Synthesis and structure of new low dimensional polymeric haloplumbate(II) complexes $[Pb_4Br_{12}(C_{40}H_{40}N_8)]$ and $[Pb_4Cl_{12}(C_{40}H_{40}N_8)]\cdot H_2O$

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New low dimensional polymeric haloplumbate(II) complexes of the dication of (4,4′-bis(imidazolyl-ylmethyl)biphenyl) were synthesised and their crystal structures determined. Complex **1,** $[Pb_4Br_{12}(C_{40}H_{40}N_8)]$, has *cis*-edge-shared, octahedral, lead bromide double chains. In compound **2** $[Pb_4Cl_{12}(C_{40}H_{40}N_8)].H_2O$, the inorganic chains are corner-shared, square pyramidal chains of lead chloride. In both compounds the organic ammoniums form regular layers that alternate with the inorganic chains. Strong hydrogen bonds of Pb–X··HN form between the organic and inorganic components in these complexes, which are always considered as an important interaction in supramolecular syntheses. The optical properties of compound **1** and compound **2** yielded photoluminescence spectra, which are attributed to the π–π^* transitions of the organic ligand.

Keywords: low dimensional, haloplumbates, organoammonium, extended chain, hydrogen bond, photoluminescence

The chemistry of haloplumbate(II) complexes with unusual structures has been extensively studied in order to rationalise correlations between structural and physical properties.[1-6] The flexibility of the Pb(II) coordination sphere and the non-stereospecific nature of the halide anions, which can be modulated by the size and hydrogen-bonding properties of the cations, allow a large span of structural arrangements to be observable in haloplumbate(II) materials.[7,8] Thus, this system can be considered an ideal candidate for investigating the change of behaviour from the low-dimensional inorganic lattice to the three-dimensional molecular network, due to presence of intercalated organic cations.[9] In the past few years, much attention has been paid to the low dimensional polymeric halometallates of lead (II) due to their semiconductor properties. Different structural, thermal and electrical properties of haloplumbate(II) systems have been obtained by using mono/diprotonated heterocyclic amines and mono/diprotonated linear amines.[10] Important relationships between organic amines and structural or physical properties of lead complexes have been found. We are interested in using different amines and haloplumbates(II) to construct new organic-inorganic hybrids.[11-13]

In formation of the ionic type of coordination compound, besides the function for overall charge neutrality, the organic components have also been considered with respect to their steric hindrance and to their hydrogen-bonding capability, making for the whole molecular framework formation.[1] A new organic amine introduced into the inorganic haloplumbate(II) framework may bring about novel structure and special physical properties.

In this paper, we report the synthesis, structural and optical properties of the complex compounds formed from the diprotonated heterocyclic amine 4,4'-bis(imidazolyl-ylmethyl)biphenyl, (denoted as L), and PbX_2 (X = Br, Cl). A few imidazoliums have been used to obtain organo-ammonium lead halide complexes. One <100>-oriented layered perovskite has been obtained with 2,2'-biimidazolium dications and PbI_2;[14] the other complex has been obtained with histaminium dications and $PbCl_2$ or $PbBr_2$.[15] In addition, the dications, imidazolium-N-(3-aminopropyl)imidazolium has also been employed to form a novel <110>-oriented layered perovskite $[PbBr_4(C_6H_{13}N_3)]$.[16] The special structure of the imidazole heterocycles and the optical properties they sometimes display, prompt study of ammonium metal halide salts. The biimidazole heterocyclic amine we use here has a linear and symmetric molecular structure that is different from the previously reported imidazolium compounds. We anticipated that such a new organic component with different steric hindrance and hydrogen-bonding capability might bring about novel polymeric inorganic complexes of PbX_2. When the biimidazolium salt (denoted as L·2HX, X = Br, Cl) was used, new structures with extended PbX_2 chains in $[Pb_4Br_{12}(C_{40}H_{40}N_8)]$ (**1**) and $[Pb_4Cl_{12}(C_{40}H_{40}N_8)]\cdot H_2O$ (**2**), sheathed on both sides by the imidazolium cations, were obtained. Compound **1** has *cis*-edge-shared, octahedral, double $PbBr_2$ chains alternating with organic ammonium dications, whereas compound **2** consists of symmetry-related $PbCl_5$ square pyramids that share their basal corners to form a polymeric tunnel-like structure. These are new members of the low dimensional polymeric haloplumbates (II) complexes and as far as we know it is the first time such a $PbBr_2$ chain as in compound **1** has been reported. Optical properties of the two compounds are also described below.

Experimental

Materials and syntheses:

$PbBr_2$ (99.999%, Aldrich) and $PbCl_2$ (99.99%), HCl (36%) and HBr (40%, Beijing Chemical Industry Co., Ltd) were used as received. 4,4'-Bis(imidazolyl-ylmethyl)biphenyl was synthesised as reported previously.[17] Elemental analysis was carried out on a Vario EL instrument. FT-IR spectra were measured with a Perking-Elmer 580B IR spectrophotometer with the KBr or KCl pellet technique. The excitation and emission spectra were taken on a Hitachi F-4500 spectrofluorimeter equipped with a 150W xenon lamp as the excitation source.

Compound **1**: Stoichiometric amounts of $PbBr_2$ (1 mmol 0.367 g) and 4,4'-bis(imidazolyl-ylmethyl)biphenyl (1 mmol 0.314 g) were added to HBr with stirring, and the obtained clear solution was slowly evaporated at room temperature; then colourless single crystals suitable for single X-ray diffraction were obtained (yield: 36.7%). Anal. Calc.: C, 19.85, N, 4.6, H, 1.7. Found: C, 19.7, N, 4.8, H, 1.9. FT-IR (cm^{-1} KBr): $\nu(NH_3^+)$: 3119, 3043, 2858; ν(imidazole, benzene): 1571, 1537, 1495; δ(Ar-H): 1074, 840, 746.

Compound **2**: a similar method to that for compound **1** was used. (yield: 45.6%). Anal. Calc.: C, 25.2, N, 5.9, H, 2.2. Found: C, 25.0, N, 5.6, H, 2.4. FT-IR (cm^{-1} KBr): $\nu(NH_3^+)$: 3279, 3110; ν(imidazole, benzene): 1610, 1571, 1537; δ(Ar-H): 1074, 838, 737.

X-ray structures

Crystal data of the two compounds are shown in Table 1. CCDC: *298957-298958.*

Diffraction intensities were collected on a Rigaku RAXIS-RAPID image plate diffractometer using the ω-scan technique with MoKa radiation (λ = 0.71069 Å). Absorption corrections were applied using the multiscan technique.[18] The structures were solved by direct methods using SHELXS-97[19] and refined by means of full-matrix least-squares techniques using the SHELXL-97 program[20] as implemented in WINGX.[21] Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms attached to carbon were generated geometrically. Analytical expressions of neutral-atom scattering factors were employed, with anomalous dispersion corrections incorporated therein.[22]

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Table 1 Crystal data for compound **1** and **2**

Crystal data	Compound **1**	Compound **2**
Empirical formula	Pb_4Br_{12} ($C_{40}H_{40}N_8$)	$Pb_4Cl_{12}(C_{40}H_{40}N_8)\cdot H_2O$
FW	2420.48	1094.98
Space group	C2/c	P-1
a (Å)	16.1153(10)	14.826(3)
b (Å)	24.1628(15)	14.935(3)
c (Å)	7.6782(5)	15.333(3)
α/ϒ	90.0	105.900(3)
β/ϒ	104.5430(10)	104.425(3)
γ/ϒ	90.0	113.223(3)
Volume/ Å	2894.0(3)	2744.9(10)
D_{calc}	2.778	2.305
Z	2	2
F(000)	2168	1756
Temperature (K)	293(2)	293(2)
R1/WR2(obsd data)	0.0285/0.0834	0.0733/0.1772

Results and discussion

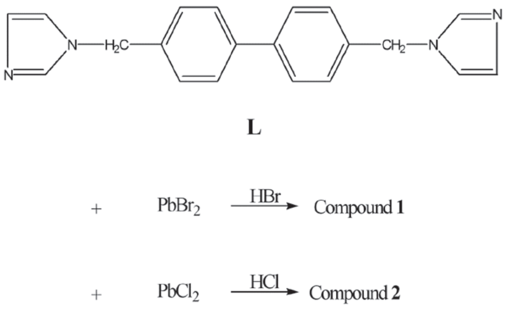
Spectral characterisation

Complexes **1** and **2** were characterised by FT-IR spectroscopy. Their IR spectra were very similar to each other and exhibited absorptions characteristic of N–H vibrations at about 2860–3300 cm^{-1} and the $\nu_{C\text{–}H}$ stretching vibration of the benzene rings in the two complexes. Several peaks were found from 1495 to 1610 cm^{-1}, which might be assigned to $\nu_{C=C}$ stretching vibrations in imidazole and benzene rings.

Structure description.

Scheme 1 shows structure of 4,4'-bis(imidazolyl-ylmethyl)biphenyl and the synthetic process for the two compounds. In acid solution, the ligand forms the imidazolium dication that interacts with lead halide chains.

The lead atoms in compound **1** take octahedral geometry and these octahedra share near edges to link double chains. Compound **1** builds up novel double chains of *cis*-edge-shared $PbBr_6$ octahedra as shown in Fig.1. In the inorganic chains there are two types of Pb atoms, defined by their location: outer Pb1 which is bonded to the terminal bromide atoms Br1; and inner Pb2 which is only bonded to the bridging bromide atoms Br2, Br3 (the Br atoms which link Pb1 and Pb2). The $PbBr_6$ octahedra of the inorganic chains are slightly distorted with the Pb–Br bond lengths ranging from 2.8965(7) to 3.1607(7) Å (Table 2). The shortest Pb–Br distances are those between terminal bromines and Pb1. The Pb–Br–Pb angles are also slightly deviated from perpendicular with Pb1 (86.10(3)–96.114(19)°) and Pb2 (83.943(19)–97.72(3)°) (Table 2). A previous study entailing PbI_2 has shown similar double chains as the $PbBr_2$ of compound **1**: in that case PbI_2 reacted with *p*-nitroaniline to form double chains of *cis*-edge-shared PbI_6 octahedra.[23] Such double chains of $PbBr_2$ have never been reported. Compared with the PbI_2 chains, the octahedra in the $PbBr_2$ chains are a little distorted [in the PbI_2 complex the Pb–I–Pb angles: Pb1 (84.7–94°) and Pb2 (83.1–91.4°)], indicating that the $PbBr_6$ octahedra are more deviating from ideal symmetry.



Scheme 1 Structure of the organic ligand 4,4'-bis(imidazolyl-ylmethyl)biphenyl

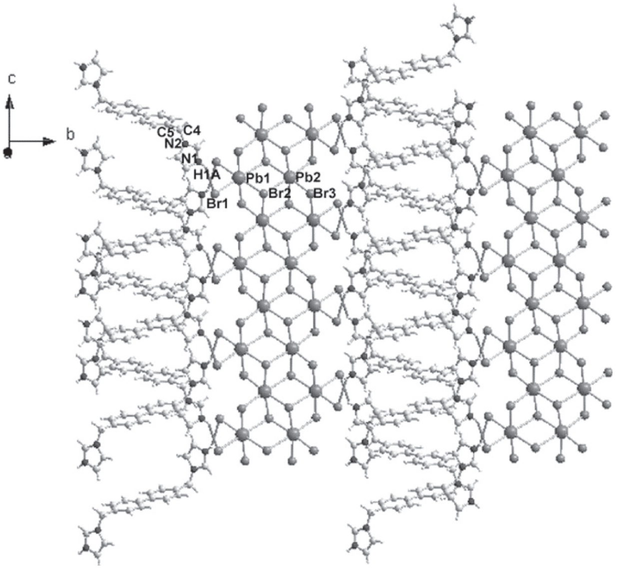


Fig. 1 Structure of compound **1** with hydrogen bonds shown.

The structure of compound **1** shows evident layer formation with organic cations and inorganic chains arranging regularly in turn viewed down the *a* axial. In acid solution, 4,4'-Bis(imidazolyl-ylmethyl)biphenyl forms ammonium dications connecting the $[Pb_2Br_6]^{2-}$ anions through hydrogen bonds and electrostatic interactions between the organic ammonium ions and axial halides in the inorganic chains. The chain packing is dictated by the steric hindrance and hydrogen bonding confinement of the diimidazole cations. Along the *c* axis, every two adjacent chains are hydrogen-bonded together *via* the $–NH_3$ moieties of the ammonium cations. Hydrogen bonds between Br1 and H1A are shown in Fig. 1 with bond lengths Br1–H1A 2.645 Å and bond angles N1–H1A–Br1 139.825°, respectively. It is a stronger hydrogen bonding interaction than in the PbI_2 counterpart in which the hydrogen bonds range from 3.56 to 3.83 Å.[23] The organic and inorganic components connect through hydrogen bonds constructing a two-dimensional network. In compound **1** the organic sheets of L·2HBr are organised in an orderly fashion, interleaving the inorganic chains. The organic ligand takes a regular chair form with bended angle C5–C4–N2 111.51° (Fig. 1).

Compound **2** crystallises in the P-1 space group. The crystal structure of compound **2** exhibits a three-dimensional network through hydrogen bonds between the chlorine of the inorganic chains and the

Table 2 Selected bond lengths (Å) and angles (°) for compound **1** (Symmetry transformations used to generate equivalent atoms: 1 –*x*,*y*,–*z* + 1/2, 2 –*x*,*y*, –*z*–1/2, 3 *x*, –*y*,*z*–1/2) and **2** (Symmetry transformations used to generate equivalent atoms: –*x* + 1,–*y* + 1,–*z* + 1)

Compound **1**	Compound **2**
Br1 Pb1 2.8965(7) Br3 Pb2 2.9731(7)	Cl4 Pb2 3.006(4) Cl7 Pb2 3.034(5)
Pb1 Br3$^{\#1}$ 3.0310(7) Pb2 Br2$^{\#2}$ 3.0398(7)	Cl9 Pb4 2.872(5) Cl11 Pb4 2.578(5)
Pb2 Br2$^{\#3}$ 3.1290(7) Pb1 Br2$^{\#1}$ 3.1607(7)	Pb2 Cl3$^{\#}$ 2.768(4) Pb4 Cl12$^{\#}$ 2.981(5)
Br1 Pb1 Br1$^{\#1}$ 87.18(3)	Pb1 Cl1 Pb4 102.64(14)
Br1 Pb1 Br3$^{\#1}$ 96.114(19)	Pb2$^{\#}$ Cl3 Pb1 99.10(14)
Br1 Pb1 Br2 93.435(19)	Pb1 Cl12 Pb4$^{\#}$ 128.84(19)
Br2 Pb1 Br2$^{\#1}$ 86.10(3)	Cl2 Pb1 Cl12 87.96(15)
Br3$^{\#2}$ Pb2 Br3 97.72(3)	Cl5 Pb2 Cl4 84.39(14)
Br3$^{\#2}$ Pb2 Br2$^{\#2}$ 90.123(18)	Cl8 Pb3 Cl9 92.68(16)
Br3$^{\#2}$ Pb2 Br2$^{\#3}$ 87.55(2)	Cl10 Pb4 Cl12$^{\#}$ 81.64(15)
Br2$^{\#2}$ Pb2 Br2$^{\#3}$ 83.943(19)	Cl11 Pb4 Cl1 82.27(14)

hydrogen of the ammonium groups. The structure of compound **2** is shown in Fig. 2. The inorganic portion of the composite could be described as made up of symmetry-related $PbCl_5$ square pyramids that share their basal corners to form a polymeric tunnel-like structure. Hydrogen bonds between chlorine and ammonium hydrogen are shown in Fig. 2. The chlorine atoms of Cl 11, Cl 5, Cl 1 and Cl 2 interact respectively with the hydrogen atoms on N1, N4, N8 and N5 with Cl–H bond lengths ranging from 2.297 to 2.606Å, and bond angles N–H–Cl ranging from 148.929 to 167.613°.

The inorganic framework shown in Fig. 3 is consists of chains with the lead atoms coordinating in square pyramidal geometry. There are four independent lead atoms in the single chain, each of which takes similar square pyramidal geometry. The Pb–Cl bond lengths range from 2.578(5) to 3.034(5) Å and the Cl–Pb–Cl bond angles in the octahedron range from 81.64(15) to 98.66(13)° (Table 2). It should be noted that two sixth Pb–Cl interactions [Pb1–Cl4 3.4003 Å and Pb3–Cl7 3.2474 Å] (shown in Fig. 3 by a dotted line) below the sum of relevant van der Waals radii are also observed. If such interactions are considered, the coordination mode of the lead atoms (Pb1, Pb3) should be described as very distorted octahedra (with the angle Cl7–Pb3–Cl7 97.52° and Cl4–Pb1–Cl4 104.27° respectively, as shown in Fig. 3). However, due to the characteristics of these bonds (length and directionality), and for clarity reasons we prefer to describe the main coordination polyhedron as square pyramid.[15b]

A $PbCl_2$ complex that has the same inorganic chains as compound **2** has been reported, and it is constructed by a macrocyclic amine of 1-aza-4,10-dithia-7-oxacyclododecane.[24] The organic ammine of 4,4'-bis(imidazolyl-ylmethyl)biphenyl in **2** is a dication in acid solution, different from the single cation reported previously. The dications in **2** bridge near inorganic chains through hydrogen bonds to construct a three-dimensional network. The chains have been described as shifting *a*/2 along [100] oriented hybrid perovskite and arranging next to each other [010] orientation.[24]

Lone pair electrons in lead (II)

The lone pair electrons in Pb(II) cations can influence the disposition of the ligands around the cations, which results in an identifiable void. This gap in the coordination sphere has been considered to take up more space on a specific region of the surface of the coordination sphere than a single bond. However, the effects of the lone pair electrons in Pb^{2+} compounds do not always cause a void in the coordination geometry. In fact this geometry can take various forms.[25] The experimental coordination geometry around lead reveals two distinct structure categories: (A) holodirected, in which the bonds to the ligand atoms are directed throughout the surface of an encompassing globe; and (B) hemidirected, in which the bonds to the ligand atoms are directed throughout only part of the globe, that is, there is an identifiable void (or gap) in the distribution of bonds to the ligands.[26-30] According to this classification the coordination geometry around lead in compound **1** can be attributed as holodirected and that in compound **2** as hemidirected.

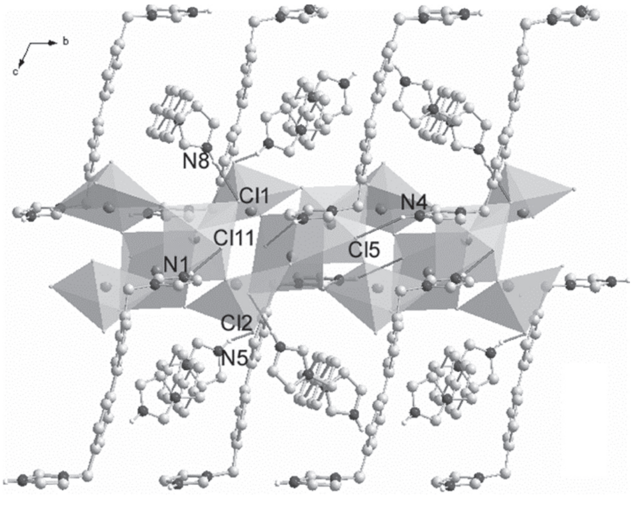


Fig. 2 Structure of compound **2** with hydrogen bonds shown.

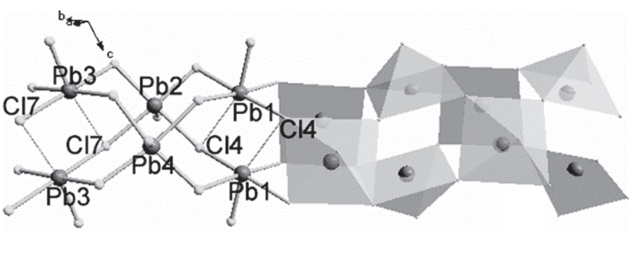


Fig. 3 Structure of compound **2** with all organic components omitted.

Optical properties

The photoluminescence spectra of compound **1** and **2** are shown in Figs 4 and 5 respectively. Compound **1** shows two emission maxima at 518 and 547 nm, upon excitation at 430 and 340 nm respectively (Fig. 4), whereas compound **2** shows two emission maxima at 465 nm and 523 nm respectively, upon excitation at 375 nm (Fig. 5). The photoluminescence of the complexes and ligand can be attributed to the π–π* transitions of 4,4'-bis(imidazolyl-ylmethyl)biphenyl.[31,32] Different interactions between the organic and inorganic components make the same organic ligand show different optical properties in the two complexes. Hydrogen bonds together with the electrostatic interactions in the two complexes make the ligand take different conformation rigidity,[33] which may change the π* energy levels of the organic ammoniums,[34-40] thereby bringing about some changes of the luminescence spectra.

Conclusion

Lead (II) can be considered an ideal candidate for investigating the changing behaviour from the low-dimensional inorganic lattice to a three-dimensional molecular network. In this paper we revealed new organoammonium lead halide salts with low dimensional lead halide chains alternating with dications of imidazoliums. The special imidazole derivative-4,4'-bis(imidazolyl-ylmethyl) biphenyl was used as organic component. Compounds **1** and **2** are new examples of low dimensional polymeric haloplumbate(II) complexes. With

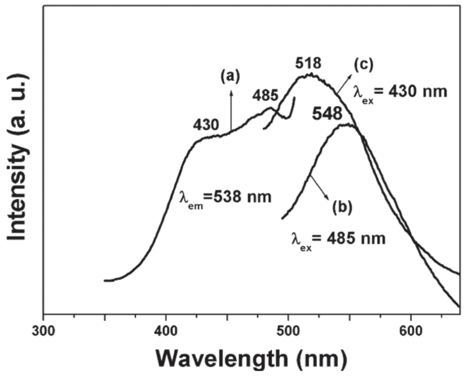


Fig. 4 Photoluminescence excitation (a) and emission (b, c) spectra of compound **1**.

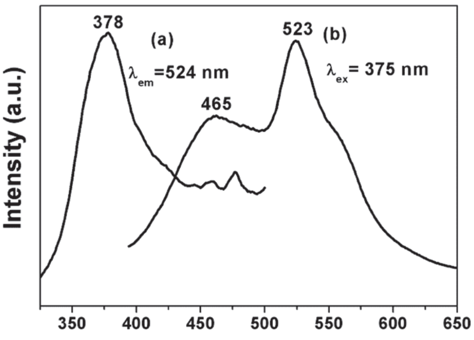


Fig. 5 Photoluminescence excitation (a) and emission (b) spectra of compound **2**.

the flexibility of the Pb(II) coordination sphere and the non-stereospecific nature of the halide anions, it is expected that other ammonium salts can be used to construct new low dimensional polymeric haloplumbate(II) frameworks.

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