

## *catena*-Poly[tetrakis(3-phenylpropylammonium) [iodoplumbate(II)-tri- $\mu$ -iodo-plumbate(II)-tri- $\mu$ -iodo-iodo-plumbate(II)-di- $\mu$ -iodo]]

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Received 7 March 2006

Accepted 10 March 2006

Online 13 April 2006

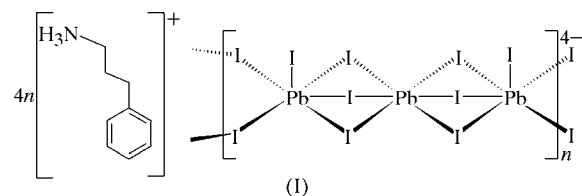
The title compound,  $\{(C_9H_{14}N)_4[Pb_3I_{10}]\}_n$ , crystallizes as an organic–inorganic hybrid. As such, the structure consists of a two-dimensional inorganic layer of  $[Pb_3I_{10}]_n^{4n-}$  ions extending along [100]. The asymmetric unit contains two independent Pb atoms, *viz.* one in a general position and the other on an inversion centre. Each Pb atom is octahedrally coordinated by six iodide ions and exhibits both face- and corner-sharing with adjacent atoms in the inorganic layer. These anionic layers alternate with 3-phenylpropylammonium cations, which hydrogen bond to the iodides. Simple face-to-edge  $\sigma$ – $\pi$  stacking interactions are observed between the aromatic rings that stabilize the overall three-dimensional structure. This net structure has only been observed five times previously.

### Comment

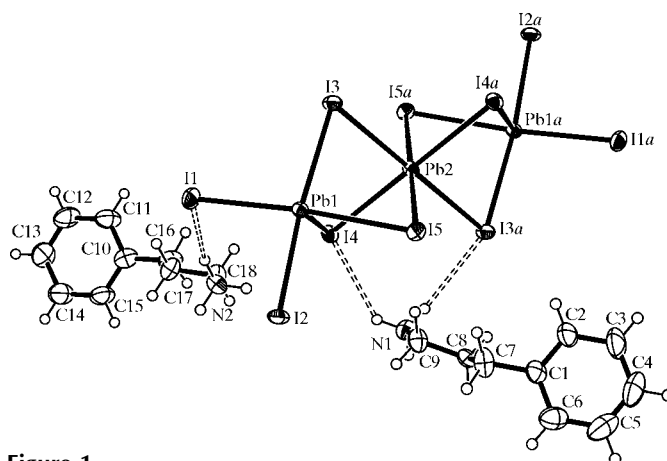
In recent years, a significant number of organic–inorganic hybrid materials based on lead and tin halide units have been prepared and studied; for reviews, see Papavassiliou (1997) and Mitzi (1999). Haloplumbates in particular have demonstrated a propensity for forming a great variety of crystalline structures. This diversity is a result of the metal–halide octahedra engaging in different combinations of face-, edge- and corner-sharing. As a result, the  $MX_6$  ( $X = Br$  and  $I$ , and  $M = Sn$  and  $Pb$ ) octahedral building blocks become severely distorted. One of the possible structural motifs forms two-dimensional layers, where chains of two or three *trans* face-sharing octahedra are connected *via* four halides on both ends. This situation can be summarized by the formula  $[M_nX_{3n+1}]^{(n+1)-}$ . To our knowledge, only one structure with  $n = 2$  has been reported; in this structure, isolated  $I^-$  anions lie between the lead iodide layers (Krautscheid *et al.*, 1998).

The case with  $n = 3$  has been observed with both lead bromide in  $(PhMe_3N)_4[Pb_3Br_{10}]$  (Wiest *et al.*, 1999) and tin iodide in  $(PhMe_3N)_4[Sn_3I_{10}]$  (Lode & Krautscheid, 2001). We

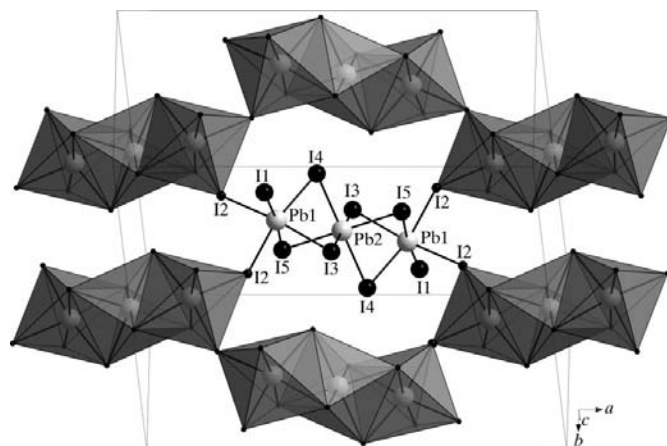
present here the synthesis and crystal structure of the title compound, (I), namely the  $n = 3$  case that has  $[Pb_3I_{10}]_n^{4n-}$  two-dimensional layers separated by 3-phenylpropylammonium cations.



The atomic numbering scheme of (I) is shown in Fig. 1. The  $[Pb_3I_{10}]_n^{4n-}$  building block has two crystallographically independent Pb atoms, *viz.* Pb1 and Pb2. Atom Pb2 is the central Pb atom and sits on an inversion centre through which the third Pb atom, Pb1( $-x + \frac{3}{2}, y + \frac{1}{2}, z$ ), is generated to complete the simplest repeat unit. The three Pb atoms are connected by sharing *trans* faces made up of  $\mu_2$ -I bridges, with atoms I3, I4 and I5 and their inversion equivalents related through Pb2. The outer octahedra on either end connect to adjacent


**Figure 1**

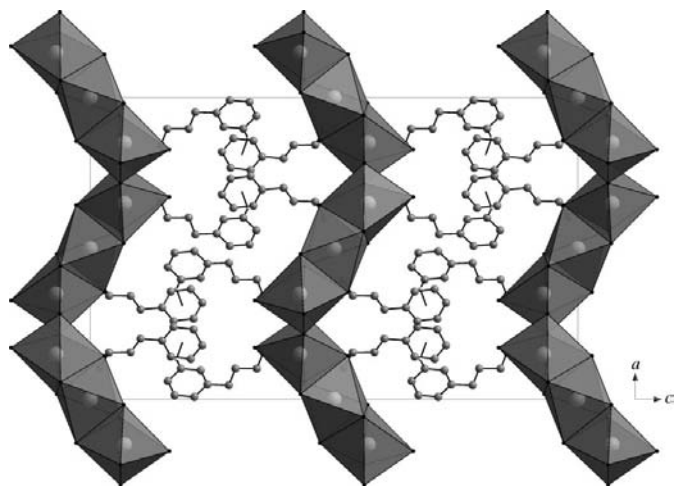
The asymmetric unit of (I) and some adjacent atoms, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms labelled with the suffix *a* are at the symmetry position ( $-x, -y, -z$ ).


**Figure 2**

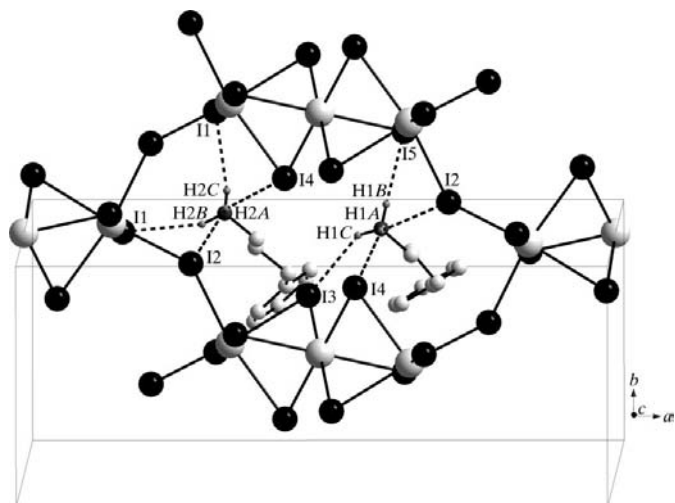
An illustration of the  $[Pb_3I_{10}]_n^{4n-}$  two-dimensional net.

$[\text{Pb}_3\text{I}_{10}]^{4-}$  units via  $\mu_2$ -I2 bridges (see Fig. 2) that are far from linear [ $\text{Pb}1^i - \text{I}2 - \text{Pb}1 = 142.51(3)^\circ$ ], in contrast to the almost linear bridges found in  $[\text{Sn}_3\text{I}_{10}]^{4-}$  [169.87(3) $^\circ$ ; Lode & Krautscheid, 2001]. The resulting inorganic layer sits in the *ab* plane and is corrugated as the trimeric units connect in an alternating *trans* fashion (see Fig. 3), as seen in  $(\text{C}_6\text{H}_5\text{NH}_3)_4[\text{Cd}_3\text{Br}_{10}]$  (Ishihara *et al.*, 1994) and  $[\text{C}_6\text{H}_5\text{CH}_2\text{SC}(\text{NH}_2)_2]_4[\text{Pb}_3\text{I}_{10}]$  (Raptopoulou *et al.*, 2002). In the other two  $n = 3$  structures mentioned above, the individual building blocks are *cis* related.

The Pb atoms show different degrees of distortion. The central Pb2 atom has three almost equal bond lengths to the I atoms [3.2006(7)–3.2090(7) Å]. This uniformity is due to the identical face-sharing that occurs with the neighbouring Pb1 atoms. The outer Pb1 octahedra are more distorted, with long Pb–I bond lengths in the range 3.2288(8)–3.3381(9) Å



**Figure 3**  
A packing diagram of (I), viewed along the *b* axis, showing the face-to-edge  $\sigma$ - $\pi$  interaction between cat1 and cat2 which forms a three-dimensional system.



**Figure 4**  
Hydrogen bridging interactions (dashed lines) between the ammonium heads and the halogen atoms of (I).

when face-sharing occurs, and short bond lengths to the corner-sharing I2 and the terminal non-bridging I1 atoms (see Table 1).

Sandwiched between the inorganic nets are two unique organic aromatic amines, denoted cat1 and cat2. Fig. 3 clearly shows the two-dimensional arrangement of the cations. Both propylammonium groups have an all-*trans* conformation, and they deviate by 9.3(11) and 14.2(11) $^\circ$  from the normal to the aromatic rings, respectively. The two ammonium groups display the same hydrogen-bonding scheme, *viz.* one bifurcated and two normal hydrogen bonds. The bifurcated bond distances are similar for atoms N1 and N2 as they both bond to atoms I4 (2.95 and 2.94 Å) and I2 (3.11 and 3.07 Å). In addition, atom N1 forms a long hydrogen bond and a short normal hydrogen bond (2.95 and 2.66 Å), as it bonds to an equatorial (I3) and an axial (I5) I atom, respectively. Atom N2, however, has two similar hydrogen bonds (2.82 and 2.84 Å), as they both bond to the axial atom I1, which is not involved in any bridging (see Fig. 4).

Between the aromatic rings of cat1 and cat2, a face-to-edge  $\sigma$ - $\pi$  interaction,  $\text{C}14 - \text{H}14 \cdots \text{C}g1(1 - x, 1 - y, 1 - z)$ , occurs with a distance of 2.92 Å and an angle of 143 $^\circ$ . This interaction is between two cations that hydrogen bond to adjacent two-dimensional nets and so form a three-dimensional system (see Fig. 3).

## Experimental

PbO (0.184 g, 0.824 mmol) and 3-phenylpropylamine (0.167 g, 1.23 mmol) were dissolved in HI (3 ml) and then heated to form a clear solution. Upon slow cooling to room temperature, yellow crystals formed. A single crystal suitable for X-ray diffraction was selected and mounted on a glass fibre. Analysis calculated for  $\text{C}_{36}\text{H}_{56}\text{I}_{10}\text{N}_4\text{Pb}_3$ : C 17.75, H 2.32, N 2.30%; found: C 18.96, H 2.55, N 2.55%.

### Crystal data

$(\text{C}_9\text{H}_{14}\text{N})_4[\text{Pb}_3\text{I}_{10}]$   
 $M_r = 2435.42$   
 Orthorhombic, *Pbca*  
 $a = 20.777(3)$  Å  
 $b = 8.4689(11)$  Å  
 $c = 33.550(5)$  Å  
 $V = 5903.3(14)$  Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 2.74$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 903 reflections  
 $\theta = 4.6$ – $56.5^\circ$   
 $\mu = 13.79$  mm<sup>-1</sup>  
 $T = 173(2)$  K  
 Rectangular block, yellow  
 0.37 × 0.21 × 0.07 mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: integration (*XPREP*; Bruker, 1999)  
 $T_{\min} = 0.073$ ,  $T_{\max} = 0.393$   
 27663 measured reflections

7120 independent reflections  
 5479 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.075$   
 $\theta_{\max} = 28^\circ$   
 $h = -27 \rightarrow 27$   
 $k = -10 \rightarrow 11$   
 $l = -44 \rightarrow 30$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.094$   
 $S = 1.14$   
 7120 reflections  
 217 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 63.008P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.49$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -2.10$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

C1—C7	1.490 (13)	I2—Pb1 <sup>i</sup>	3.1217 (8)
C7—C8	1.556 (15)	I2—Pb1	3.1492 (8)
C8—C9	1.508 (15)	I3—Pb2	3.2078 (7)
C9—N1	1.521 (14)	I3—Pb1	3.2288 (8)
C10—C16	1.513 (14)	I4—Pb2	3.2090 (7)
C16—C17	1.523 (18)	I4—Pb1	3.3077 (8)
C17—C18	1.483 (16)	I5—Pb2	3.2006 (7)
C18—N2	1.496 (16)	I5—Pb1	3.3381 (9)
I1—Pb1	3.1197 (9)		

 Symmetry code: (i)  $-x + \frac{3}{2}, y - \frac{1}{2}, z$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...I4	0.91	2.95	3.655 (9)	136
N1—H1A...I2 <sup>i</sup>	0.91	3.11	3.676 (9)	122
N1—H1B...I5 <sup>ii</sup>	0.91	2.66	3.561 (9)	172
N1—H1C...I3 <sup>iii</sup>	0.91	2.95	3.750 (10)	148
N2—H2A...I4	0.91	2.94	3.641 (9)	135
N2—H2A...I2 <sup>i</sup>	0.91	3.07	3.629 (10)	122
N2—H2B...I1 <sup>i</sup>	0.91	2.82	3.677 (9)	159
N2—H2C...I1	0.91	2.84	3.680 (11)	155

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

All H atoms were allowed for in idealized positions in the riding-model approximation (C—H = 0.95 and 0.99 Å), with their  $U_{\text{iso}}(\text{H})$  values fixed at  $1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{N})$ .

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-Plus* (Bruker, 1999) and *SHELXTL* (Bruker, 1999); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

The University of the Witwatersrand is thanked for the award of a research grant and for providing the infrastructure required to carry out this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3008). Services for accessing these data are described at the back of the journal.

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