

Poly[bis[2-(1-cyclohexenyl)ethylammonium] di- μ -iodo-diodo-plumbate(II)]

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 20 March 2006

Accepted 18 April 2006

Online 15 June 2006

The title compound, $(C_8H_{16}N)_2[PbI_4]$, crystallizes as an inorganic–organic hybrid perovskite, adopting the unusual $2a_p \times 2a_p$ superstructure. As such, the structure consists of two-dimensional sheets of corner-sharing PbI_6 octahedra in the ab plane, separated by bilayers of 2-(1-cyclohexenyl)ethylammonium cations. The ethylammonium groups are not in the plane of the cyclohexenyl rings.

Comment

The hybrid perovskites $(C_6H_5C_2H_4NH_3)_2[PbX_4]$ ($X = Cl, Br$ and I) have been investigated extensively for their photoluminescence, electroluminescence and non-linear optical properties (Mitzi, 1999a, and references therein). The hybrid perovskites are natural quantum-well structures as they consist of inorganic semiconducting layers of $[MX_4]^{2-}$ perovskite sheets and organic ammonium cation $(R-NH_3)^+$ bilayers. Highly efficient electroluminescence has been found in the related materials $(C_6H_5C_4H_8NH_3)_2[PbI_4]$ and $(C_6H_9C_2H_4NH_3)_2[PbI_4]$ (Hattori *et al.*, 1996). The latter and the title

compound, (I), which contains a six-membered ring with a $C=C$ bond, showed high luminescence, exceeding 4000 cd m^{-2} . The reason for the high electroluminescence observed is the nature of the organic carrier transport material, in this case the $C_6H_9C_2H_4NH_3^+$ cation (Hattori *et al.*, 1996). In this study, we present the detailed crystal structure of the hybrid perovskite (I) (Fig. 1).

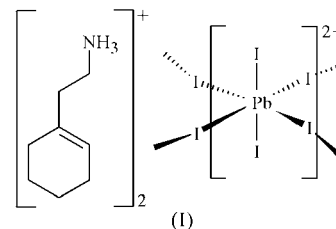


Fig. 2 clearly underlines a bidimensional arrangement in which two layers of non-interdigitated 2-(1-cyclohexenyl)ethylammonium ions are embedded between two consecutive inorganic PbI_6 sheets, forming an alternated inorganic–organic layered structure. The Pb atoms are aligned from layer to layer, resulting in an eclipsed arrangement of adjacent layers. In the direction perpendicular to the layers, the crystal cohesion is achieved at one end of the organic molecules by $N-H \cdots I$ hydrogen bridges, related to the NH_3 polar groups. There are van der Waals forces between molecules [the nearest neighbor distance is $3.792(18) \text{ \AA}$]. In the direction parallel to the layers, the cohesion is achieved by strong ionic bonds between equatorial I and Pb atoms, giving the classical perovskite structural arrangement. An interesting feature of this hybrid perovskite is that the triclinic unit-cell dimensions parallel to the perovskite layers are twice the simple cubic perovskite lattice parameter of $(CH_3NH_3)[PbI_3]$ [$a_p = 6.3285(4) \text{ \AA}$; Mitzi, 1999b]. Most layered inorganic–organic hybrid perovskites show the $2^{1/2}a_p \times 2^{1/2}a_p$ superstructure not the unusual $2a_p \times 2a_p$ structure observed here (Mitzi, 1999b).

The inorganic layer is built up from characteristic corner-sharing PbI_6 octahedra. The asymmetric unit consists of Pb atoms, Pb1 and Pb2, on general positions and eight I atoms, *viz.* atoms I1–I4 occupying the axial positions and I5–I8

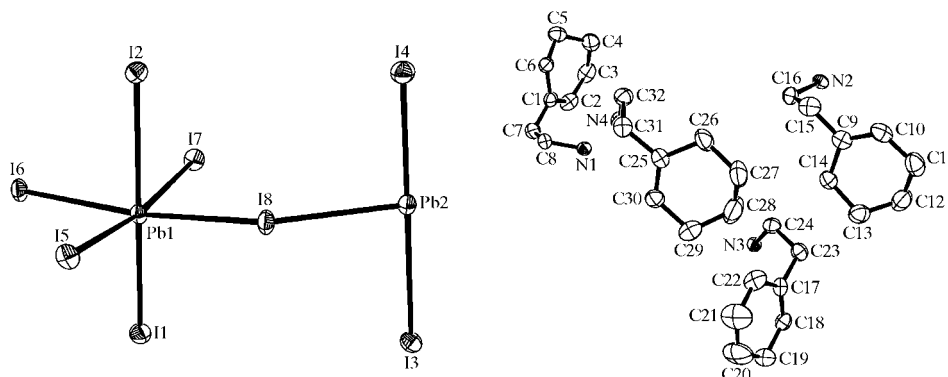


Figure 1

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

metal-organic compounds

occupying the equatorial positions in the octahedra. The four equatorial I atoms are corner-shared by neighboring octahedra. As shown in the projection perpendicular to the layers, along the *c* axis, the PbI_6 octahedra are rotated relative to each other (Fig. 3). The degree of rotation ranges from 148.632 (15) to 150.948 (15) $^\circ$, as there are four different bridging I atoms. Furthermore, the perovskite layers are corrugated. The tilt angle is 2.462° for Pb1 and 2.543° for Pb2. The coordination geometry around the Pb atoms shows axial compression of the octahedral geometry, with the bridging distances longer than the axial distances. The bridging lead–iodine bond distances are in a narrow range for both Pb1 and Pb2 [3.1626 (5)– 3.1858 (5) \AA ; Table 1]. The longest bond distances are to the

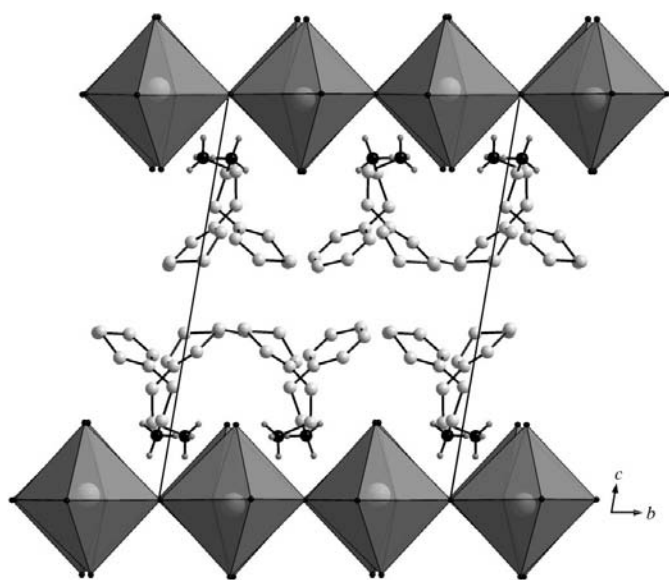


Figure 2
A packing diagram of (I), viewed along the *a* axis.

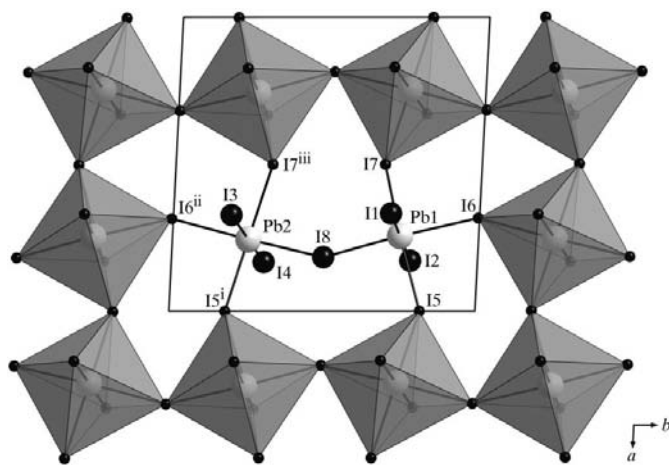


Figure 3
An illustration of the two-dimensional PbI_6 sheets, viewed down the *c* axis. The symmetry codes are as in Table 1.

axial atoms I2 and I3 [3.3889 (6) and 3.3947 (6) \AA , respectively], whereas the shortest distances are to the I atoms *trans* to them, *viz.* I1 [3.0626 (6) \AA] and I4 [3.0622 (6) \AA]. The size of the parallelograms that make up the voids depends on which bridging I atoms are used. There are four unique voids and the edge lengths range from 4.427 (12) to 4.556 (12) \AA . The bond angles between *cis*- and *trans*-related I atoms within the octahedra all deviate from ideality. The *cis* angles range from 84.050 (13) to 96.074 (16) $^\circ$. The *trans* angles between the bridging I atoms deviate more from 180° [171.223 (13)– 172.639 (14) $^\circ$] than those between the axial halides [179.490 (12) and 179.558 (12) $^\circ$].

There are four unique 2-(1-cyclohexenyl)ethylammonium molecules in the asymmetric unit and their atomic numbering schemes are shown in Fig. 1. All four amine groups are well ordered between the layers; these groups are labeled cat1 (containing atom N1), cat2 (N2), cat3 (N3) and cat4 (N4). Three of the 1-cyclohexenyl rings are not planar. The r.m.s. deviation from the planes is 0.3041 (1) \AA for cat1, 0.3095 (1) \AA for cat2, 0.2591 (1) \AA for cat3 and the least for cat4 [0.0586 (1) \AA]. When viewing the cations perpendicular to the 1-cyclohexenyl rings, with the ethylammonium groups pointing towards you, they are bent towards the right for cat1, cat2 and cat4, and to the left for cat3. The direction is always to the side with the double bond. Furthermore, the terminal ethylammonium C and N atoms are not in the plane of the ring but in a J-shaped conformation, similar to the phenylethylammonium molecules in $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2[\text{PbCl}_4]$ (Mitzi, 1999*a*). Consequently, the 1-cyclohexenyl rings are slanted towards the layers (33.916 , 35.053 , 37.179 and 37.994° , respectively, for cat1–cat4).

The hydrogen bridges (Table 2) between the organic and inorganic entities adopt the terminal configuration for all four unique ammonium groups, *i.e.* two H atoms bond to axial I atoms and the third H atom to a bridging I atom (see Fig. 4). The $\text{H}\cdots\text{A}$ distances to the terminal halides range from 2.75 to 2.93 \AA and to the bridging halides from 2.78 to 2.84 \AA .

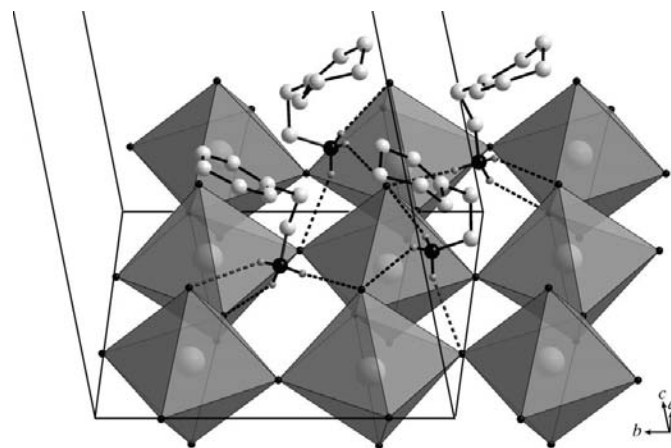


Figure 4
Hydrogen bridging interactions (dashed lines) between the ammonium heads and the halogen atoms of (I).

Experimental

PbI₂ (0.101 g, 0.219 mmol) was dissolved in 47% HI (4 ml) in a sample vial. 2-(1-Cyclohexenyl)ethylamine (0.055 g, 0.454 mmol) was added and the precipitate was dissolved with methanol (9 ml). Crystals were grown by slow evaporation over a period of a few days. An orange single crystal suitable for X-ray diffraction analysis was selected and studied. Analysis calculated for C₁₆H₃₂I₄N₂Pb: C 19.87, H 3.33, N 2.90%; found: C 19.81, H 3.19, N 3.00%.

Crystal data

(C₈H₁₆N)₂[PbI₄] $V = 2584.8 (4) \text{ \AA}^3$
 $M_r = 967.23$ $Z = 4$
 Triclinic, $P\bar{1}$ $D_x = 2.485 \text{ Mg m}^{-3}$
 $a = 12.2053 (11) \text{ \AA}$ Mo $K\alpha$ radiation
 $b = 12.3053 (11) \text{ \AA}$ $\mu = 11.31 \text{ mm}^{-1}$
 $c = 18.3182 (17) \text{ \AA}$ $T = 173 (2) \text{ K}$
 $\alpha = 80.629 (6)^\circ$ Plate, orange
 $\beta = 72.455 (6)^\circ$ $0.48 \times 0.44 \times 0.04 \text{ mm}$
 $\gamma = 89.961 (6)^\circ$

Data collection

Bruker SMART CCD area-detector 42465 measured reflections
 diffractometer 12456 independent reflections
 φ and ω scans 10208 reflections with $I > 2\sigma(I)$
 Absorption correction: integration $R_{\text{int}} = 0.075$
 (XPREP; Bruker, 1999) $\theta_{\text{max}} = 28^\circ$
 $T_{\text{min}} = 0.03, T_{\text{max}} = 0.570$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 9.0173P]$
 $R[F^2 > 2\sigma(F^2)] = 0.035$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.093$ $(\Delta/\sigma)_{\text{max}} = 0.002$
 $S = 1.05$ $\Delta\rho_{\text{max}} = 1.26 \text{ e \AA}^{-3}$
 12456 reflections $\Delta\rho_{\text{min}} = -3.13 \text{ e \AA}^{-3}$
 415 parameters
 H-atom parameters constrained

Table 1

Selected interatomic distances (Å).

Pb1—I1	3.0626 (6)	Pb2—I4	3.0622 (6)
Pb1—I7	3.1636 (5)	Pb2—I5 ⁱ	3.1626 (5)
Pb1—I5	3.1772 (5)	Pb2—I7 ⁱⁱⁱ	3.1750 (5)
Pb1—I6	3.1843 (5)	Pb2—I8	3.1848 (5)
Pb1—I8	3.1858 (5)	Pb2—I6 ⁱⁱ	3.1856 (5)
Pb1—I2	3.3889 (6)	Pb2—I3	3.3947 (6)

Symmetry codes: (i) $-x + 2, -y + 1, -z$; (ii) $x, y - 1, z$; (iii) $-x + 1, -y + 1, -z$.

H atoms were refined in idealized positions in the riding-model approximation, with C—H = 0.95 (CH) and 0.99 Å (CH₂), and N—H = 0.91 Å [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{N})$]. The highest residual peak is 1.96 Å from atom H1A.

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1A...I6	0.91	2.84	3.649 (5)	149
N1—H1B...I2	0.91	2.92	3.683 (5)	142
N1—H1C...I3 ⁱⁱⁱ	0.91	2.78	3.656 (5)	161
N2—H2A...I8	0.91	2.83	3.644 (5)	150
N2—H2B...I3	0.91	2.93	3.685 (5)	142
N2—H2C...I2 ⁱ	0.91	2.79	3.659 (5)	160
N3—H3A...I7	0.91	2.78	3.628 (6)	155
N3—H3B...I4 ⁱⁱⁱ	0.91	2.83	3.626 (5)	148
N3—H3C...I2 ⁱⁱⁱ	0.91	2.76	3.644 (5)	166
N4—H4A...I5	0.91	2.78	3.623 (6)	154
N4—H4B...I3 ^{iv}	0.91	2.75	3.647 (6)	167
N4—H4C...I1	0.91	2.82	3.626 (5)	148

Symmetry codes: (i) $-x + 2, -y + 1, -z$; (iii) $-x + 1, -y + 1, -z$; (iv) $x, y + 1, z$.

Data collection: SMART-NT (Bruker, 1998); cell refinement: SMART-NT; data reduction: 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).

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: TR3004). 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.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
 Hattori, T., Taira, T., Era, M., Tsutsui, T. & Saito, S. (1996). *Chem. Phys. Lett.* **254**, 103–108.
 Mitzi, D. B. (1999a). *J. Solid State Chem.* **145**, 694–704.
 Mitzi, D. B. (1999b). *Prog. Inorg. Chem.* **48**, 1–121.
 Sheldrick, G. M. (1997). SHELXL97 and SHELXS97. University of Göttingen, Germany.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.