Mousdis *et al.* (2000). The bond angles around Pb vary between 84.770 (8) and 95.230 (8)°, while the *trans* angles are all 180°, as required by symmetry. The bridging angle Pb–I1–Pb^{iv} is 155.43 (1)° (Table 1), which is an indication of the rotation and tilt between adjacent octahedra. The 1-phenylethylammonium cation is hydrogen bonded to two axial and one equatorial halide ions (Table 2). The two axial hydrogen

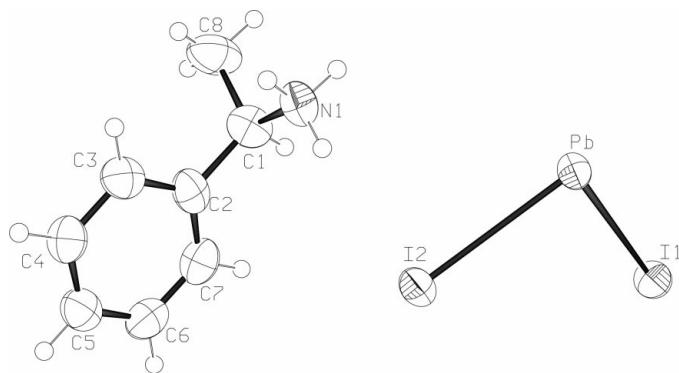


Figure 1
The asymmetric unit of (I), with crystallographic numbering and 50% probability displacement ellipsoids.

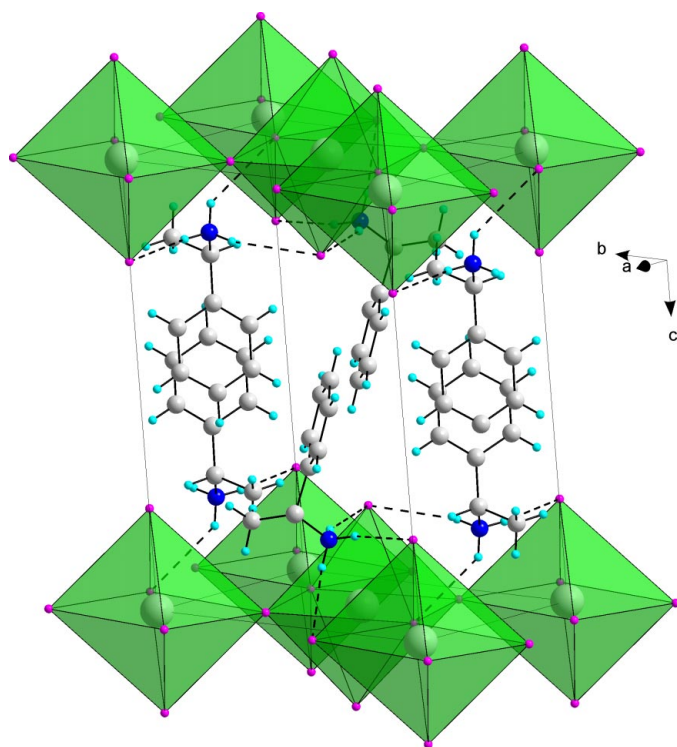


Figure 2
A packing diagram of (I), including hydrogen bonds.

bonds are similar in length to the average lengths reported by Steiner (1998) in his database study of hydrogen bonds involving halide ions. The hydrogen bond to the equatorial iodide anion possibly involves some bifurcation to another equatorial iodide. Within the organic layer, adjacent aromatic rings are separated by a centroid-to-centroid distance of 3.712 (3) Å, which is suggestive of π -stacking interactions.

Experimental

The crystal used in this study was obtained by slow evaporation of an acetonitrile solution that contained the stoichiometrically required amounts of lead nitrate and 1-phenylethylamine, together with an excess of hydroiodic acid.

Crystal data

(C₈H₁₂N)₂[PbI₄]
 $M_r = 959.16$
 Monoclinic, $P2_1/a$
 $a = 8.7935$ (11) Å
 $b = 9.3913$ (11) Å
 $c = 14.6428$ (18) Å
 $\beta = 100.093$ (2)°
 $V = 1190.5$ (3) Å³
 $Z = 2$

$D_x = 2.676$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 870 reflections
 $\theta = 3.0$ –28.2°
 $\mu = 12.27$ mm⁻¹
 $T = 293$ (2) K
 Rhomboid, orange
 0.30 × 0.26 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: numerical (XPREP; Bruker, 1999)
 $T_{\min} = 0.072$, $T_{\max} = 0.161$
 8011 measured reflections

2950 independent reflections
 2580 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -11 \rightarrow 11$
 $k = -9 \rightarrow 12$
 $l = -18 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(\text{that})] = 0.024$
 $wR(F^2) = 0.057$
 $S = 1.05$
 2950 reflections
 107 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 0.4657P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.006$
 $\Delta\rho_{\text{max}} = 0.83$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.52$ e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.00101 (9)

Table 1

Selected geometric parameters (Å, °).

I1–Pb	3.2609 (4)	Pb–I1 ⁱⁱ	3.3227 (4)
I2–Pb	3.1896 (5)	Pb–I1 ⁱⁱⁱ	3.3227 (4)
Pb–I1 ⁱ	3.2609 (4)		
Pb–I1–Pb ^{iv}	155.425 (11)	I1–Pb–I1 ⁱⁱ	93.532 (9)
I2–Pb–I1	90.531 (8)	I1 ⁱⁱ –Pb–I1 ⁱⁱⁱ	180.000 (10)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (iv) $\frac{1}{2}-x, y-\frac{1}{2}, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–HNA \cdots I2	0.89	2.78	3.605 (4)	154
N1–HNB \cdots I2 ^v	0.89	2.83	3.671 (4)	158
N1–HNC \cdots I1 ⁱⁱ	0.89	3.00	3.710 (4)	138

Symmetry codes: (ii) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (v) $\frac{1}{2}+x, \frac{3}{2}-y, z$.

All H atoms were refined in idealized positions in the riding-model approximation and with their isotropic displacement parameters fixed to $1.2U_{\text{eq}}$ of the equivalent isotropic displacement parameter of the atoms to which they are bonded.

Data collection: SMART-NT (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and DIAMOND (Brandenburg, 1999); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON (Spek, 2002).

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