

Two packing motifs based upon chains of edge-sharing  $\text{PbI}_6$  octahedra

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Received 18 August 2006

Accepted 27 September 2006

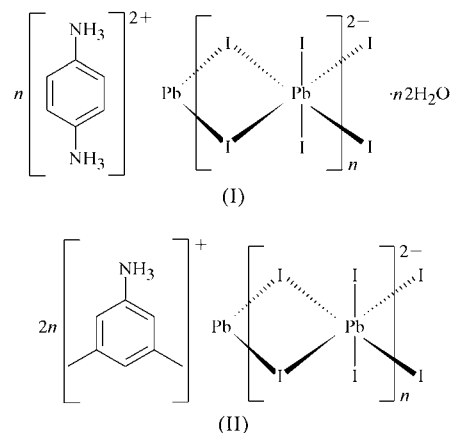
Online 22 November 2006

The compounds *catena*-poly[*p*-phenylenediammonium [[diiodolead(II)]-di- $\mu$ -iodo] dihydrate],  $\{(\text{C}_6\text{H}_{10}\text{N}_2)[\text{PbI}_4] \cdot 2\text{H}_2\text{O}\}_n$ , (I), and *catena*-poly[bis(3,5-dimethylanilinium) [[diiodolead(II)]-di- $\mu$ -iodo]],  $\{(\text{C}_8\text{H}_{12}\text{N})_2[\text{PbI}_4]\}_n$ , (II), crystallize as organic-inorganic hybrids. As such, the structures consist of chains of  $[\text{PbI}_2]^-$  units extending along the *c* axis in (I) and along the *b* axis in (II). The asymmetric unit in (I) contains one Pb atom on a site of  $2/m$  symmetry, two I atoms and a water molecule on mirror planes, and a *p*-phenylenediammonium molecule that sits around a site of  $2/m$  symmetry with the C and N atoms on a mirror plane. In (II), the Pb atom is on a twofold axis and the two I atoms are on general positions. Each Pb atom is octahedrally coordinated to six I atoms, arranged as chains of edge-sharing octahedra. Both compounds undergo hydrogen-bonding interactions between the ammonium groups and the I atoms. In addition, there are hydrogen bonds between the water molecules and the ammonium groups and halides in (I), and between the ammonium groups and the ring systems in (II).

## Comment

In recent years, a significant number of organic-inorganic hybrid materials based on metal halide units have been prepared and studied. Haloplumbates in particular have demonstrated a propensity for forming a great variety of crystalline structures by self-assembly from suitable solution mixtures. It has been shown that their structures can vary considerably, ranging from systems based on isolated inorganic polyhedra (Billing & Lemmerer, 2006*a*) to ones containing extended chains, as in  $(\text{C}_4\text{H}_{12})_2[\text{PbI}_3]\text{I} \cdot 2\text{H}_2\text{O}$  (Billing & Lemmerer, 2006*b*), right up to two- or three-dimensional networks (Billing & Lemmerer, 2006*c*). For systems containing extended chains, such chains may be formed by one, two or three bridging halides, referred to as corner-, edge- and face-sharing polyhedra, respectively. The most desired structure type, due to its suspected electroluminescence, photoluminescence and non-linear optical properties, is based on the  $\text{K}_2\text{NiF}_4$  type system, which has two-

dimensional layers of corner-sharing divalent metal halide octahedra, separated by organic compounds with primary ammonium cations, as in  $(\text{C}_8\text{H}_{16}\text{N})_2[\text{PbI}_4]$  (Billing &



Lemmerer, 2006*d*). The organic cations can either consist of alkylammonium chains or systems containing aromatic groups, with either a monoammonium ( $\text{R}-\text{NH}_3^+$ ) or a diammonium ( $^+\text{H}_3\text{N}-\text{R}-\text{NH}_3^+$ ) group. One of the simplest aromatic systems with a primary amine is aniline, which has been incorporated into the two-dimensional type system with copper(II) chloride (Larsen, 1974). The diammonium version,

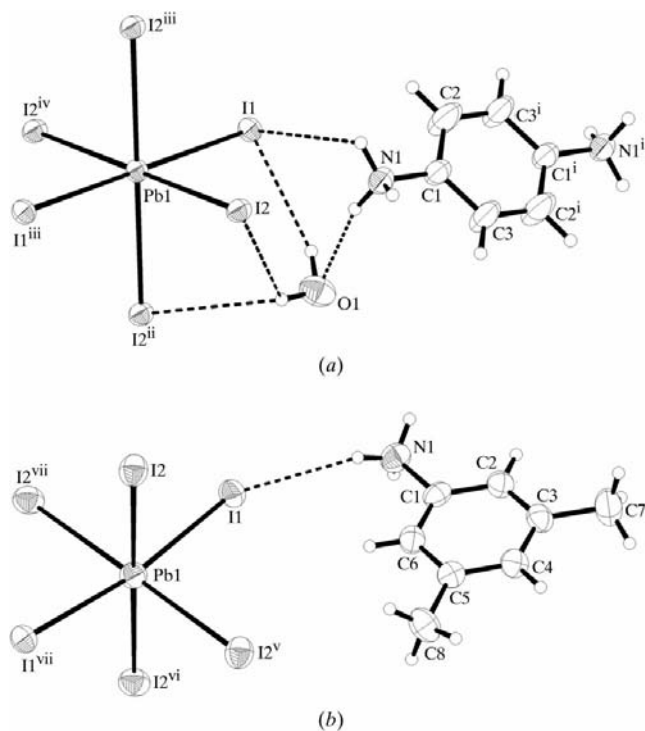


Figure 1

The asymmetric units of (a) (I) and (b) (II), showing the atomic numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only one position of the disordered  $\text{NH}_3^+$  group is shown. [Symmetry codes: (i)  $1-x, 1-y, z$ ; (ii)  $x, y, -1+z$ ; (iii)  $1-x, -y, z$ ; (iv)  $1-x, 1-x, -y, -1+z$ ; (v)  $x, -1+y, z$ ; (vi)  $-x, -1+y, \frac{1}{2}-z$ ; (vii)  $-x, y, \frac{1}{2}-z$ .]

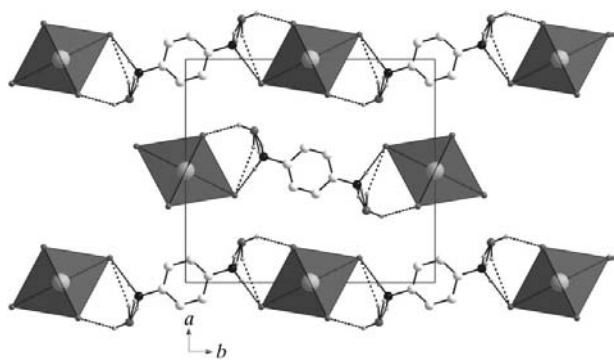
*viz.* *p*-phenylenediammonium, has also crystallized out in the  $K_2NiF_4$ -type system with a variety of metal halides, as in  $(H_3NC_6H_4NH_3)[CdBr_4]$  (Ishihara *et al.*, 1996) and  $(H_3NC_6H_4NH_3)[CuCl_4]$  (Bourne & Mangombo, 2004). Continuing this work, we wished to investigate the packing of the hybrid compound with *p*-phenylenediamine and lead(II) iodide, and to study the influence of the methyl groups bonded to the aniline backbone in a second compound with lead(II) iodide.

The two compounds reported here, *viz.*  $(H_3NC_6H_4NH_3)[PbI_4] \cdot 2H_2O$  (I) (Fig. 1*a*), and  $(C_8H_9NH_3)_2[PbI_4]$  (II) (Fig. 1*b*), adopt the same one-dimensional inorganic motif, albeit with different counter-ions to give unique packing arrangements. The inorganic chain consists of edge-shared  $PbI_6$  octahedra, so these structures differ from the  $K_2NiF_4$  archetype. Other one- and two-dimensional motifs that use the *p*-phenylenediammonium cation and lead(II) halides that have been reported to date include the twin anionic chains of *cis* edge-sharing  $\{[Pb_2I_6]^{2-}\}_\infty$  (Chakravarthy & Guloy, 1997) and the double-layer sheet of face-sharing square antiprisms of eight-coordinate lead(II) chloride (Bourne & Mangombo, 2004). To

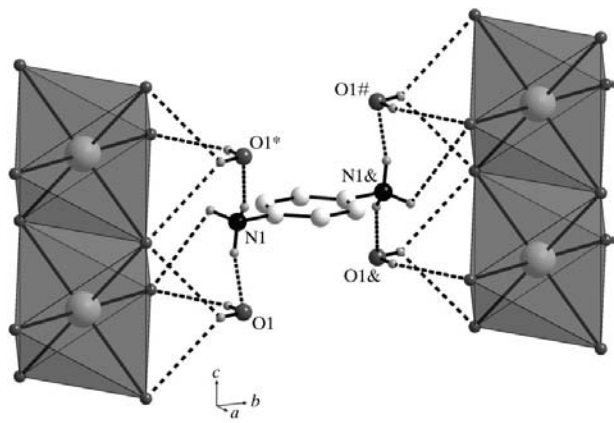
the best of our knowledge, there are only two previously reported cases of *trans* edge-sharing octahedral chains for lead(II) iodide, where square-pyramidal  $PbI_5$  units are connected to form infinite one-dimensional chains. The reported counter-ions are tetrahedral  $(Pr_4N)^+$  and octahedral  $[Mg(dmf)_6]^{2+}$  (dmf is dimethylformamide; Krautscheid & Vielsack, 1998). The bridging Pb—I bond distances lie over a larger range with the former counter-ion [3.1017 (9)–3.4553 (9) Å] compared with the more symmetrical bond-length range [3.1836 (5)–3.2407 (6) Å] when the latter, bulkier, counter-ion is included in the hybrid structure (Krautscheid & Vielsack, 1998). *trans*-Edge-sharing has also been reported for mercury; a one-dimensional chain of alternating octahedral and tetrahedral mercury(II) chloride units is formed when the counter-ion is  $(CH_3)_3NH^+$  (Salah *et al.*, 1983), while the lone H atom interacts with the  $Cl^-$  anions *via* hydrogen bonding.

The asymmetric part of the anionic layer of (I) contains a Pb atom on a site of  $2/m$  symmetry and two I atoms on mirror planes. Within a given  $PbI_6$  octahedron, the symmetry generates four equivalent positions for atom I2, in what is defined as the equatorial plane, and two equivalent positions for atom I1, deemed to be axial. Edge sharing between adjacent octahedra occurs through the equatorial I atoms only. The chains run parallel to the *c* axis, while the axial I atoms lie in the (001) plane, with an angle of  $26.50 (1)^\circ$  between the  $I1 \cdots I1^{iii}$  vector and the *b* axis [symmetry code: (iii)  $1 - x, -y, z$ ]. The coordination geometry around the Pb atom shows the typical axial compression of the octahedral geometry, with the bridging Pb1—I2 distances [3.2429 (6) Å] longer than the axial Pb1—I1 distances [3.1895 (8) Å]. The angle between all *cis*-related I atoms deviates by  $0.457 (17)^\circ$  from  $90^\circ$ , with all *trans* angles equal to  $180^\circ$  (Table 1).

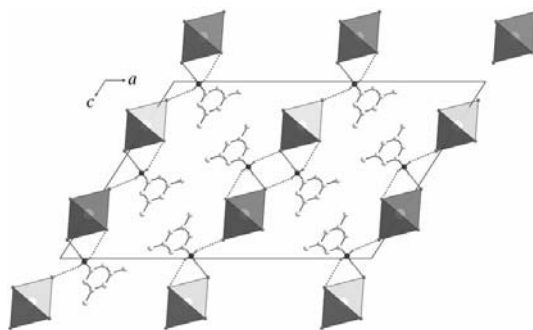
The *p*-phenylenediammonium cation in (I) sits around a site of  $2/m$  symmetry with the C and N atoms on a mirror plane (Fig. 1*a*). The cations all lie parallel to the (001) plane and are rotated by  $16.57 (12)^\circ$  away from the *b* axis, measured through the  $N1 \cdots N1$  vector. Adjacent aromatic rings are separated by a centroid-to-centroid distance of  $4.585 (1)$  Å, which is too



**Figure 2**  
A packing diagram of (I), viewed along the *c* axis. Hydrogen bonds between the three components are shown as dashed lines.



**Figure 3**  
A magnified view of the edge-sharing  $PbI_6$  octahedra in (I) and the hydrogen bonds (dashed lines). Atoms marked with an asterisk (\*), a hash (#) or an ampersand (&) are at the symmetry positions  $(x, y, 1 + z)$ ,  $(1 - x, 1 - y, 1 + z)$  and  $(1 - x, 1 - y, z)$ , respectively.



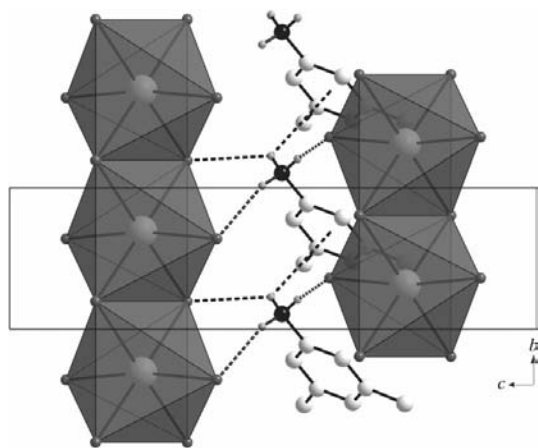
**Figure 4**  
A packing diagram of (II), viewed along the *b* axis, showing the alternating organic-inorganic layers and the N—H $\cdots$ I hydrogen bonds (dashed lines).

large to be considered as representing  $\pi$ - $\pi$  stacking interactions.

Fig. 2 clearly displays the one-dimensional inorganic motif adopted by (I), in which each *p*-phenylenediammonium molecule is surrounded by four one-dimensional chains of inorganic  $\text{PbI}_6$  octahedra in a chessboard-like pattern. In other words, the cations occupy the channels created by the anionic edge-sharing chains. In the direction of the *b* axis, crystal cohesion is achieved by a single  $\text{N}-\text{H}\cdots\text{I}$  hydrogen bond on either end of the organic molecule, related to the  $\text{NH}_3$  polar groups. The water molecules, which lie on mirror planes, are embedded between the organic and inorganic moieties and held in place by  $\text{O}-\text{H}\cdots\text{I}$  and  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds. Within the inorganic chains, cohesion is achieved by strong ionic bonds between equatorial  $\text{I}^-$  and  $\text{Pb}^{2+}$  ions.

There is only one hydrogen bond between the N-donor atom and the halide acceptor atom of (I), instead of three as found in the  $\text{K}_2\text{NiF}_4$ -type systems. Nevertheless, the chains of edge-sharing octahedra are connected by the cations along the *b* axis in the sequence  $\text{Ar}-\text{N1}-\text{H1C}\cdots\text{I1}-\text{Pb1}-\text{I1}\cdots\text{H1C}-\text{N1}-\text{Ar}$  (Fig. 2). The two remaining H atoms of the ammonium head group bond to the O atom of the water molecule. The two hydrogen bonds are related by a mirror plane on which the *p*-phenylenediammonium cation lies, and hence the  $\text{O1}\cdots\text{H1B}-\text{N1}-\text{H1A}\cdots\text{O1}$  donor-acceptor distances are almost identical (1.93 and 1.94 Å) (Fig. 3). The H atoms on the water molecule themselves both bond to the equatorial and axial I atoms of the octahedra (Table 2).

In (II), the coordination geometry around the Pb atom (Table 3) and the edge-sharing  $\text{PbI}_6$  chain geometry is essentially the same as in (I), except that the Pb atom sits on a twofold axis, while all other atoms are on general positions. The chains run parallel to the *b* axis and the vector through the axial I atoms makes an angle of  $6.74$  ( $12^\circ$ ) with the *c* axis. The angles between *cis*- and *trans*-related I atoms deviate significantly from  $90$  and  $180^\circ$ , respectively.



**Figure 5**

A magnified view of the edge-sharing  $\text{PbI}_6$  octahedra in (II) and the  $\text{N1}-\text{H1C}\cdots\pi$  hydrogen bond between the organic cations along the *b* axis.

Compound (II) has a different packing arrangement to (I). In this case, hydrocarbon layers of 3,5-dimethylanilinium molecules alternate with ionic layers of edge-sharing  $\text{PbI}_6$  octahedra running along the *b* axis (Fig. 4). In the directions of the *a* and *c* axes, crystal cohesion between the inorganic and organic layers is achieved by three  $\text{N}-\text{H}\cdots\text{I}$  hydrogen bonds, related to the  $\text{NH}_3$  polar groups. There are  $\text{N}-\text{H}\cdots\pi$  interactions between neighbouring ring systems perpendicular to the hydrogen bonds. In the direction parallel to the inorganic chains, cohesion is again achieved by strong ionic bonds between equatorial I and Pb atoms.

The three H atoms form hydrogen bonds between two neighbouring chains. Atom H1C forms a weak hydrogen bond to the equatorial atom I1, but a stronger bond to the ring system of an adjacent 3,5-dimethylanilinium molecule of 2.95 Å. The  $\text{C}-\text{H}\cdots\pi$  angle is  $110.35$  ( $24^\circ$ ). The remaining two H atoms form hydrogen bonds to two axial halides of adjacent chains, with shorter donor-acceptor distances of 2.57 and 2.84 Å (Fig. 5). The 3,5-xyliidinium cation sits on a general position. The atomic numbering scheme is shown in Fig. 1(b). Within the organic layers, the molecules are stacked head-to-tail along the  $[101]$  direction at a dihedral angle of  $87.3$  ( $1^\circ$ ), and head-to-head along the  $[001]$  direction.

## Experimental

For the preparation of (I),  $\text{PbI}_2$  (0.200 g, 0.434 mmol) was dissolved in 47% HI (7 ml) in a test tube.  $\text{NH}_2\text{C}_6\text{H}_4\text{NH}_2$  (0.043 g, 0.398 mmol) was then added and the resulting precipitate dissolved by refluxing for 12 h at 393 K. The solution was then cooled slowly to room temperature at a rate of  $2\text{ K h}^{-1}$ . A brown single crystal suitable for X-ray diffraction analysis was selected and studied. Analysis calculated for  $\text{C}_6\text{H}_{14}\text{I}_4\text{N}_2\text{Pb}$ : C 8.37, H 1.64, N 3.25%; found: C 8.23, H 1.79, N 3.13%. For the preparation of (II),  $\text{PbI}_2$  (0.060 g, 0.130 mmol) was dissolved in 47% HI (2 ml) in a round-bottomed flask.  $\text{C}_8\text{H}_9\text{NH}_2$  (0.040 g, 0.330 mmol) was then added and the resulting precipitate dissolved by refluxing for 12 h at 363 K. The solution was then cooled slowly to room temperature at a rate of  $2\text{ K h}^{-1}$ . A yellow single crystal suitable for X-ray diffraction analysis was selected and studied. Analysis calculated for  $\text{C}_{16}\text{H}_{24}\text{I}_4\text{N}_2\text{Pb}$ : C 20.04, H 2.52, N 2.92%; found: C 19.96, H 2.48, N 2.89%.

## Compound (I)

### Crystal data

$(\text{C}_6\text{H}_{10}\text{N}_2)[\text{PbI}_4]\cdot 2\text{H}_2\text{O}$   
 $M_r = 860.98$   
 Orthorhombic,  $Pnmm$   
 $a = 12.952$  (3) Å  
 $b = 14.489$  (3) Å  
 $c = 4.5851$  (10) Å  
 $V = 860.4$  (3) Å<sup>3</sup>

$Z = 2$   
 $D_x = 3.323\text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 $\mu = 16.97\text{ mm}^{-1}$   
 $T = 173$  (2) K  
 Polyhedral, brown  
 $0.5 \times 0.37 \times 0.3\text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: integration (*XPRED* in *SAINT-Plus*; Bruker, 1999)  
 $T_{\min} = 0.012$ ,  $T_{\max} = 0.059$

5460 measured reflections  
 1168 independent reflections  
 1095 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.056$   
 $\theta_{\max} = 28^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 2.0341P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.081$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.11$	$\Delta\rho_{\max} = 2.36 \text{ e } \text{\AA}^{-3}$
1168 reflections	$\Delta\rho_{\min} = -1.02 \text{ e } \text{\AA}^{-3}$
49 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.0204 (9)

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I).

Pb1—I1	3.1895 (8)	Pb1—I2	3.2429 (6)
I1—Pb1—I2 <sup>i</sup>	89.543 (17)	I1 <sup>i</sup> —Pb1—I2 <sup>i</sup>	90.457 (17)

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

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1C $\cdots$ I1	0.91	3.18	3.611 (6)	111
N1—H1A $\cdots$ O1 <sup>ii</sup>	0.91	1.94	2.794 (7)	156
N1—H1B $\cdots$ O1	0.91	1.93	2.794 (7)	158
O1—H6 $\cdots$ I2 <sup>iii</sup>	0.95	3.16	3.771 (7)	124
O1—H7 $\cdots$ I1	0.95	2.99	3.901 (8)	160

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

### Compound (II)

#### Crystal data

$(\text{C}_8\text{H}_{12}\text{N})_2[\text{PbI}_4]$	$Z = 4$
$M_r = 959.16$	$D_x = 2.665 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 30.1215 (19) \text{ \AA}$	$\mu = 12.22 \text{ mm}^{-1}$
$b = 4.6111 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 20.4599 (12) \text{ \AA}$	Plate, yellow
$\beta = 122.725 (3)^\circ$	$0.2 \times 0.13 \times 0.02 \text{ mm}$
$V = 2390.7 (3) \text{ \AA}^3$	

#### Data collection

Bruker SMART CCD area-detector diffractometer	11071 measured reflections
$\varphi$ and $\omega$ scans	2871 independent reflections
Absorption correction: integration ( <i>XPREP</i> in <i>SAINT-Plus</i> ; Bruker, 1999)	2337 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.174, T_{\max} = 0.782$	$R_{\text{int}} = 0.044$
	$\theta_{\max} = 28^\circ$

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.024$	$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2]$
$wR(F^2) = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{\max} = 0.005$
2871 reflections	$\Delta\rho_{\max} = 0.59 \text{ e } \text{\AA}^{-3}$
108 parameters	$\Delta\rho_{\min} = -1.08 \text{ e } \text{\AA}^{-3}$

**Table 3**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II).

Pb1—I1	3.1984 (3)	Pb1—I2 <sup>i</sup>	3.2728 (4)
Pb1—I2	3.2426 (4)		
I1—Pb1—I1 <sup>ii</sup>	171.556 (13)	I1—Pb1—I2 <sup>i</sup>	92.250 (9)
I1—Pb1—I2	87.785 (9)	I1 <sup>ii</sup> —Pb1—I2 <sup>i</sup>	93.752 (9)
I1 <sup>ii</sup> —Pb1—I2	86.269 (9)		

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

**Table 4**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ I1	0.89	2.84	3.663 (4)	155
N1—H1B $\cdots$ I1 <sup>iii</sup>	0.89	2.57	3.432 (4)	165
N1—H1C $\cdots$ I2 <sup>iv</sup>	0.89	3.15	3.789 (4)	131

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

For compound (I), all H atoms were found in a difference map. For 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, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{O})$ . H atoms bonded to C and N atoms were refined in idealized positions in the riding-model approximation, with Ar—H = 0.95  $\text{\AA}$  and N—H = 0.91  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{N})$ . There is a close contact between atom H7 of the water molecule and atoms H1A and H1B of the ammonium group (1.77 and 1.52  $\text{\AA}$ , respectively). The position of H7 is justified as it then forms a hydrogen bond to atom I1. The short intermolecular H $\cdots$ H contacts are due to the acute angle between the donor atom N1, atom O1 and the I1 acceptor atom. For compound (II), all H atoms were refined using a riding model, with Ar—H = 0.93  $\text{\AA}$ , C—H = 0.96  $\text{\AA}$  and N—H = 0.89  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{N})$ . The  $\text{NH}_3$  and  $\text{CH}_3$  groups were allowed to rotate but not to tip in both compounds. The highest residual peaks are 0.82  $\text{\AA}$  from atom Pb1 in (I) and 0.87  $\text{\AA}$  from I2 in (II).

For both compounds, 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, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

The University of the Witwatersrand and the National Research Fund (GUN 2069064) are thanked for the award of a research grant and for providing the infrastructure required to do this work. AL thanks Professor D. C. Levendis and Dr M. A. Fernandes for help with handling the disorder in compound (I).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3041). Services for accessing these data are described at the back of the journal.

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