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Preparation, structure and optical properties of $[CH_3SC(=NH_2)NH_2]_3PbI_5$, $[CH_3SC(=NH_2)NH_2]_4Pb_2Br_8$ and $[CH_3SC(=NH_2)NH_2]_3PbCl_5{\cdot}CH_3SC(=NH_2)NH_2Cl$

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The preparation, crystal structures and optical absorption spectra of $[CH_3SC(=NH_2)NH_2]_3PbI_5$ **1**, $[CH_3SC(=NH_2)NH_2]_4Pb_2Br_8$ **2** and $[CH_3SC(=NH_2)NH_2]_3PbCl_5{\cdot}CH_3SC(=NH_2)NH_2Cl$ **3** are reported. Compounds **1** and **3** consist of deformed PbX_6 octahedra, which share opposite corners to form quasi-zero-dimensional or one-dimensional infinite chains along the *a*-axis. Compound **2** consists of Pb_2Br_9 units which are connected with two neighbouring units by non-opposite Br atoms; in this way, infinite zigzag chains are formed. A blue shift of the excitonic absorption bands, in comparison to those of systems with higher dimensionality, is observed.

Introduction

A great problem of solid state chemistry is the correlation of physical properties with the structural features of a particular compound or class of compounds. From this point of view, low-dimensional (LD) compounds play an important role, because the properties that arise, when the interactions between atoms or molecules are confined to one or two dimensions, make theoretical models much simpler.[1]

In the class of inorganic–organic hybrid materials a novel family of (LD) materials has been described, in which the inorganic part is confined, by intercalating organic units, in two, one or zero dimensions[1–16] (for a review see ref. 11). These compounds are involved in various fundamental as well as more applied studies, related to their structural,[1,3,5–9] optical,[2–4,11,13,16] transport,[3,6,11] and other physical properties.[1–16] Recently, much attention has been devoted to a family of such compounds, the haloplumbate and halotin perovskites, due to their special structural features and physical properties. The haloplumbate perovskites family can be classified in four different classes.[2,11] The $APbX_3$ class [where A is amine-H^+ or (diamine-2H)$_{0.5}{}^+$; $X=I$, Br, Cl]. These compounds form a three-dimensional (3D) network. The A_2PbX_4 class, which has a two-dimensional (2D) character and consists of layers of four-coplanar-corner sharing octahedra, separated by layers of amines. By the use of different size of amines, or by a combination of them, we can tailor the thickness of the organic or inorganic layer. The A_3PbX_5 class, which is one-dimensional (1D) and the A_4PbX_6 class, that gives zero-dimensional materials (0D). The energy-gap value (E_g) of these systems increases and the low-energy peaks, which are due to the lowest free excitonic states, are shifted to higher energies as the dimensionality decreases (3D→2D→1D→0D) (see ref. 11 and references cited therein).

In contrast to the A_2PbX_4 class, that has been studied extensively, little work has been done with the A_3PbX_5[14] class, owing to the lack of materials. To the best of our knowledge one salt of this family has been reported so far: $[NH_2C(I)=NH_2]_3PbI_5$.[14]

Here, we report the synthesis, structure and the UV–VIS optical absorption spectra, of three new salts: $[CH_3SC(=NH_2)NH_2]_3PbI_5$ **1**, $[CH_3SC(=NH_2)NH_2]_4Pb_2Br_8$ **2** and $[CH_3SC(=NH_2)NH_2]_3PbCl_5{\cdot}CH_3SC(=NH_2)NH_2Cl$ **3**. The results are compared with those observed from similar LD compounds based on inorganic units.

Experimental

Starting materials and apparatus

The following starting materials were used without further purification; PbO (Ferak 01 881), thiourea (Ferak zur Analyse 01 525), methyl iodide (Fluka puriss 67690), hydroiodic acid (57%) (Merck 341), hydrobromic acid (47%) (Merck 304), hydrochloric acid (25%) (Merck 312). Crystal X-ray intensity data were collected on a Crystal Logic[17] dual goniometer diffractometer using graphite-monochromated Mo-Kα radiation. Unit cell dimensions were determined and refined by using the angular setting of 24 automatically centered reflections in the range $11<2\theta<24$. Intensity data were recorded using a θ-2θ scan. Three standard reflections monitored every 97 reflections showed less than 3% variation and no systematic decay. Lorentz, polarization and absorption correction were applied using Crystal Logic Software. The structures were solved by Patterson methods using SHELXS-86[18] and refined by full-matrix least-squares techniques with SHELXL-93.[19] Hydrogen atoms were not located. All non hydrogen atoms were refined anisotropically, except the C(10), C(1), C(2), C(4), C(9), N(5), N(6) atoms of compound **3**. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/110.

Optical absorption spectra were recorded on a Varian model 2390 spectrometer.

Preparation of compounds

The $[CH_3SC(=NH_2)NH_2]I$ salt was prepared by refluxing 7.6 g (0.1 mol) of thiourea and 14.2 g (0.1 mol) methyl iodide in 50 ml CH_3CN for 2.5 h. The solution was cooled at 0 °C and 18.5 g of white crystals of the desired product were precipitated. The crystals were filtered off and washed with diethyl ether [yield 85%; mp 116 °C; ^1H NMR (D_2O), δ 2.67J. The $[CH_3SC(=NH_2)NH_2]Br$ salt was prepared by refluxing a solution of 7.6 g (0.1 mol) of thiourea and 20 ml of HBr in 30 ml methanol for 5 h. The solution was condensed to 5 ml and cooled at 0 °C to give 5.1 g of a white crystalline precipitate. The precipitate was filtered off and washed with diethyl ether [yield 30%; mp 102 °C; ^{1}H NMR (D_2O), δ 2.66J.

The $[CH_3SC(=NH_2)NH_2]_3PbI_5$ salt was prepared by refluxing a solution of 0.654 g (3 mmol) of $[CH_3SC(=NH_2)NH_2]I$ and 0.223 g (1 mmol) of PbO in 20 ml of 57% HI for 0.5 h. The solution was left to cool at room temperature to give 0.844 g of yellow–orange crystals. The crystals were recrystallized from 57% HI (yield 76%; mp 199–201 °C).

The $[CH_3SC(=NH_2)NH_2]_4Pb_2Br_8$ salt was prepared by the following two methods:

(*a*) by refluxing a solution of 0.436 g (2 mmol) of $[CH_3SC(=NH_2)NH_2]I$ and 0.223 g (1 mmol) of PbO in 20 ml of 47% HBr for 3 h. The solution was left to cool at room temperature to give 0.425 g of white crystals (yield 60%; mp 157 °C).

(*b*) by refluxing a solution of 0.342 g (2 mmol) of $[CH_3SC(=NH_2)NH_2]Br$ and 0.223 g (1 mmol) of PbO in 20 ml of 47% HBr for 3 h. The solution was left to cool at room temperature to give 0.354 g of white crystals (yield 50%; mp 157 °C).

The $[CH_3SC(=NH_2)NH_2]_3PbCl_5 \cdot [CH_3SC(=NH_2)NH_2]Cl$ salt was prepared by refluxing 0.436 g (2 mmol) of $[CH_3SC(=NH_2)NH_2]I$ and 0.112 g (0.5 mmol) of PbO in 20 ml of 25% HCl for 3 h. The solution was filtered and left to concentrate at room temperature. After the evaporation of the solvent three different types of crystals were obtained, *i.e.*, PbI_2, an organic material and some colourless prismatic crystals of the required compound (yield ≈5%).

Results and discussion

Morphology of materials

The compounds studied herein were prepared in a pure single crystal form. The crystals were large enough for X-ray crystal structure determination and investigation of their physical properties.

Crystal structure

Packing diagrams of compounds **1**–**3** are shown in Fig. 1–3 respectively. A summary of crystal, intensity collection and refinement data for the three compounds is given in Table 1. Selected bonds and angles of the three compounds are listed in Tables 2–4. Compound **1** crystallizes in the orthorhombic system. As can be seen from the packing diagram of Fig. 1, it consists of distorted PbI_6 octahedra (bond distances and angles are given in Table 2). This distortion is probably caused by the stereochemical activity of the lead lone pair.[20] Each octahedron shares opposite corners [I(3) atoms], forming infinite one-dimensional chains extending along the *a* axis. The Pb—I(3)—Pb angle is 174.98° indicating that the chain is almost linear. The structure is similar to that of $CaCrF_5$, $(NH_4)_2MnF_5$, $[NH_2C(I)=NH_2]_3SnI_5$ and $[NH_2C(I)=NH_2]_3PbI_5$.[14] In **1** the distances of the I(3) atom connecting the Pb atoms are different (3.882, 3.037 Å), in contrast to $[NH_2C(I)=NH_2]_3PbI_5$ where the distances are almost the same (3.182, 3.243 Å). The $CH_3SC(=NH_2)NH_2$ cations are arranged around the inorganic chains, and thus separate them. The two C—N bond lengths are almost equal (Table 2), indicating that the cations have a resonance structure $[CH_3SC(\overset{...}{-}NH_2)_2]$. The compound is considered to be a quasi-zero dimensional system (q-0D).

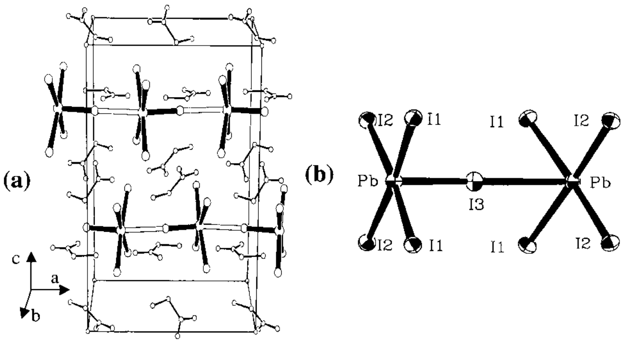

Fig. 1 (a) Packing diagram of $[CH_3SC(=NH_2)NH_2]_3PbI_5$, showing the detailed structure and the PbI_5 (thick bonds) chains. (b) A drawing of two connected PbI_5 units showing the atoms and the 50% probability ellipsoids.

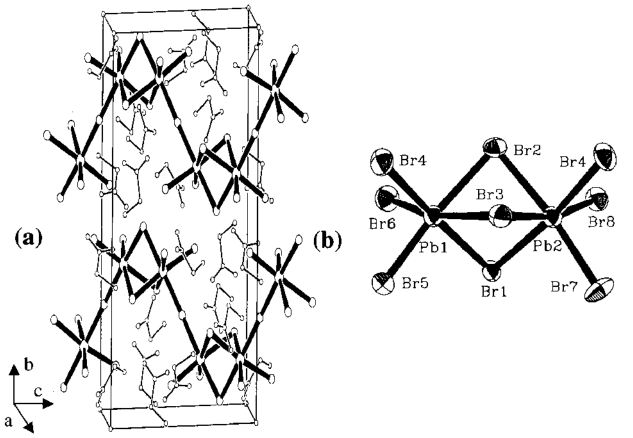

Fig. 2 (a) Packing diagram of $[CH_3SC(=NH_2)NH_2]_4Pb_2Br_8$, showing the detailed structure and the Pb—Br zigzag chains (thick bonds). (b) A drawing of the Pb_2Br_9 unit showing the atoms and the 50% probability ellipsoids.

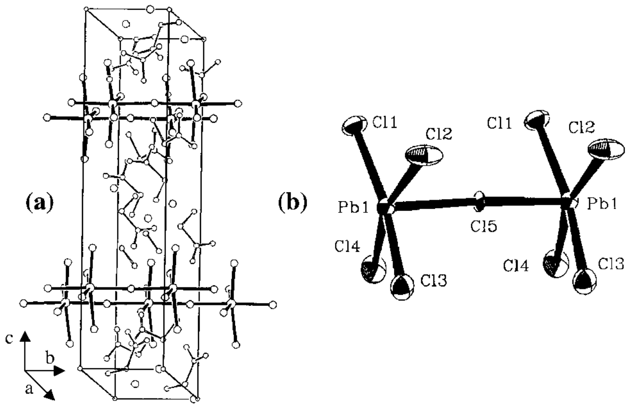

Fig. 3 (a) Packing diagram of $[CH_3SC(=NH_2)NH_2]_3PbCl_5 \cdot [CH_3SC(=NH_2)NH_2]Cl$ along the *a* axis, showing the detailed structure and the $PbCl_5$ chains (thick bonds). (b) A drawing of two connected $PbCl_5$ units showing the atoms and the 50% probability ellipsoids.

Compound **2** crystallizes in the monoclinic system. As is shown in the packing diagram (Fig. 2) it is built up of Pb_2Br_9 units. These units are composed from two face-sharing octahedra. Each unit is connected with two neighbouring units by sharing the non-opposite Br(4) atoms; in this way infinite zigzag chains are formed.

Compound **3** crystallizes in the monoclinic system. It has a compositional formula of $[CH_3SC(=NH_2)NH_2]_4PbCl_6$, but based on its structure, we can formulate it as $[CH_3SC(=NH_2)NH_2]_3PbCl_5 \cdot [CH_3SC(=NH_2)NH_2]Cl$. As can be seen from the packing diagram of Fig. 3, it consists of two crystallographically independent inorganic chains. These chains are similar to those of **1**, but for **3** the two bridging distances [Pb(1)—Cl(5) for the first chain and Pb(2)—Cl(10) for the second chain] are almost equal (2.863, 2.893 and 2.811, 2.941 Å). These chains are separated by columns of

Table 1 Summary of crystal, intensity collection and refinement data

	1	**2**	**3**
empirical formula	$C_6H_{21}I_5N_6PbS_3$	$C_8H_{28}Br_8N_8Pb_2S_4$	$C_8H_{28}Cl_6N_8PbS_4$
M_w	1115.16	1418,288	784.53
a/Å	13.661(9)	12.476(9)	19.556(9)
b/Å	10.009(6)	22.43(1)	5.748(3)
c/Å	18.60(1)	13.120(8)	49.55(2)
β/degrees	107.77(2)	91.15(2)	
V/Å^3	2544(3)	3496(4)	5569(5)
Z	4	4	8
μ/mm^{-1}	12.949	19.016	6.948
$D_c(D_m)$/kg m^{-3}	2912(2880)	2694(2660)	1871(1860)
space group	*Pnam*	$P2_1/n$	$C2$
θ range/degrees	0–25.01	0–24.83	0–24.24
scan range 2θ/degrees	$2.3+\alpha_1\alpha_2$ separation	$2.4+\alpha_1\alpha_2$ separation	$2.4+\alpha_1\alpha_2$ separation
scan mode	θ–2θ	θ–2θ	θ–2θ
speed/degrees min^{-1}	2.7	2.0	3.2
refl. collected/independent	4120(2314)	4770(4528)	8082(7974)
R_{int}	0.03181	0.0290	0.0346
GOF	1.110	1.067	1.075
$R(R_w)$	0.0294(0.0725)	0.0450(0.1232)	0.0569(0.1576)

Table 2 Bond lengths (Å) and angles (degrees) for compound **1**

Pb—I(1)	3.037(2)	N(1)—C(2)	1.297(11)
Pb—I(3′)	3.882(2)	N(2)—C(2)	1.291(13)
Pb—I(2)	3.189(2)	S(2)—C(4)	1.732(6)
Pb—I(1)	3.248(2)	S(2)—C(3)	1.782(7)
S(1)—C(2)	1.725(7)	N(3)—C(4)	1.296(8)
S(1)—C(1)	1.797(8)	N(4)—C(4)	1.309(8)
I(3)—Pb—I(2)	93.73(2)	N(2)—C(2)—N(1)	119.0(8)
I(2′)—Pb—I(2)	89.39(6)	N(2)—C(2)—S(1)	115.8(7)
I(2)—Pb—I(1′)	89.26(5)	N(1)—C(2)—S(1)	125.2(7)
I(3)—Pb—I(1)	91.66(2)	C(4)—S(2)—C(3)	102.8(3)
I(2)—Pb—I(1)	174.515(13)	N(3)—C(4)—N(4)	120.5(6)
I(1′)—Pb—I(1)	91.59(6)	N(3)—C(4)—S(2)	122.8(5)
C(2)—S(1)—C(1)	102.3	N(4)—C(4)—S(2)	116.7(5)

Primed atoms related to unprimed equivalents by x, y, $-z+3/2$.

Table 3 Selected bond lengths (Å) and angles (degrees) for compound **2**

Pb(1)—Br(6)	2.910(3)	Pb(2)—Br(3)	3.027(2)
Pb(1)—Br(5)	2.943(2)	Pb(2)—Br(1)	3.101(2)
Pb(1)—Br(4′)	3.027(2)	Pb(2)—Br(7)	3.117(3)
Pb(1)—Br(1)	3.053(2)	Pb(2)—Br(8)	3.132(3)
Pb(1)—Br(2)	3.220(2)	Pb(2)—Br(2)	3.165(3)
Pb(2)—Br(4)	2.992(2)	Br(4)—Pb(1″)	3.027(2)
Br(6)—Pb(1)—Br(5)	91.81(6)	Br(3)—Pb(2)—Br(7)	93.42(6)
Br(6)—Pb(1)—Br(4′)	90.10(8)	Br(1)—Pb(2)—Br(7)	89.46(6)
Br(5)—Pb(1)—Br(4′)	92.35(7)	Br(4)—Pb(2)—Br(8)	85.29(7)
Br(6)—Pb(1)—Br(1)	96.12(7)	Br(3)—Pb(2)—Br(8)	166.62(6)
Br(5)—Pb(1)—Br(1)	88.91(6)	Br(1)—Pb(2)—Br(8)	92.22(6)
Br(4′)—Pb(1)—Br(1)	173.61(6)	Br(7)—Pb(2)—Br(8)	99.73(6)
Br(6)—Pb(1)—Br(2)	91.38(6)	Br(4)—Pb(2)—Br(2)	85.75(7)
Br(5)—Pb(1)—Br(2)	174.92(5)	Br(3)—Pb(2)—Br(2)	79.88(5)
Br(4′)—Pb(1)—Br(2)	91.59(7)	Br(1)—Pb(2)—Br(2)	86.99(6)
Br(1)—Pb(1)—Br(2)	86.82(6)	Br(7)—Pb(2)—Br(2)	172.39(6)
Br(4)—Pb(2)—Br(3)	90.46(7)	Br(8)—Pb(2)—Br(2)	87.1(5)
Br(4)—Pb(2)—Br(1)	172.43(6)	Pb(1)—Br(1)—Pb(2)	81.37(6)
Br(3)—Pb(2)—Br(1)	90.36(6)	Pb(2)—Br(2)—Pb(1)	77.85(5)
Br(4)—Pb(2)—Br(7)	98.01(7)	Pb(2)—Br(4)—Pb(1″)	171.49(10)

Symmetry transformations used to generate equivalent atoms: ′ $x+1/2$, $-y+1/2$, $z+1/2$. ″ $x-1/2$, $-y+1/2$, $z-1/2$.

$CH_3SC(=NH_2)NH_2$ to which the Cl^- anions are hydrogen bonded. The structure of this compound is similar to that of $[NH_2C(I)=NH_2]_3PbI_5$.[14]

Optical properties

Fig. 4 shows the optical absorption spectra of thin deposits[21] of compounds **1**–**3** at room temperature. Low energy excitonic peaks occur at 408 (3.04), 360 (3.44) and 316 nm (3.92 eV) for the compounds **1**–**3**, respectively. Assuming that the energy gap (E_g) occurs at the dip, which is close to the excitonic band, one can estimate the values of the excitonic binding energy (E_b) of the materials. Thus we found $E_g = 3.369$ eV, $E_b = 330.3$ meV, for **1**, $E_g = 3.936$ eV, $E_b = 492.1$ meV for **2** and $E_g = 4.593$ eV, $E_b = 668.5$ meV for **3**. As it can be seen, the excitonic peak positions and the band-gaps are shifted to lower energies in order I < Br < Cl, while the excitonic binding energy is increased in the same order.

The excitonic peak position (E_{ex}) and the band gap values of **1** are between those of similar 1D compounds, *e.g.*, for $[NH_2C(I)=NH_2]_3PbI_5$, $E_{ex} = 2.70$ eV (460 nm), $E_g = 3.18$ eV[22] and 0D compounds, *e.g.*, for $(CH_3NH_3)_4PbI_6{\cdot}2H_2O$, $E_{ex} = 3.33$ eV (372 nm), $E_g = 3.87$ eV,[2] confirming the q-0D character of **1**.

Compound **2** has excitonic peak position (E_{ex}) and band gap value in between those of similar 2D compounds, *e.g.*, for $(C_9H_{19}NH_3)_2PbBr_4$, $E_{ex} = 3.15$ eV (394 nm), $E_g = 3.87$ eV[2] and 0D compounds, *e.g.*, for $(CH_3NH_3)_4PbBr_6{\cdot}2H_2O$, $E_{ex} = 3.97$ eV (312 nm), $E_g \geq 4.77$ eV,[2] confirming its 1D character. To our knowledge, no other similar 1D material with Br has been studied to enable direct comparison.

The only other similar salts with Cl, that have been studied, are the 2D compounds $(C_9H_{19}NH_3)_2PbCl_4$ and $[Ph(CH_2)_2NH_3]_2PbCl_4$, which have $E_{ex} = 3.75$ eV (331 nm) that is lower than those of **3** as expected from its 1D character.

The optical properties of similar tin based compounds indicate similar structures and the preparation, structure and optical properties of such compounds will be published elsewhere.[23]

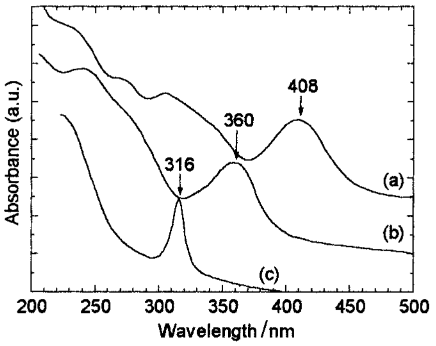

Fig. 4 Optical absorption spectra of (a) **1**, (b) **2** and (c) **3**.

Table 4 Selected bond lengths (Å) and angles (degrees) for compound **3**

Pb(1)—Cl(2)	2.794(7)	Pb(2)—Cl(7)	2.804(7)
Pb(1)—Cl(3)	2.834(8)	Pb(2)—Cl(10′)	2.811(12)
Pb(1)—Cl(5′)	2.863(12)	Pb(2)—Cl(6)	2.846(8)
Pb(1)—Cl(4)	2.886(7)	Pb(2)—Cl(9)	2.866(8)
Pb(1)—Cl(5)	2.893(12)	Pb(2)—Cl(8)	2.931(8)
Pb(1)—Cl(1)	2.922(7)	Pb(2)—Cl(10)	2.941(12)
Cl(2)—Pb(1)—Cl(3)	88.9(2)	Cl(7)—Pb(2)—Cl(10′)	92.5(3)
Cl(2)—Pb(1)—Cl(5′)	83.2(3)	Cl(7)—Pb(2)—Cl(6)	88.1(2)
Cl(3)—Pb(1)—Cl(5′)	95.3(3)	Cl(10′)—Pb(2)—Cl(6)	84.5(2)
Cl(2)—Pb(1)—Cl(4)	164.5(3)	Cl(7)—Pb(2)—Cl(9)	165.0(3)
Cl(3)—Pb(1)—Cl(4)	84.2(2)	Cl(10′)—Pb(2)—Cl(9)	100.8(3)
Cl(5′)—Pb(1)—Cl(4)	83.6(2)	Cl(6)—Pb(2)—Cl(9)	86.2(2)
Cl(2)—Pb(1)—Cl(5)	91.2(3)	Cl(7)—Pb(2)—Cl(8)	92.2(2)
Cl(3)—Pb(1)—Cl(5)	86.1(3)	Cl(10′)—Pb(2)—Cl(8)	84.0(3)
Cl(5′)—Pb(1)—Cl(5)	174.2(3)	Cl(6)—Pb(2)—Cl(8)	168.5(3)
Cl(4)—Pb(1)—Cl(5)	102.1(2)	Cl(9)—Pb(2)—Cl(8)	96.1(2)
Cl(2)—Pb(1)—Cl(1)	92.6(2)	Cl(7)—Pb(2)—Cl(10)	83.9(3)
Cl(3)—Pb(1)—Cl(1)	170.4(3)	Cl(10′)—Pb(2)—Cl(10)	176.1(3)
Cl(5′)—Pb(1)—Cl(1)	94.3(2)	Cl(6)—Pb(2)—Cl(10)	97.1(2)
Cl(4)—Pb(1)—Cl(1)	96.6(2)	Cl(9)—Pb(2)—Cl(10)	83.0(3)
Cl(5)—Pb(1)—Cl(1)	84.3(2)	Cl(8)—Pb(2)—Cl(10)	94.4(3)

Symmetry transformations used to generate equivalent atoms: $'\,x,y+1,z$.

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