

Bis(pentane-1,5-diammonium) decaiodotriplumbate(II)

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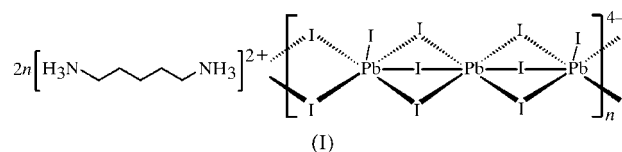
The title compound, $\{(\text{NH}_3\text{C}_5\text{H}_{10}\text{NH}_3)_2[\text{Pb}_3\text{I}_{10}]\}_n$, crystallizes as an organic–inorganic hybrid. As such, the structure consists of extended chains of $[\text{Pb}_3\text{I}_{10}]_n^{4n-}$ ions extending along [111]. The asymmetric unit contains two independent Pb atoms: one is in a general position and the other is on an inversion centre. Each Pb atom is octahedrally coordinated by six iodide ions and exhibits both face- and edge-sharing with adjacent atoms in the inorganic chain. The organic counter-ion, *viz.* pentane-1,5-diammonium, lies in channels formed by the chains and interacts with these chains *via* $\text{N}-\text{H}\cdots\text{I}$ hydrogen bonding.

Comment

In recent years, a significant number of organic–inorganic hybrid materials based on metal–halide units have been prepared and studied [for reviews, see Papavassiliou (1997) and Mitzi (1999)]. Haloplumbates, in particular, have demonstrated a propensity for forming a variety of crystalline structures by self-assembling from suitable solution mixtures. It has been shown that these structures can vary considerably, ranging from systems based on isolated molecules, to those containing infinite chains, as in $(\text{Me}_4\text{N})[\text{PbI}_3]$ (Contreras *et al.*, 1983), right up to two- or three-dimensional networks (Mitzi, 1999). The lead iodide octahedra can be connected in one of three ways, *viz.* face-sharing between two equatorial halides and one axial halide, edge-sharing between two equatorial halides, and corner-sharing *via* a single halide. It is also possible to have combinations of the various types of sharing in one chain, as in $[\text{Na}(\text{DMF})_3]_4[\text{Pb}_6\text{I}_{16}]$ (DMF is dimethylformamide) and $[\text{PrN}(\text{C}_2\text{H}_4)_3\text{NPr}][\text{Pb}_2\text{I}_6]$, in which the octahedra simultaneously share common faces, edges and vertices (Krautscheid *et al.*, 2001). The chains formed by the octahedra can be described by the shorthand notation $(f_m e)_n$ for m adjacent face-sharing octahedra, f , connected by octahedra sharing an edge, denoted e . Structures with $m = 3$ have been synthesized for lead iodide (Krautscheid & Vielsack, 1997; Maxcy *et al.*, 2003) and tin iodide (Lode & Krautscheid, 2001) octahedra. The case with $m = 1$ contains PbI_6 octahedra that

share a face with PbI_5 square pyramids, which in turn share an edge.

Pentadamine has previously been incorporated into the layered perovskite structure type. For example, single-crystal structures of $(\text{NH}_3\text{C}_5\text{H}_{10}\text{NH}_3)\text{CuX}_4$ ($X = \text{Cl}$ and Br ; Garland *et al.*, 1990) have been determined. In general, the hybrid perovskite family displays structural phase transitions resulting from conformational changes within the amine groups between the layers, as well as the slipping of layers with respect to one another. The temperatures at which the phase changes occur are dependent on the length of the chain, as can be seen for $[\text{NH}_3(\text{CH}_2)_n\text{NH}_3]\text{CdCl}_4$ ($n = 3, 4$ and 5 ; Kind *et al.*, 1981).



We present here the crystal structure of the title compound, (I), an $m = 3$ case, which contains $[\text{Pb}_3\text{I}_{10}]_n^{4n-}$ chains extending approximately along [111], with the pentadamine ion as counter-cation (Fig. 1). The asymmetric unit contains two crystallographically independent Pb atoms, *viz.* atoms Pb1 and Pb2. Each face-sharing monomer unit consists of two Pb2 octahedra and one Pb1 octahedron, where the central Pb1 octahedron is connected to the Pb2 octahedra by shared faces. The Pb2 octahedra are linked *via* edge-sharing at both ends to adjacent monomers. The overall repeat pattern can be represented as $(f_2 e)_3$ (Fig. 2).

Atom Pb1 is located on a centre of inversion, chosen for convenience as that at the centre of the unit cell, and is bonded to three unique halide atoms, *viz.* I1, I2 and I3, which then complete the full octahedron through the inversion centre. At the centre of a quadrilateral formed by atoms Pb2, I4, Pb2A and I4A [Pb2A and I4A are at the symmetry position $(-x, -y, -z)$]; Fig. 1] is a second inversion centre, chosen for convenience as the cell origin. Atom Pb2 is bonded to four unique

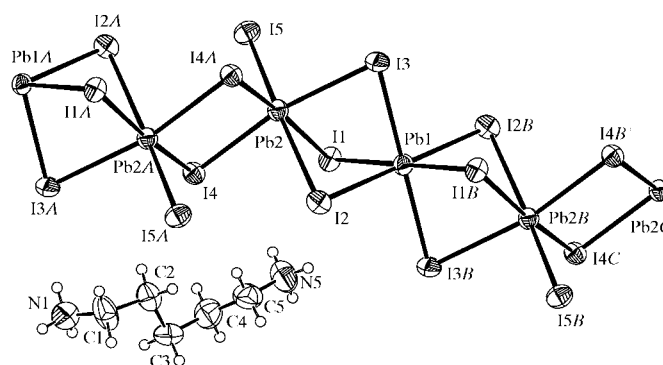


Figure 1

The asymmetric unit of (I) and some adjacent atoms, showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. Atoms labelled with the suffixes A, B and C are at the symmetry positions $(-x, -y, -z)$, $(1-x, 1-y, 1-z)$ and $(1+x, 1+y, 1+z)$, respectively.

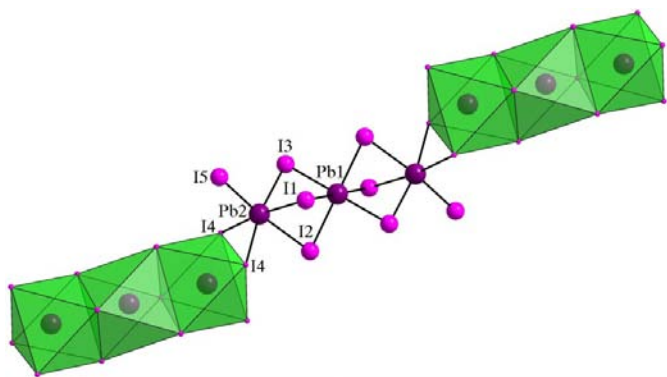


Figure 2
An illustration of the $(\text{Pb}_3\text{I}_{10})_n^{4n-}$ chain.

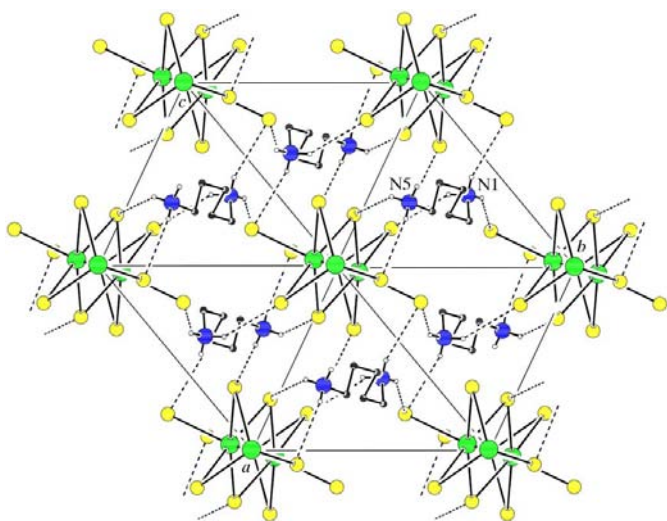


Figure 3
The crystal packing of (I), viewed along [111], showing the pseudo-hexagonal packing and the N—H...I hydrogen bonding (dashed lines).

halides, the extra halide, I4, being responsible for the edge-sharing between the Pb2 octahedra. This second inversion centre then generates the second I4 halide involved in edge-sharing. The metal–halide bond distances are very similar, possibly because of the lower strain imposed by the simpler sharing. Atoms I1, I2 and I3 participate in the face-sharing between the Pb1 and Pb2 octahedra. Axial atom I5 is the only halide not involved in any bonding to adjacent octahedra and has the shortest Pb—I distance [3.1221 (12) Å].

Atom Pb1 has a more regular coordination geometry, as it lies on an inversion centre, which ensures that all *trans* angles are exactly 180°; the Pb1 octahedron shares *trans* faces with the two adjacent Pb2 octahedra. Atom Pb2, in contrast, has a more distorted environment, with all *cis* and *trans* angles different (Table 1).

One unique inorganic chain runs through the unit cell along the body diagonal from (0, 0, 0) to (1, 1, 1). The Pb1 octahedron is located at the centre of the unit cell, with the two Pb2 octahedra located along the body diagonal and related by the inversion centres at (0, 0, 0) and (1, 1, 1). In the crystal

structure, the cations occupy channels that run parallel to the anion chains. Each diammonium cation is hydrogen bonded to three different chains in a pseudo-trigonal pattern. One anion chain lies along the body diagonal and the other two run through the corners of the unit cell in a pseudo-hexagonal pattern (Fig. 3).

Both ammonium groups on the cation form three hydrogen bonds to I atoms of the anion chains (details are given in Table 2). Ammonium atom N1 connects three chains, atom I5 being a bifurcated acceptor. The ammonium group containing atom N2 bonds to two chains. It connects *via* a short and a long hydrogen bond to atoms I2 and I4, respectively, and to a second chain *via* the N2—H2B...I1(−*x*, 1 − *y*, 1 − *z*) interaction.

The pentadiazonium ion exhibits two types of conformational arrangement between the four possible torsion angles. There are antiperiplanar C1—C2—C3—C4 and C3—C4—C5—N5 angles of 174.0 (15) and −179.2 (14)°, and synclinal (*gauche*) C2—C3—C4—C5 and N1—C1—C2—C3 angles of 59 (2) and −71 (2)°.

Experimental

PbI₂ (0.125 g, 0.271 mmol) and C₅H₁₆N₂ (0.031 g, 0.507 mmol) were added to HI (3 ml) and the mixture was heated until all the components had dissolved. The solution was allowed to cool to room temperature, whereupon yellow plate-shaped crystals formed. A single crystal suitable for X-ray diffraction analysis was selected and studied. Analysis calculated for C₁₀H₃₂I₁₀N₄Pb₃: C 5.72, H 1.54, N 2.67%; found: C 5.74, H 1.63, N 2.73%.

Crystal data

(C₅H₁₆N₂)₂[Pb₃I₁₀]
 $M_r = 2098.97$
 Triclinic, $P\bar{1}$
 $a = 8.8543$ (15) Å
 $b = 11.1457$ (19) Å
 $c = 11.5725$ (19) Å
 $\alpha = 109.624$ (3)°
 $\beta = 106.173$ (3)°
 $\gamma = 107.339$ (3)°
 $V = 931.4$ (3) Å³

$Z = 1$
 $D_x = 3.742$ Mg m^{−3}
 Mo $K\alpha$ radiation
 Cell parameters from 849 reflections
 $\theta = 2.6$ – 25°
 $\mu = 21.82$ mm^{−1}
 $T = 293$ (2) K
 Plate, yellow
 0.30 × 0.24 × 0.03 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: by integration (*XPREP* in *SAINTE-Plus*; Bruker, 1999)
 $T_{\min} = 0.026$, $T_{\max} = 0.643$
 5061 measured reflections

3257 independent reflections
 2593 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$
 $\theta_{\max} = 25^\circ$
 $h = -10 \rightarrow 7$
 $k = -13 \rightarrow 13$
 $l = -11 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.104$
 $S = 1.10$
 3257 reflections
 127 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 4.4173P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.25$ e Å^{−3}
 $\Delta\rho_{\min} = -1.19$ e Å^{−3}
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00170 (19)

Table 1

Selected geometric parameters (Å, °).

Pb1—I2	3.1998 (11)	Pb2—I4 ⁱ	3.1718 (12)
Pb1—I3	3.2226 (10)	Pb2—I1	3.3102 (12)
Pb1—I1	3.2275 (10)	Pb2—I2	3.3187 (12)
Pb2—I5	3.1221 (12)	Pb2—I3	3.3222 (11)
Pb2—I4	3.1680 (10)		
I4 ⁱ —Pb2—I1	172.40 (3)	I4—Pb2—I3	169.37 (3)
I5—Pb2—I2	168.97 (3)		

 Symmetry code: (i) $-x, -y, -z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots I3 ⁱ	0.89	3.02	3.806 (15)	149
N1—H1B \cdots I5 ⁱⁱ	0.89	2.93	3.669 (16)	142
N1—H1C \cdots I5 ⁱⁱⁱ	0.89	2.92	3.672 (15)	143
N5—H5A \cdots I1 ^{iv}	0.89	2.79	3.668 (14)	169
N5—H5B \cdots I2	0.89	2.87	3.531 (14)	132
N5—H5C \cdots I4	0.89	3.31	4.001 (16)	136

 Symmetry codes: (i) $-x, -y, -z$; (ii) $x-1, y, z-1$; (iii) $-1-x, -y, -z$; (iv) $-x, 1-y, 1-z$.

All H atoms were allowed for in idealized positions in the riding-model approximation [$C-H = 0.97$ Å, $N-H = 0.89$ Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$].

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *XPREP* in *SAINT-Plus* (Bruker, 1999); 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, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1746). Services for accessing these data are described at the back of the journal.

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