

## Octakis(3-propylammonium) octadeca-iodopentaplumbate(II): a new layered structure based on layered perovskites

David G. Billing\* and Andreas Lemmerer

School of Chemistry, University of the Witwatersrand, Private Bag 3, PO Wits 2050, South Africa

Correspondence e-mail: andy@hobbes.gh.wits.ac.za

Received 31 March 2006

Accepted 20 April 2006

Online 16 May 2006

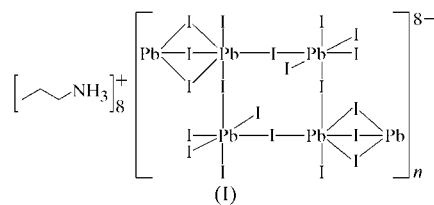
The title compound,  $(C_3H_{10}N)_8[Pb_5I_{18}]$ , crystallizes as an inorganic–organic hybrid. As such, the structure consists of two-dimensional sheets of corner- and face-sharing  $[PbI_6]^{4-}$  octahedra, separated by layers of 3-propylammonium cations, which hydrogen bond to the I atoms. The asymmetric unit contains six independent Pb atoms; four are on general positions and the other two are on special positions, *viz.* a centre of inversion and a twofold axis. The inorganic sheets show a never before seen motif.

### Comment

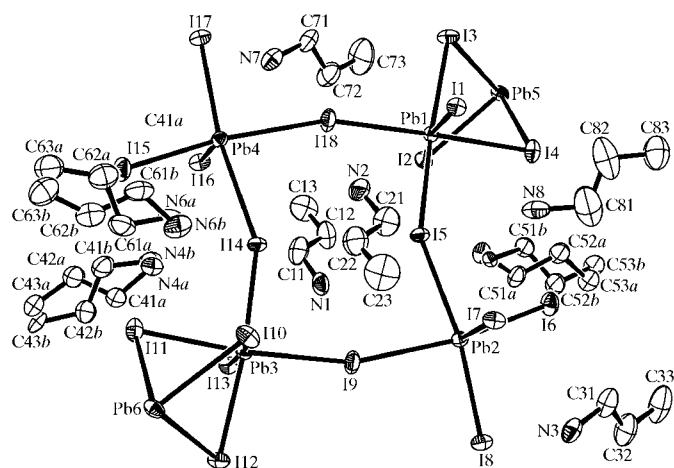
Compounds belonging to the hybrid system  $(C_3H_7NH_3)_2[MCl_4]$  ( $M = Cu, Mn, Cd, Pd$  and  $Pb$ ) have been extensively investigated for their phase behaviour (Mitzi, 1999; Depmeier, 1981; Doudin & Chapuis, 1990; Meresse & Daoud, 1989; Willett & Willett, 1977; Chapuis, 1978). The hybrid perovskites consist of inorganic semiconducting layers of  $[MX_4]^{2-}$  perovskite sheets and organic ammonium cation  $(RNH_3)^+$  bilayers. When trying to synthesize the compound  $(C_3H_7NH_3)_2[PbI_4]$ , a different inorganic motif was observed. A view of the asymmetric unit of the title compound, (I), is given in Fig. 1. Instead of the expected sheets of purely corner-sharing octahedra, the lead iodide layers can be built up from  $PbI_6$  octahedra linked *via* corners into nominal zigzag chains that are *trans* to each other along the crystallographic *b* axis. Adjacent parallel chains are linked *via* face-shared octahedra to create infinite sheets parallel to the (201) plane through the unit cell.

Fig. 2 clearly displays the two-dimensional arrangement in which layers of 3-propylammonium molecules are embedded between two consecutive inorganic  $[Pb_5I_{18}]$  sheets, forming an alternating organic–inorganic layered structure. In the direction perpendicular to the layers, the crystal cohesion is achieved by  $N-H \cdots I$  hydrogen bridges, related to the  $NH_3$

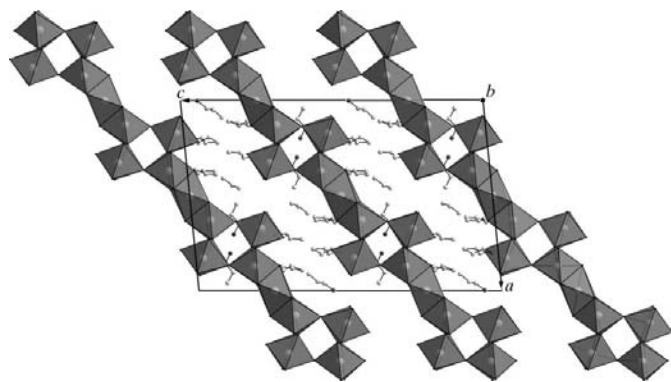
polar groups. There are no van der Waals forces between adjacent molecules. In the direction parallel to the layers, the cohesion is achieved by strong ionic bonds between axial and equatorial I and Pb atoms.



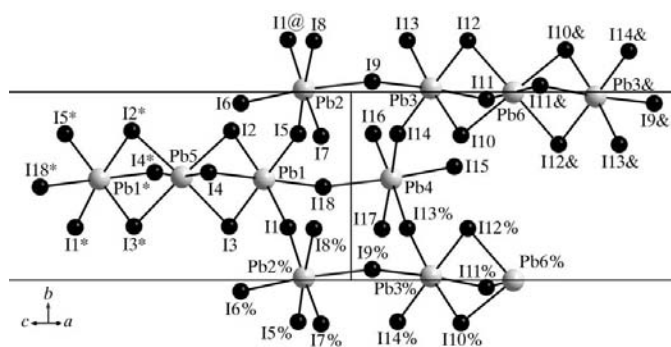
The inorganic layer is built up from corner- and face-sharing  $PbI_6$  octahedra (see Fig. 3). The asymmetric unit consists of four Pb atoms on general positions that undergo corner-sharing of *cis*-related I atoms to form a square, similar to the corner-sharing hybrid perovskites. The sequence is  $Pb1-I5-Pb2-I9-Pb3-I14-Pb4-I18-Pb1$ , *i.e.* the Pb atoms are at the corners. Two of these corner-shared squares are connected to each other *via* atoms I1 and I13. This generates another square, where the sequence is now  $Pb1-I1-Pb2-I9-Pb3-I13-Pb4-I18-Pb1$ , which is at right angles to the former square because I1 is *cis* to I5 and I13 is *cis* to I14. The squares then form a zigzag sequence, running along the *b* axis. The two Pb atoms that are at opposite ends of the squares, *viz.* Pb1 and Pb3, connect adjacent zigzag squares *via* atoms Pb5 and Pb6, respectively, on special positions, by sharing faces. Atoms I2, I3 and I4 make up the face shared between atoms Pb1 and Pb5, and, similarly, atoms I10, I11 and I12 are shared by atoms Pb3 and Pb6. The Pb atoms show different degrees of distortion (Table 1). The central face-sharing atoms Pb5 and Pb6 each have three unique Pb–I bond lengths only by virtue of their special positions on a twofold axis and a centre of inversion, respectively. All six bond lengths are in a narrow


**Figure 1**

The asymmetric unit of (I), showing the atomic numbering scheme of the inorganic moieties and the eight organic cations. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.



**Figure 2**  
The packing of (I), viewed along the *b* axis.



**Figure 3**  
An illustration of the  $[\text{Pb}_5\text{I}_{18}]_n^{8-}$  two-dimensional net. Atoms marked with an asterisk (\*), ampersand (&), percentage sign (%) or '@' sign (@) are at the symmetry positions  $(-x, y, -z + \frac{1}{2})$ ,  $(-x + 1, -y + 2, -z)$ ,  $(x, y - 1, z)$  and  $(x, y + 1, z)$ , respectively.

range from 3.2154 (13) to 3.2486 (14) Å. The largest range of bond lengths is observed for atoms Pb2 and Pb4, which only undergo corner-sharing with three I atoms. The I atoms that are not involved in any sharing with adjacent octahedra, namely atoms I6, I7 and I8 for Pb2, and atoms I15, I16 and I17 for Pb4, have the shortest bond lengths [3.0341 (14)–3.0886 (15) Å]. In contrast, the bond lengths to the corner-shared I atoms are the longest in the structure [3.3462 (14)–3.4415 (14) Å]. The Pb1 and Pb3 octahedra, which have three I atoms involved in corner-sharing and three I atoms face-sharing, have a narrow range for all six Pb–I bonds [3.1546 (14)–3.2394 (14) Å], regardless of which type of sharing they are involved in.

There are eight crystallographically independent 3-propylammonium cations in the asymmetric unit (cat1 containing atom N1, *etc.*), which fill the gaps between the lead iodide systems; cat4, cat5 and cat6 are disordered. The cations are maximally extended with the moduli of the N–C–C–C torsion angles in the 160 (5)–179.3 (17)° range. The cations are held in place above the gaps by hydrogen-bonding interactions with the I atoms. Cat1, cat2, cat3, cat7 and cat8 have two simple N–H···I bonds and a bifurcated bond. The hydrogen bonds of the three disordered cations are also listed

in Table 2. The hydrogen–acceptor distances range from 2.74 to 3.30 Å.

## Experimental

$\text{PbI}_2$  (0.092 g, 0.200 mmol) was dissolved in 47% HI (2 ml) in a sample vial. Isopropylamine (0.026 g, 0.427 mmol) was added and the precipitate was dissolved by refluxing for 2 h at 363 K. The solution was cooled slowly at a rate of 2 K  $\text{h}^{-1}$  to room temperature. A yellow single crystal suitable for X-ray diffraction analysis was selected and studied. Analysis calculated for  $\text{C}_{24}\text{H}_{80}\text{I}_{18}\text{N}_8\text{Pb}_5$ : C 7.58, H 2.12, N 2.95%; found: C 7.63, H 2.27, N 3.04%

### Crystal data

$(\text{C}_3\text{H}_{10}\text{N})_8[\text{Pb}_5\text{I}_{18}]$   
 $M_r = 3801.11$   
 Monoclinic,  $P2_1/c$   
 $a = 23.988$  (5) Å  
 $b = 8.754$  (5) Å  
 $c = 37.986$  (5) Å  
 $\beta = 95.718$  (5)°  
 $V = 7937$  (5) Å<sup>3</sup>

$Z = 4$   
 $D_x = 3.181$  Mg  $\text{m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 17.60$   $\text{mm}^{-1}$   
 $T = 173$  (2) K  
 Needle, yellow  
 $0.44 \times 0.06 \times 0.06$  mm

### Data collection

Bruker SMART-NT CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: integration (*XPREP*; Bruker, 1999)  
 $T_{\min} = 0.076$ ,  $T_{\max} = 0.392$

52039 measured reflections  
 13878 independent reflections  
 9140 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.090$   
 $\theta_{\max} = 25^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.108$   
 $S = 1.00$   
 13878 reflections  
 625 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.004$   
 $\Delta\rho_{\max} = 2.21$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.85$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Pb1–I1	3.2345 (14)	Pb3–I12	3.1899 (14)
Pb1–I2	3.2106 (14)	Pb3–I13	3.2394 (14)
Pb1–I3	3.1546 (14)	Pb3–I14	3.2225 (14)
Pb1–I4	3.1943 (12)	Pb4–I13 <sup>ii</sup>	3.4333 (14)
Pb1–I5	3.2221 (14)	Pb4–I14	3.3796 (13)
Pb1–I18	3.2197 (13)	Pb4–I15	3.0699 (12)
Pb2–I1 <sup>i</sup>	3.4415 (14)	Pb4–I16	3.0351 (14)
Pb2–I5	3.3462 (14)	Pb4–I17	3.0788 (15)
Pb2–I6	3.0753 (12)	Pb4–I18	3.3779 (13)
Pb2–I7	3.0341 (14)	Pb5–I2	3.2154 (13)
Pb2–I8	3.0886 (15)	Pb5–I3	3.2359 (14)
Pb2–I9	3.3741 (13)	Pb5–I4	3.2486 (14)
Pb3–I9	3.1977 (13)	Pb6–I10	3.2234 (12)
Pb3–I10	3.1781 (14)	Pb6–I11	3.2397 (14)
Pb3–I11	3.2098 (13)	Pb6–I12	3.2335 (14)

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

H atoms bonded to C and N atoms were refined in idealized positions in the riding-model approximation, with C–H distances of 0.98 and 0.99 Å for methyl and methylene H atoms, respectively, N–H distances of 0.91 Å, and  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$  (for  $\text{CH}_2$  H atoms) or  $1.5U_{\text{eq}}(\text{C}, \text{N})$  (for  $\text{CH}_3$  and  $\text{NH}_3$  H atoms). The conformational disorder around cations cat4, cat5 and cat6 was resolved by finding alternative positions from the difference Fourier map for all C

**Table 2**  
Hydrogen-bond geometry (Å, °).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N1—H1A···I1 <sup>i</sup>	0.91	3.20	3.795 (13)	125
N1—H1B···I14	0.91	2.99	3.732 (13)	140
N1—H1B···I13	0.91	3.20	3.793 (13)	125
N1—H1C···I5	0.91	2.80	3.701 (13)	169
N2—H2A···I14	0.91	2.79	3.694 (15)	173
N2—H2B···I5	0.91	3.01	3.713 (14)	135
N2—H2B···I1	0.91	3.14	3.768 (15)	128
N2—H2C···I13 <sup>ii</sup>	0.91	3.08	3.765 (13)	133
N3—H3A···I8	0.91	2.74	3.631 (14)	166
N3—H3B···I7 <sup>iii</sup>	0.91	2.89	3.678 (12)	146
N3—H3B···I7	0.91	3.17	3.759 (14)	125
N3—H3C···I9 <sup>iii</sup>	0.91	2.76	3.623 (16)	160
N4A—H4AA···I15	0.91	2.78	3.68 (10)	174
N4A—H4AB···I17 <sup>i</sup>	0.91	2.97	3.70 (8)	138
N4A—H4AB···I16	0.91	3.16	3.80 (5)	130
N4A—H4AC···I13	0.91	3.02	3.77 (8)	141
N4A—H4AC···I14	0.91	3.23	3.88 (4)	130
N4B—H4BA···I17 <sup>i</sup>	0.91	2.67	3.56 (14)	168
N4B—H4BB···I13	0.91	3.24	3.94 (13)	136
N4B—H4BC···I15	0.91	2.93	3.66 (16)	138
N4B—H4BC···I16	0.91	3.01	3.61 (9)	125
N5A—H5AA···I1 <sup>i</sup>	0.91	3.04	3.83 (7)	146
N5A—H5AB···I3 <sup>i</sup>	0.91	2.94	3.69 (7)	142
N5A—H5AB···I2	0.91	2.93	3.52 (6)	123
N5A—H5AC···I4	0.91	3.05	3.96 (7)	179
N5B—H5BA···I1 <sup>i</sup>	0.91	3.16	3.79 (4)	128
N5B—H5BA···I3 <sup>i</sup>	0.91	3.22	3.95 (5)	139
N5B—H5BB···I2	0.91	3.10	3.85 (4)	142
N5B—H5BC···I6	0.91	2.70	3.60 (4)	168
N6A—H6AA···I12 <sup>ii</sup>	0.91	3.00	3.87 (7)	162
N6A—H6AB···I15	0.91	3.02	3.66 (6)	129
N6A—H6AB···I13 <sup>ii</sup>	0.91	3.12	3.73 (5)	126
N6A—H6AC···I11	0.91	3.03	3.77 (6)	140
N6A—H6AC···I14	0.91	3.30	3.92 (4)	127
N6B—H6BA···I11	0.91	2.93	3.71 (8)	146
N6B—H6BB···I10	0.91	2.95	3.64 (5)	134
N6B—H6BB···I12 <sup>ii</sup>	0.91	3.26	3.67 (8)	110
N6B—H6BC···I13 <sup>ii</sup>	0.91	3.08	3.88 (8)	147
N7—H7A···I17 <sup>iv</sup>	0.91	2.81	3.631 (15)	150
N7—H7B···I16 <sup>iv</sup>	0.91	2.90	3.669 (14)	144
N7—H7B···I17	0.91	3.14	3.754 (13)	127
N7—H7C···I18	0.91	2.74	3.645 (16)	171
N8—H8A···I1	0.91	2.91	3.751 (14)	154
N8—H8B···I8 <sup>ii</sup>	0.91	2.93	3.717 (15)	146
N8—H8B···I7	0.91	3.11	3.689 (14)	123
N8—H8C···I6	0.91	2.90	3.679 (12)	145

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

and N atoms that make up the propylammonium chains. These atoms were then refined anisotropically together with their site occupancy such that the sum of the occupancies for the two chains summed to unity. H-atom positions were then calculated for the respective atoms using a riding model as above. For cat4 the major to minor ratio was 60:40%, for cat5 the major to minor ratio was 57:43%, and for cat6 the major to minor ratio was 54:46%.

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).

The authors thank the University of the Witwatersrand and the National Research Foundation of South Africa for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3016). Services for accessing these data are described at the back of the journal.

## References

- Brandenburg, K. (1999). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.
- Bruker (1998). *SMART-NT*. Version 5.050. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SAINT-Plus*. Version 6.02 (including *XPREP*). Bruker AXS Inc., Madison, Wisconsin, USA.
- Chapuis, G. (1978). *Acta Cryst.* **B34**, 1506–1512.
- Depmeier, W. (1981). *Acta Cryst.* **B37**, 330–339.
- Doudin, B. & Chapuis, G. (1990). *Acta Cryst.* **B46**, 175–180.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Meresse, A. & Daoud, A. (1989). *Acta Cryst.* **C45**, 194–196.
- Mitzi, D. B. (1999). *Prog. Inorg. Chem.* **48**, 1–121.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2002). *PLATON*. Utrecht University, The Netherlands.
- Willett, R. D. & Willett, J. J. (1977). *Acta Cryst.* **B33**, 1639–1641.