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Bis(propane-1,2-diammonium) hexaiodoplumbate(II) trihydrate

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Key indicators

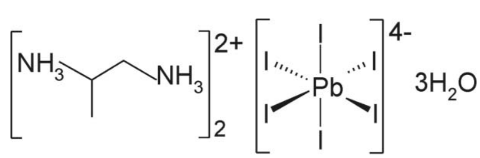
Single-crystal X-ray study
T = 173 K
Mean σ(b–I) = 0.001 Å
Disorder in main residue
R factor = 0.030
wR factor = 0.059
Data-to-parameter ratio = 27.8

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

The title compound, $[NH_3CH_2CH(NH_3)CH_3]_2[PbI_6]\cdot3H_2O$, crystallizes as an organic–inorganic hybrid, consisting of alternating inorganic and organic layers. The ionic layer consists of isolated $[PbI_6]^{4-}$ octahedra. The hydrocarbon layer has one propane-1,2-diammonium cation in the asymmetric unit which links to the ionic layer *via* hydrogen bonding. Two solvent water molecules lie between the anions and cations. The Pb atom lies on a centre of inversion.

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). It has been shown that their structures can vary considerably, ranging from systems based on isolated molecules to ones containing extended chains, as in $[Me_4N][PbI_3]$ (Contreras *et al.*, 1983), right up to two- or three-dimensional networks (Mitzi, 1999). Very few cases have been reported of the zero-dimensional form, where the metal halide units exist isolated from each other and connect *via* hydrogen bonds to the organic counter-ion. Often, water molecules are able to coordinate to the two charged components, as in $(CH_3NH_3)_4PbI_6\cdot2H_20$ (Vincent *et al.*, 1986). We present here the crystal structure of the title compound, (I).



(I)

The unit cell of (I) contains four isolated $[PbI_6]$ octahedra and the hydrocarbon layer is comprised of propane-1,2-diammonium cations and isolated water molecules. Between the two layers, crystal cohesion is achieved by N—H···I, N—H···O, O—H···I and O—H···O hydrogen bonds.

The asymmetric unit of (I) consists of a Pb atom on a special position and three I^- ions occupying general positions. The full octahedral coordination is completed through the inversion centre at the Pb atom. The coordination geometry around the Pb atom is characterized by short and long Pb—I bonds. The Pb—I bond lengths for the I^- ions engaged in multiple hydrogen bonds are longest. Atom I1, which acts as an acceptor atom five times, has the longest bond [3.2361 (6) Å]. Atoms I2 and I3 act as acceptor atoms three times and twice, respectively, and have distances of 3.2071 (6) and 3.1935 (6) Å, respectively. The angles between *cis*-related I^-

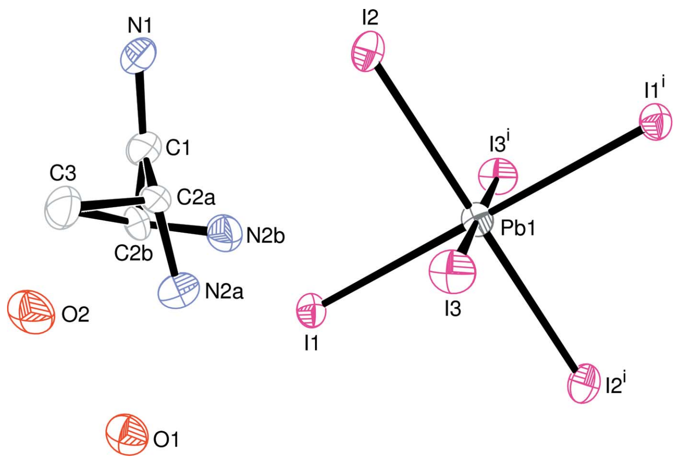


Figure 1
The asymmetric unit of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted. Both disorder components are shown **[Please check added text]** [Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.]

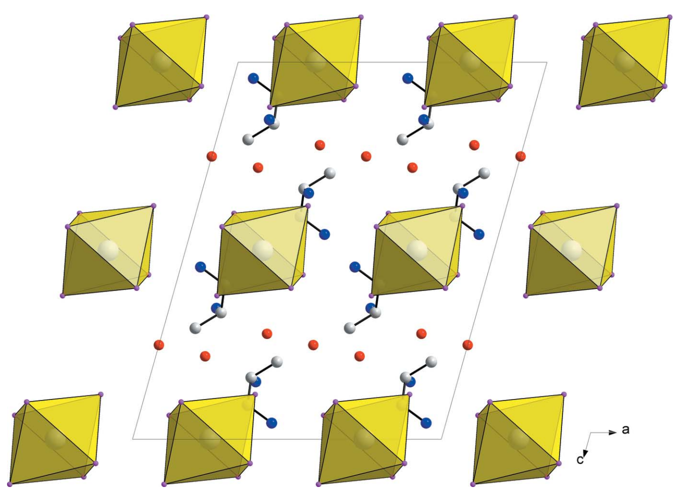


Figure 2
A packing diagram for (I).

ions deviate from 90° by 3.177 (17)° at most, whereas the *trans* angles are all 180°.

The propane-1,2-diammonium cations in the asymmetric unit occupy general positions and the atomic numbering scheme is shown in Fig. 1. The first and last C atoms of the propane chain are well ordered but the second C atom and its ammonium group are disordered.

The two ammonium groups on the propane chain display different hydrogen-bonding interactions with I^- ions and O atoms. Atom N1 is hydrogen bonded to three I^- ions *via* three normal hydrogen bonds. Atom N2, which is disordered over two positions, bridges to I^- ions and to atom O2 on one of the water molecules *via* five normal and one bifurcated hydrogen bond. Hydrogen-bonding acceptor distances range from 2.52 to 2.98 Å for the N—H···I pairs and from 1.83 to 2.49 Å for the N—H···O2 pairs. The two O atoms of the solvent water molecules form hydrogen bonds to I^- ions and O atoms. Atom O1 forms hydrogen bonds only to I1 and I3, with O1—H···I

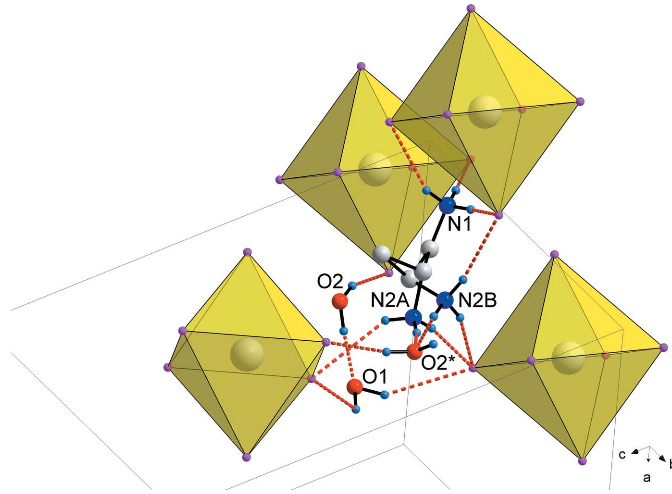


Figure 3
Hydrogen-bonding interactions (dashed lines) between the ammonium headgroups, I^- ions and O atoms. The O atom labelled with an asterisk (*) is at the symmetry position ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$).

distances of 2.93 (6) and 3.31 (9) Å, respectively. Atom O2 forms hydrogen bonds to the other water molecule (O2—H···O1 = 1.86 Å) and to I2 (2.61 Å).

Experimental

PbI_2 (0.220 g, 0.477 mmol) was dissolved in 47% HI (3 ml) in a round-bottomed flask. $NH_2CH_2CH(NH_2)CH_3$ (0.200 g, 2.70 mmol) was then added and the precipitate which formed was dissolved by refluxing for 12 h at 363 K. The solution was slowly cooled to room temperature at 2 K h^{-1}. A colourless crystal suitable for X-ray diffraction studies was selected and studied. Analysis calculated for $C_6H_{30}I_6N_4O_3Pb$: C 6.13, H 2.57, N 4.77%; found: C 6.22, H 2.56, N 4.73%.

Crystal data

$(C_3H_{12}N_2)_2[PbI_6]\cdot 3H_2O$
$M_r = 1174.93$
Monoclinic, $C2/c$
$a = 15.093$ (3) Å
$b = 9.297$ (2) Å
$c = 19.142$ (4) Å
$\beta = 105.664$ (4)°
$V = 2586.3$ (9) $Å^3$
$Z = 4$
$D_x = 3.018$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 13.69$ mm^{-1}
$T = 173$ (2) K
Block, colourless
0.22 × 0.18 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: integration (*XPREP*; Bruker, 1999)
$T_{min} = 0.105$, $T_{max} = 0.216$
8378 measured reflections
3119 independent reflections
2629 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 28°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.059$
$S = 1.05$
3119 reflections
112 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0027P)^2 + 27.3459P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.23$ e $Å^{-3}$
$\Delta\rho_{min} = -1.63$ e $Å^{-3}$

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···I1^{i}	0.91	2.9	3.753 (5)	158
N1—H1*B*···I1^{ii}	0.91	2.74	3.629 (5)	167
N1—H1*C*···I2^{iii}	0.91	2.96	3.733 (6)	144
N2*A*—H2*AA*···O2^{iv}	0.91	1.98	2.859 (13)	164
N2*A*—H2*AB*···I1	0.91	2.52	3.416 (10)	170
N2*A*—H2*AC*···O2	0.91	2.49	3.241 (15)	140
N2*A*—H2*AC*···I3^{v}	0.91	2.98	3.681 (12)	135
N2*B*—H2*BA*···I1	0.91	2.96	3.805 (9)	155
N2*B*—H2*BB*···O2^{iv}	0.91	1.83	2.735 (10)	176
N2*B*—H2*BC*···I2^{iii}	0.91	2.84	3.718 (9)	162
O1—H11···I1^{vi}	0.95	2.93	3.755 (5)	147
O1—H11···I3^{v}	0.95	3.31	3.7684 (14)	112
O2—H21···O1	0.95	1.86	2.803 (7)	173
O2—H22···I2^{ii}	0.94	2.61	3.506 (5)	158

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

All H atoms were found in a difference map. For H atoms bonded to O atoms, restraints were used to obtain reasonable values for O—H distances and H—O—H angles The 1,2-distances were restrained to 0.95 Å and the 1,3-distance to 1.5 Å using DFIX and DANG, respectively. Finally, these H atoms were refined using a riding model, with $U_{iso}(H) = 1.2U_{iso}(O)$. H atoms bonded to C and N atoms were refined in idealized positions in the riding-model approximation, with C—H = 0.98 Å for methyl H, 0.99 Å for methylene H and 1.00 Å for methine H and N—H = 0.91 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(N)$. The conformational disorder around atoms C2 and N2 was resolved by finding alternative positions from the difference Fourier map for the respective atoms. These atoms were then refined anisotropically together with their site occupancy such that the sum of the occupancies for the two alternative atom positions equalled 1. H-atom positions were then calculated for the respective atoms using a riding model. The ratio of major to minor components is 0.580 (11):0.420 (11). The highest resudual peak is 0.70 Å from I3 and the deepest hole is 0.73 Å from I3.

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, 2003).

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