Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis[*N*-(1-naphthyl)ethylenediammonium] hexaiodoplumbate(II)

Ying-Ying Zheng, Gang Wu, Hong-Zheng Chen and Mang Wang*

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

Correspondence e-mail: wmang@zju.edu.cn

Received 26 December 2006
Accepted 12 January 2007

Key indicators

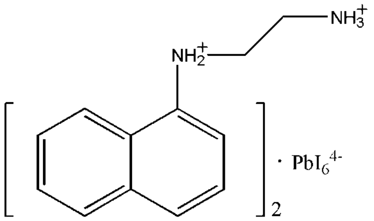
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
R factor = 0.020
wR factor = 0.050
Data-to-parameter ratio = 23.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_{12}H_{16}N_2)_2[PbI_6]$, is an organic–inorganic salt, with two doubly protonated *N*-(1-naphthyl)-ethylenediamine groups as the cations and one octahedral hexaiodoplumbate(II) as the anion. The stucture consists of alternating inorganic and organic layers parallel to the *bc* plane. Simple face-to-face aromatic stacking interactions occur between parallel naphthalene systems in the organic layers, and N—H···I hydrogen bonds between the ethylenediammonium groups and PbI_6^{4-} octahedra stabilize the structure. The slightly distorted PbI_6 octahedra are isolated from each other, with the Pb atom located on a centre of inversion.

Comment

In recent years, numerous organic–inorganic salts and hybrid materials based on metal halide units have been prepared and studied; for reviews, see Papavassiliou (1997) and Mitzi (2001). Most of these structures can be derived by taking *n*-layer thick slices from along a selected crystallographic direction of the idealised three-dimensional cubic perovskite structure and stacking these slabs in alternation with organic cationic layers. The common possibilities for the orientation of the inorganic slab include the [100], [110] and [111] directions. The [100]-oriented compounds have been extensively studied, but there are only a few reports dealing with the other two. So far, the [111]-oriented systems have been stabilized only with relatively simple organic cations such as in $(CH_3NH_3)_3[Bi_2Br_9]$, $[NH_2(CH_3)_2]_3[Sb_2Cl_9]$ (Zaleski & Pietraszko, 1996), $[NH(CH_3)_3]_3[Sb_2Cl_9]$ (Kallel & Bats, 1985) and $[(CH_3)_2NH_2]_2[SnCl_6]$ (Ben Ghozlen *et al.*, 1981). In the present study, we combined the π-conjugated chromophore *N*-(1-naphthyl)ethylenediamine with lead(II) iodide in a concentrated HI solution for the first time and found that the resulting title salt, $(C_{12}H_{16}N_2)_2[PbI_6]$, (I), has the rare [111]-oriented structure.



(I)

As illustrated in Fig. 1, the crystal structure of compound (I) is composed of alternating organic and inorganic sheets nearly parallel to the *bc* plane. The naphthalene ring systems are parallel to each other, and along the *a* axis the aromatic rings

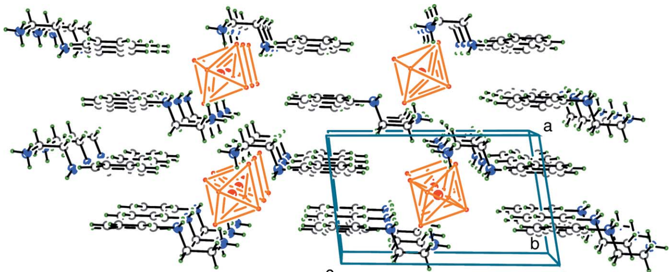


Figure 1
The packing of the title compound, viewed along the *b* axis.

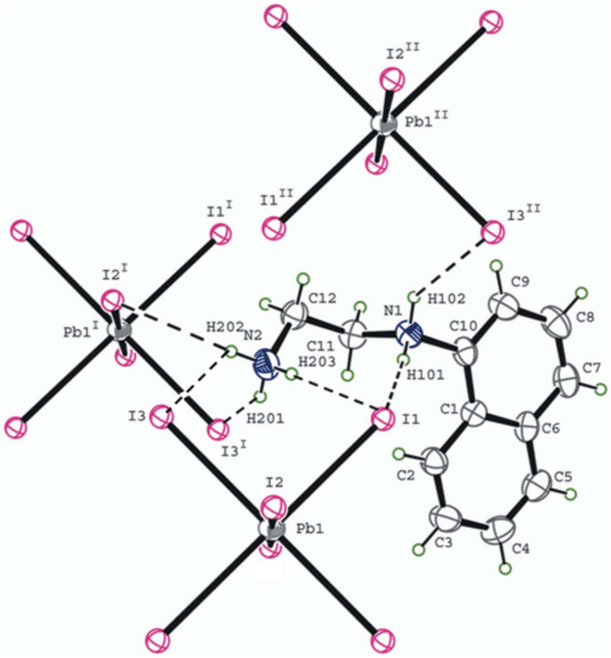


Figure 2
A view of the N—H···I hydrogen-bonding scheme, indicated by dashed lines. Displacement ellipsoids are displayed at the 50% probability level. [Symmetry codes: (I) $-x, -y+1, -z+1$; (II) $-x+1, -y, -z+1$.]

are almost directly above or below each other. The centroid-to-centroid distance of 3.626 (5) Å between adjacent naphthalene ring systems results in the typical face-to-face aromatic π–π interaction.

In the inorganic layers, the isolated $[PbI_6]^{4-}$ anions display a slightly distorted octahedral configuration, with the Pb atoms located on centres of inversion. The Pb—I bond lengths (Table 1) are in the range 3.1875 (18)–3.2380 (19)Å.

The resulting hydrogen-bonding network between the I atoms of the inorganic layer and the H atoms of the $NH_2CH_2CH_2NH_3^{2+}$ groups of the organic layer stabilizes the crystals structure of (I) and is illustrated in Fig. 2. One doubly protonated organic cation interacts with three PbI_6^{4-} octahedra. Details of the hydrogen-bonding geometry are listed in Table 2.

Experimental

Compound (I) was prepared by reacting PbI_2 (1 mmol; Shanghai Chemical Reagent Corporation, 98%) and $C_{12}H_{14}N_2\cdot 2HI$ (2 mmol; Acros Organics, 98%) in a concentrated aqueous HI solution (10 ml, 45wt%; Shanghai Chemical Reagent Corporation) at room temperature for 10 min. The resulting solution was heated to 383 K and then slowly cooled to room temperature. Yellow chunky crystals precipitated which were then filtered off and washed with acetonitrile. The crystals were moderately air-stable at room temperature, remaining unchanged over 2 d. However, as a general precaution, all reactions were carried out under a nitrogen atmosphere and all solvents were degassed before use. Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3008 (ν_{as} C—H), 2902 (ν_{as} N—H), 2778 (ν_{as} N—H), 1604 (δ CH_2), 1544 (δ NH_2). Chemical analysis, calculated: C 21.47, H 2.38, N 4.06%; found: C 21.52, H 2.42, N 4.09%.

Crystal data

$(C_{12}H_{16}N_2)_2[PbI_6]$
$M_r = 1345.17$
Triclinic, $P\overline{1}$
$a = 8.467$ (4) Å
$b = 8.732$ (5) Å
$c = 12.921$ (7) Å
$\alpha = 80.49$ (2)°
$\beta = 79.691$ (18)°
$\gamma = 62.36$ (2)°
$V = 829.0$ (7) Å^3
$Z = 1$
$D_x = 2.694$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 10.71$ mm^{-1}
$T = 298$ (1) K
Chunk, yellow
0.33 × 0.27 × 0.20 mm

Data collection

Rigaku R-AXIS RAPID CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.046$, $T_{max} = 0.118$
8214 measured reflections
3772 independent reflections
3449 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.050$
$S = 1.01$
3772 reflections
161 parameters
H-atom parameters constrained
$w = 1/[0.0001F_o^2 + 1.12\sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.63$ e Å^{-3}
$\Delta\rho_{min} = -1.42$ e Å^{-3}
Extinction correction: Larson (1970), equation 22
Extinction coefficient: 18.6 (11)

Table 1
Selected geometric parameters (Å, °).

Pb1—I1	3.2380 (19)	Pb1—I3	3.1938 (18)
Pb1—I2	3.1875 (18)		
I1—Pb1—I1^{i}	180	I2—Pb1—I2^{i}	180
I1—Pb1—I2	86.444 (5)	I2—Pb1—I3^{i}	87.425 (6)
I1—Pb1—I3	89.799 (6)	I3—Pb1—I3^{i}	180

Symmetry code: (i) $-x+1, -y+1, -z+1$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H101···I1	0.86	2.73	3.568 (4)	166
N1—H102···I3^{ii}	0.86	3.07	3.744 (5)	137
N2—H201···I3^{iii}	0.86	2.99	3.695 (5)	141
N2—H202···I3	0.86	3.16	3.698 (6)	123
N2—H202···I2^{iii}	0.86	2.86	3.595 (5)	145
N2—H203···I1	0.86	2.75	3.604 (4)	171

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

Acta Cryst. (2007). E**63**, m504–m506 Zheng *et al.* • $(C_{12}H_{16}N_2)_2[PbI_6]$ **m505**

All H atoms were placed in calculated positions, with C—H(methylene) = 0.93 Å, C—H(aromatic) = 0.97 Å and N—H = 0.86 Å, and included in the final cycles of the refinement in the riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(carrier atom). The deepest electron-density hole in the final Fourier map is located 1.08 Å from Pb1.

Data collection: *PROCESS-AUTO* (Rigaku,1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

This work was supported by project Nos. 50225312, 50318001, 50433020 and 50503021, and by the Main International Cooperation Project of the Natural Science Foundation of China. We thank Jianming Gu for help with the crystallographic analysis.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Ben Ghozlen, M. H., Daoud, A. & Bats, J. W. (1981). *Acta Cryst.* B**37**, 1415–1416.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Kallel, A. & Bats, J. W. (1985). *Acta Cryst.* C**41**, 1022–1024.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Mitzi, D. B. (2001). *J. Chem. Soc. Dalton. Trans.* pp. 1–21.

Papavassiliou, G. C. (1997). *Prog. Solid State Chem.* **25**, 125–270.

Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2004). *CrystalStructure*. Version 3.7.0. Rigaku/MSC, The Woodlands, Texas, USA.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Zaleski, J. & Pietraszko, A. (1996). *Acta Cryst.* B**52**, 287–295.

m506 Zheng *et al.* • $(C_{12}H_{16}N_2)_2[PbI_6]$ *Acta Cryst.* (2007). E**63**, m504–m506