Synthesis and structure of a new layered organic–inorganic compound containing unique chains of PbI$_2$

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Synthesis and crystal structure of [C$_6$H$_{10}$N$_2$]Pb$_2$I$_6$·3thf which contains a novel lead iodide polymeric anion with a double-chain structure.

There is increasing interest in the study of magnetic, electronic and optoelectronic properties of low-dimensional organic–inorganic hybrid compounds.[1–3] Studies suggest that complex systems consisting of organic and inorganic components have great potential for the creation of functional materials utilizing the wide variety of properties associated with each component.[4,5] Lead(ii) iodide compounds are of particular interest due to their significant third-order optical non-linear properties.[6–9]

Although there is significant interest in the physical properties of low-dimensional lead iodide compounds, relevant information regarding their crystal structure, properties and synthesis is limited.[10–12] Our current research is focused on the synthesis of low-dimensional organic–inorganic post-transition-metal iodides with the possibility of incorporating interesting properties associated with the organic and inorganic moieties. This research is motivated by the possibility of tuning properties of inorganic solid-state materials by incorporating polarizable organic moieties. Moreover, important structure–property relationships between low-dimensional structural derivatives and their parent inorganic material can be established.

The compound [C$_6$H$_{10}$N$_2$]Pb$_2$I$_6$·3thf **1** was prepared by reacting *p*-nitroaniline and PbI$_2$ in solution. The synthesis of **1** starts with dissolving *p*-nitroaniline (0.59 g, 4.33 mmol) and lead(ii) iodide (1.00 g, 2.17 mmol) in 8 ml of concentrated 57 mass% aqueous hydriodic acid diluted with acetonitrile. The addition of hydriodic acid increases the solubility of PbI$_2$ in polar organic solvents. The resulting solution was warmed to 60 °C and slowly cooled to 20 °C during which the solution turns dark red-brown, and the formation of a brown precipitate was observed. The precipitate was collected and redissolved in tetrahydrofuran (thf) at 60 °C. The resulting clear red–brown solution was allowed to slowly cool, from 60 to −10 °C over 7 days, and orange parallelepiped crystals were formed. The air-sensitive orange crystals were preserved in the mother-liquor. All reactions were carried out under nitrogen atmosphere and all solvents were degassed before use. Direct reaction of *p*-phenylenediammine and PbI$_2$ in acetonitrile–HI and/or thf does not lead to the formation of compound **1** and could be attributed to the low solubility of the diamine in the organic–HI solvents.

Compound **1** crystallizes in space group *P*$\bar{1}$.† The asymmetric unit was found to consist of a [Pb$_2$I$_6$]$^{2-}$ unit (part of a polymeric chain), two half-molecules of *p*-phenylenediammonium dications, [C$_6$H$_{10}$N$_2$]$^{2+}$, situated about inversion centres, and three molecules of thf solvent. One of the thf molecules was found to be significantly disordered over two distinct sites, with population factors of 70 : 30. The crystal structure of **1** features double chains of *cis*-edge-sharing PbI$_6$ octahedra, [Pb$_2$I$_6^{2-}$]$_\infty$, that run along the *a* axis, as shown in Fig. 1. There are three types of I atoms defined by their connectivity to Pb: terminal [I(5), I(6)], double bridged [I(3), I(4)] and triple bridged [I(1), I(2)]. Also, there are two types of Pb atoms, defined by their location in the chain: 'outer' [Pb(1)], bonded to terminal

iodides; and 'inner' [Pb(2)] bonded only to bridging iodides. The shortest Pb–I distances (3.05, 3.13 Å) are those between the terminal iodides and Pb(1). The I–Pb–I angles are nearly perpendicular around Pb(1) (84.7–94°) and Pb(2) (83.1–91.4°) with the 'outer' PbI$_6$ octahedra exhibiting the largest deviation from ideal symmetry. The structure of the polymeric anion, [Pb$_2$I$_6^{2-}$]$_\infty$, can be regarded as a < 110 > section of the layered CdI$_2$ type structure. The lead iodide chain is reminiscent of the antimony iodide chains in [PPh$_4$]Sb$_3$I$_{10}$ and [(Me$_2$N)$_3$C$_3$]Sb$_3$I$_{10}$.[13] These [Sb$_3$I$_{10}^{1-}$]$_\infty$ complex chains are structural derivatives of the CdI$_2$ type structure but differ in the way the layered structure is excised into chains. The lead iodide double chains in **1** correspond to the higher-order double chain [M$_2$I$_6$]$_\infty$ which has not been previously observed. It is important to note that the polymeric anion chain in **1** constitutes a direct structural link between molecular lead iodide complexes to the inorganic solid compound PbI$_2$ (CdI$_2$ type).

An important aspect of the crystal structure of **1** is its organic–inorganic heterostructure. It is dominated by cooperative hydrogen bonding between *p*-phenylenediamine dications with terminal and double-bridging iodines of the inorganic double chain as shown in Fig. 2. The hydrogen bond distances range from 3.56 to 3.83 Å suggesting that any interaction between them is not very strong.[14] The two half-molecules of organic dications in the asymmetric unit generate two inequivalent dications. One type of dication acts as bridge between nearest neighbouring [Pb$_2$I$_6$]$^{2-}$ double chains through hydrogen bonding interactions between the amino group and the terminal iodides. These extended interactions result in stair-like layers formed by hydrogen-bonded dications and [Pb$_2$I$_6^{2-}$]$_\infty$ chains. The stair-like layered organic–inorganic heterostructure lies nearly parallel to the < 011 > plane as shown in Fig. 3. The remaining *p*-phenylenediamine dications and solvent molecules (thf) lie between the layers of hydrogen-bonded organic cations and inorganic chains.

During the initial stages of this research, our intention was to introduce push–pull type cations and molecules like *p*-nitroaniline into PbI$_2$. However, in addition to the protonation of the amine groups, we observe that *p*-nitroaniline is reduced to
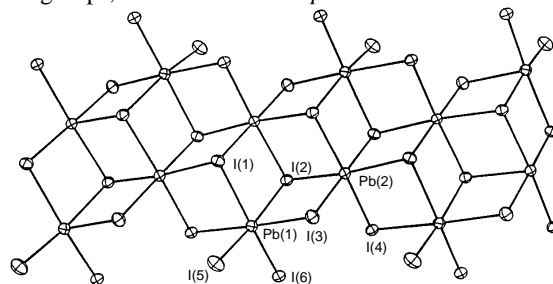

Fig. 1 ORTEP representation of the structure of the linear polymeric chain in **1** (ellipsoids are drawn at 50% probability). Important distances (Å) and angles (°) are: Pb(1)–I(1) 3.378(1); Pb(1)–I(2) 3.458(1), Pb(1)–I(3) 3.178(2), Pb(1)–I(5) 3.052 (2), Pb(1)–I(6) 3.126(1), Pb(2)–I(2) 3.264(2), Pb(2)–I(3) 3.178(2), Pb(2)–I(4) 3.154(1), I(1)–Pb(1)–I(2) 86.4(1), I(1)–Pb(1)–I(3) 93.3(1), I(1)–Pb(1)–I(5) 87.9(1), I(1)–Pb(1)–I(6) 169.3(1), I(2)–Pb(1)– I(3) 84.1(1), I(2)–Pb(1)–I(5) 174.1(1), I(2)–Pb(1)–I(6) 85.7(1), I(3)–Pb(1)–I(6) 93.1(1), I(2)–Pb(2)–I(3) 88.0(1), I(2)–Pb(2)–I(4) 91.4(1), I(3)–Pb(1)–I(5) 94.0(1).

p-phenylenediamine in the presence of hydriodic acid and PbI_2. The well known reduction of nitroarenes to primary arylamines in the presence of metal (Sn, Zn, or Fe) and acid (HCl) involves the oxidation of the metals.[15] In this work, the reduction of the nitro group involves oxidation of the iodide ions ($2I^- \rightarrow I_2$). The formation of I_2 is observed from the dark red colour of the solution upon the reaction of the inorganic and organic components. Furthermore, the observed reduction of the nitro group by iodide is catalysed by the metal iodide, PbI_2. This is indicated by several follow-up experiments wherein catalytic amounts of the metal iodide were needed to initiate the nitro reduction/iodide oxidation reaction. An examination of known oxidation potentials of Pb^{II} and I^- ($Pb^{2+} \rightarrow Pb^{4+} + 2e^-$, $E^\circ = -1.69$ V; $2I^- \rightarrow I_2 + 2e^-$, $E^\circ = -0.53$ V)[16] further supports the better reducing ability of I^-. The overall nitroaniline/I^- redox reaction is given by eqn. (1).

$$p\text{-}H_2NC_6H_4NO_2 + 6HI \rightarrow p\text{-}H_2NC_6H_4NH_2 + 3I_2 + 2H_2O \quad (1)$$

The IR spectrum of **1** recorded in KBr contains characteristic bands associated with the phenyl group and a very broad band at 3200 cm^{-1} indicating the presence of protonated amine groups. Furthermore, the characteristic band associated with the aromatic nitro group, around 1300 cm^{-1}, is not observed.

The synthesis of **1**, a direct structural derivative of PbI_2, is just the first member of a family of compounds with low-
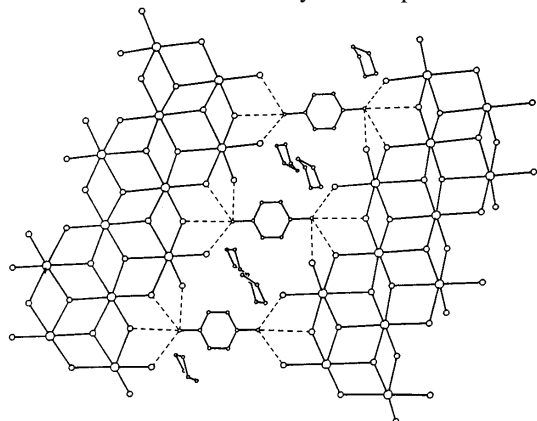

Fig. 2 View of two nearest neighbouring $[Pb_2I_6^{2-}]\infty$ chains and the bridging *p*-phenylenediamine dications. Hydrogen-bonding interactions, represented by the nearest N···I distances that range between 3.65 and 3.83 Å, are indicated by dashed lines.
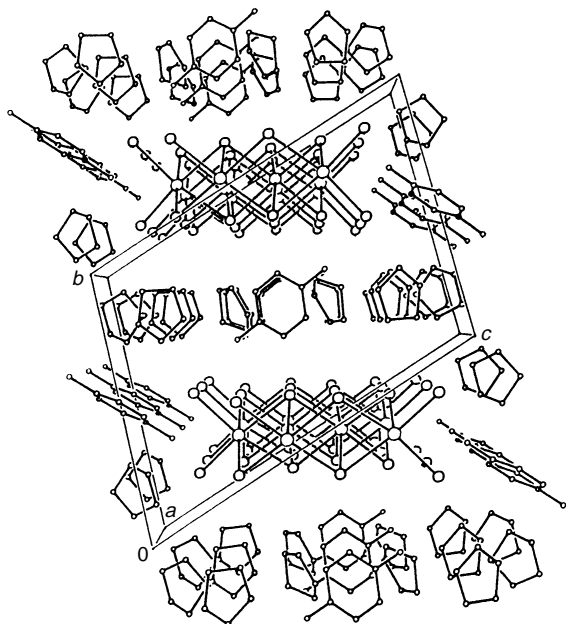

Fig. 3 A plot of the structure showing the unit-cell packing as viewed into the *a* axis. Only the major orientation of the disordered thf is shown.

dimensional chain structures derived from the layered PbI_2 structure. Its novel layered heterostructure attests to the importance of cooperative hydrogen bonding in the crystal structures of organic–inorganic halides. Studies are under way to relate the optical properties of **1** to the unique properties of PbI_2.

Footnotes

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