metal-organic compounds

catena-Poly[bis(tert-butylammonium) [plumbate(II)-tri-μ-iodo] iodide dihydrate]

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The title compound, $\{(C_4H_{12}N)_2[PbI_3]I\cdot2H_2O\}_n$, crystallizes as an organic–inorganic hybrid. The six-coordinate Pb atom lies on a centre of inversion and all the I atoms lie on mirror planes; the two independent cations both lie across mirror planes. The structure contains anionic chains along [100] of fused $[PbI_3]^-$ units forming face-sharing octahedra. Four cations enclose channels occupied by isolated iodide ions and water molecules of hydration.

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). Haloplumbates in particular have demonstrated a propensity for forming a great variety of crystalline structures by self-assembling from suitable solution mixtures. It has been shown that their structures can vary considerably, ranging from systems based on isolated molecules to systems containing extended chains, as in $(Me_4N)[PbI_3]$ (Contreras *et al.*, 1983), right up to two- or three-dimensional networks (Mitzi, 1999). For systems containing extended chains, these chains may be formed by one, two or three bridging halides. A search of the Cambridge Structural Database (Version 5.27, November 2005 release; Allen 2002) indicated that most crystal structures with tertiary butylammonium groups have isolated octahedra, as in $SnCl_6$ (Ghozlen *et al.*, 1991), $TeCl_6$ (Ishida & Kashino, 1992) and $TeBr_6$ (Baker *et al.*, 1995), or isolated $SnCl_4$ tetrahedra (Ishida & Kashino, 1993). To the best of our knowledge, only two structures have a one-dimensional system, *viz.* $(C_4H_{12}N)_2Sb_2Cl_8$, which has edge-sharing chains of square-pyramidal $SbCl_5$ (Belz *et al.*, 1992) units, and $[(t\text{-}C_4H_{12}N)CdBr_3]_2\cdot H_2O$, which has edge-sharing chains of trigonal-bipyramidal $CdBr_5$ units (Ishihara *et al.*, 1999).

The title compound, (I), has a one-dimensional arrangement in which chains of face-sharing PbI_6 octahedra run along the unit cell (see Fig. 1). The channels in between the chains

are occupied by *tert*-butylammonium molecules, an isolated I atom on a mirror plane at $y = \frac{1}{4}$ (I4), and water molecules of hydration (Fig. 2). In the direction perpendicular to the chains, the crystal cohesion is achieved by N—H···I, N—H···O and O—H···I hydrogen bridges. In the direction parallel to the chains, the cohesion is achieved by strong ionic bonds between the I and Pb atoms.


(I)
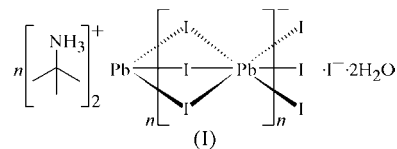
The inorganic motif is built up from characteristic face-sharing PbI_6 octahedra, which form infinite chains along the *b* axis. One unique inorganic chain runs through the centre of the unit cell. The asymmetric unit consists of a Pb atom on a centre of inversion and three I atoms, all on special positions, with I1 and I3 lying on the mirror plane at $y = \frac{3}{4}$ and I2 on the
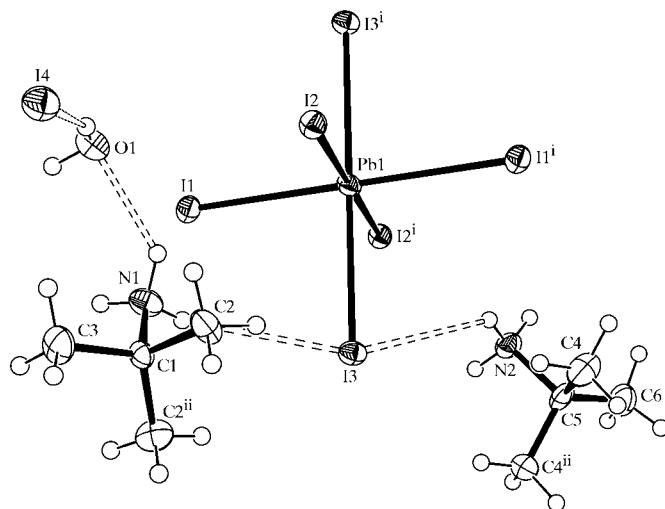
Figure 1
The asymmetric unit of (I), showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. The H atoms on N1 and N2 are disordered and only one set is shown at each site. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x, -y + \frac{3}{2}, z$.]
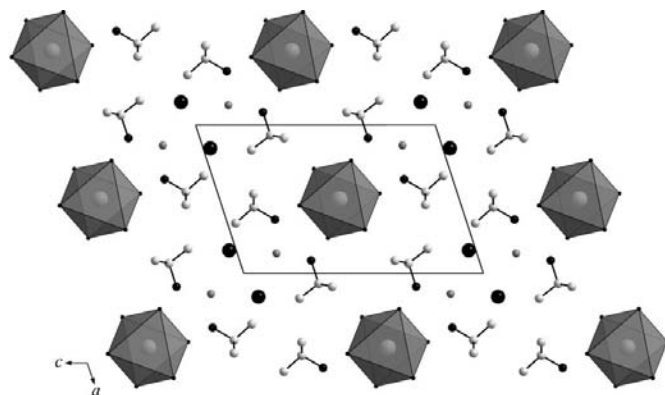
Figure 2
The packing of (I), viewed along the *b* axis.
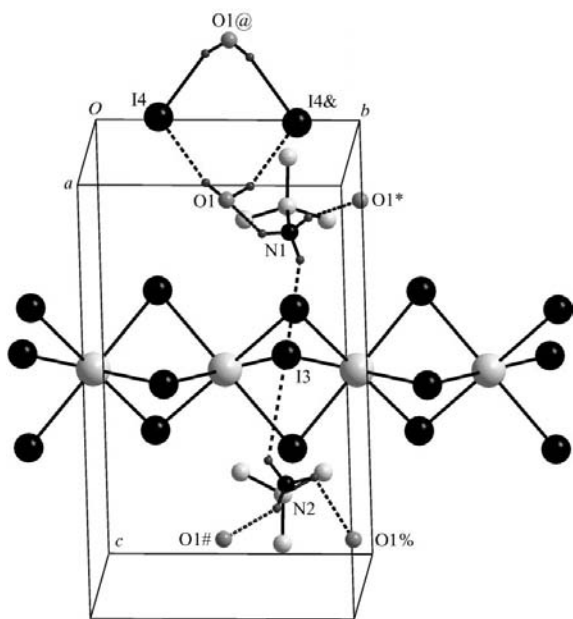
Figure 3
A magnified view of the face-sharing PbI_6 octahedra and hydrogen-bonding scheme. Atoms labelled with an ampersand (&), a percentage sign (%), a hash (#), an asterisk (*) and an 'at' sign (@) are at the symmetry positions $(-x, y + \frac{1}{2}, z)$, $(-x + 1, y + \frac{1}{2}, -z + 1)$, $(-x + 1, -y + 1, -z + 1)$, $(x, -y + \frac{3}{2}, z)$ and $(-x, -y + 1, -z)$, respectively.

mirror plane at $y = \frac{1}{4}$. Within the chains, the shared face consists of these three halides. The octahedra are somewhat distorted, with all three unique Pb—I distances different (Table 1), while the bond angles between *cis* ligands range from 83.346 (16) to 96.654 (16)°.

There are two unique *tert*-butylammonium cations in the asymmetric unit, labelled cat1 (containing atom N1) and cat2 (containing atom N2). In cat1, atoms N1, C1 and C3 lie on the mirror plane at $y = \frac{3}{4}$ and atom C2 occupies a general position. In cat2, atoms N2, C5 and C6 lie on the mirror plane at $y = \frac{1}{4}$, with atom C4 in a general position.

The two unique cations in the asymmetric unit interact with the inorganic chains *via* long N—H···I3 hydrogen bridges; the distances are 3.21 and 3.25 Å, respectively, for cat1 and cat2 (Table 2 and Fig. 3). The last two H atoms on the ammonium head groups bridge to the O atom of the water molecule of hydration. The N—H···O distances range from 2.05 to 2.48 Å. Lastly, the H atoms on the water molecule bridge towards the isolated I atom to form a symmetrical ring with graph-set notation $R_2^2(8)$, with donor–acceptor distances of 2.73 and 2.78 Å.

Experimental

PbI_2 (0.126 g, 0.273 mmol) was dissolved in 47% HI (2 ml) in a sample vial. Thereafter, $C(CH_3)_3NH_2$ (0.050 g, 0.684 mmol) was added and the precipitate was dissolved by refluxing for 12 h at 363 K. The solution was cooled slowly to room temperature at a rate of 2 K h^{-1}. A yellow single crystal suitable for X-ray diffraction analysis was selected and studied. Analysis calculated for $C_8H_{28}I_4N_2O_2Pb$: C 10.7, H 3.1, N 3.1%; found: C 10.8, H 3.3, N 3.2%.

Crystal data

$(C_4H_{12}N)_2[PbI_3]I \cdot 2H_2O$	$Z = 2$
$M_r = 899.11$	$D_x = 2.673$ Mg m^{-3}
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation
$a = 9.7917$ (10) Å	$\mu = 13.08$ mm^{-1}
$b = 7.9649$ (8) Å	$T = 173$ (2) K
$c = 15.0594$ (16) Å	Needle, yellow
$\beta = 107.985$ (3)°	$0.28 \times 0.1 \times 0.09$ mm
$V = 1117.1$ (2) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	5842 measured reflections
φ and ω scans	2878 independent reflections
	2416 reflections with $I > 2\sigma(I)$
Absorption correction: integration (*XPREP*; Bruker, 1999)	$R_{int} = 0.074$
$T_{min} = 0.174$, $T_{max} = 0.388$	$\theta_{max} = 28°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 0.2377P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.07$	$\Delta\rho_{max} = 2.67$ e Å^{-3}
2878 reflections	$\Delta\rho_{min} = -2.32$ e Å^{-3}
96 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Pb1—I3	3.1953 (5)	Pb1—I2	3.2355 (6)
Pb1—I1	3.2263 (6)		
I3—Pb1—I1^i	92.706 (16)	I3—Pb1—I2	93.491 (15)
I3—Pb1—I1	87.294 (16)	I1—Pb1—I2	96.654 (16)
I3—Pb1—I2^i	86.509 (15)	I1—Pb1—I2^i	83.346 (16)

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—H1A···I3	0.91	3.21	4.016 (10)	148
N1—H1B···O1	0.91	2.21	2.936 (9)	136
N1—H1C···O1^{ii}	0.91	2.05	2.936 (9)	164
N2—H2A···O1^i	0.91	2.16	2.958 (9)	147
N2—H2B···I3	0.91	3.25	3.905 (10)	131
N2—H2C···O1^{iii}	0.91	2.48	2.958 (9)	113
O1—H2···I4	0.86	2.73	3.572 (6)	165
O1—H1···I4^{iv}	0.86	2.78	3.570 (6)	154

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

All H were found in a difference map. For the H atoms bonded to O atoms, restraints were used to obtain reasonable O—H distances and H—O—H angles. Finally, these H atoms were refined using a riding model [$U_{iso}(H) = 1.2U_{eq}(O)$]. H atoms bonded to C and N atoms were refined in idealized positions using the riding-model approximation, with C—H distances of 0.98 Å, N—H distances of 0.91 Å and $U_{iso}(H)$ values of $1.5U_{eq}(C,N)$. The highest residual peak is 0.83 Å from atom Pb1.

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3019). Services for accessing these data are described at the back of the journal.

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