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FULL PAPER

Discrete and polymeric iodoplumbates with Pb_3I_{10} building blocks: $[Pb_3I_{10}]^{4-}$, $[Pb_7I_{22}]^{8-}$, $[Pb_{10}I_{28}]^{8-}$, ${}^{1}_{\infty}[Pb_3I_{10}]^{4-}$ and ${}^{2}_{\infty}[Pb_7I_{18}]^{4-}$

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Received 1st April 1999, Accepted 16th June 1999

Iodoplumbate complexes were obtained by reaction of PbI_2 with sodium iodide in polar organic solvents and precipitation with large cations. With diammonium cations $[R_3N(CH_2)_nNR_3]^{2+}$ a series of polynuclear iodoplumbates could be isolated and characterized by single crystal X-ray diffraction. While $[Bu_3N(CH_2)_4NBu_3]_2[Pb_3I_{10}]$ **1**, $[Bu_3N(CH_2)_4NBu_3]_4[Pb_7I_{22}]$ **2** and $[Bu_3N(CH_2)_4NBu_3]_4[Pb_{10}I_{28}]$ **3** contain discrete anions, the iodoplumbates $[Me_3N(CH_2)_5NMe_3]_2[Pb_3I_{10}]$ **4** and $[Pr_3N(CH_2)_5NPr_3]_2[Pb_7I_{18}]$ **5** consist of one-dimensional and two-dimensional co-ordination polymers, respectively. The $[Pb_3I_{10}]^{4-}$ anion in **1** can be regarded as a building block for the structures of **2**, **4**, **5** and, slightly modified, of **3**. In spite of their related structures and similar compositions, these complexes are formed selectively and in good yield under appropriate reaction and crystallization conditions.

Introduction

The compound PbI_2 reacts with iodide in polar organic solvents forming iodoplumbate anions, which can be crystallized in the presence of large counter ions such as quaternary ammonium, phosphonium or diammonium cations. In this way polynuclear iodoplumbates can be isolated, which contain, with exception of the discrete anions in $[Bu_4N]_8[Pb_{18}I_{44}]$,[1] one-, two- or three-dimensional polymeric anions.[2–4] For example, in $[Me_3N(CH_2)_2NMe_3]_2[Pb_3I_{10}]$[4] Pb_3I_{11} units are linked by common I atoms to form infinite zigzag chains. In $[Me_3N(CH_2)_2NMe_3]_3[Pb_3I_9]_2$ these chains are condensed to give a two-dimensional network.[4] Regarding their composition this class of compounds can be considered as a link between the mononuclear complex $[PbI_6]^{4-}$ and the corresponding binary solid PbI_2. Generally the physical properties of such low dimensional compounds differ from those of the parent compound. In this respect only few iodoplumbates have been investigated. For example the absorption edge is shifted to higher energies compared to 2.36 eV in the photoconductor PbI_2. Some derivatives of lead iodide show very efficient electroluminescence.[5] Most of these investigations of physical properties, however, have been conducted on thin films and not using structurally characterized single crystals. Thus often there is not enough information about the structures of the iodoplumbates. Recently we showed that their structures strongly depend on the conditions of synthesis and crystallization.[1–4] In many cases small variations of the reaction parameters allow selective formation of different products. This fact is impressively shown in the products of the reaction of PbI_2 with NaI and $[Bu_3N(CH_2)_4NBu_3][PF_6]_2$ in DMF, on which we report in this paper.

Results and discussion

Variation of the molar ratio of the starting compounds PbI_2, NaI and $[Bu_3N(CH_2)_4NBu_3][PF_6]_2$ and the crystallization conditions leads to the formation of three iodoplumbates $[Bu_3N(CH_2)_4NBu_3]_2[Pb_3I_{10}]$ **1**, $[Bu_3N(CH_2)_4NBu_3]_4[Pb_7I_{22}]$ **2** and $[Bu_3N(CH_2)_4NBu_3]_4[Pb_{10}I_{28}]$ **3**. They contain discrete complex anions whose structures are related to each other and show analogies to those in $[Me_3N(CH_2)_2NMe_3]_2[Pb_3I_{10}]$ and $[Me_3N(CH_2)_2NMe_3]_3[Pb_3I_9]_2$.[4] Structurally related to **1**–**3** are $[Me_3N(CH_2)_5NMe_3]_2[Pb_3I_{10}]$ **4** and $[Pr_3N(CH_2)_5NPr_3]_2[Pb_7I_{18}]$ **5**, which are formed under similar reaction conditions with counter ions of different size, eqns. (1)–(3).

$$PbI_2 + NaI + [Bu_3N(CH_2)_4NBu_3][PF_6]_2 \xrightarrow{DMF} [Bu_3N(CH_2)_4NBu_3]_2[Pb_3I_{10}]\ \mathbf{1} + [Bu_3N(CH_2)_4NBu_3]_4[Pb_7I_{22}]\ \mathbf{2} + [Bu_3N(CH_2)_4NBu_3]_4[Pb_{10}I_{28}]\ \mathbf{3} \quad (1)$$

$$PbI_2 + NaI + [Me_3N(CH_2)_5NMe_3][PF_6]_2 \xrightarrow{DMF} [Me_3N(CH_2)_5NMe_3]_2{}^{1}_{\infty}[Pb_3I_{10}]\ \mathbf{4} \quad (2)$$

$$PbI_2 + NaI + [Pr_3N(CH_2)_5NPr_3][PF_6]_2 \xrightarrow{DMF} [Pr_3N(CH_2)_5NPr_3]_2{}^{2}_{\infty}[Pb_7I_{18}]\ \mathbf{5} \quad (3)$$

Yellow platelets of complex **1**, yellow rods of **2** and orange-red crystals of **3** crystallize by slow condensation of diethyl ether into the DMF solution. In solutions richer in NaI the formation of **1** is preferred. Addition of THF to the reaction solution before condensation of diethyl ether yields **2** selectively. Layering of the DMF solution with toluene or ethanol instead of diethyl ether leads to crystals of **3** in good yield.

According to the crystal structure analysis, in complex **1** (space group $P\bar{1}$) three Pb atoms approximately form an equilateral triangle (Fig. 1; Pb···Pb 429.40–441.01(8) pm). The atoms Pb1 and Pb2 are co-ordinated by iodide ligands in a distorted octahedral fashion, whereas Pb3 has square pyramidal co-ordination. The asymmetrically μ_3-bridging atoms I1 and I2 are situated above and below the Pb_3 triangle, whereby I2 is shifted significantly towards Pb3 (Pb1–I2 366.0(1), Pb2–I2 340.87(9), Pb3–I2 298.5(1) pm). The bond length Pb3–I2 is unusually short for a triply bridging iodide ligand; this contraction can be attributed to the absence of a ligand *trans* to I2. The stronger bond of I2 to Pb3 leads to weaker and significantly longer bonds to Pb1 and Pb2. Thus I2 is involved in the shortest as well as in the longest Pb–I bond in **1**. The μ ligands I3, I4 and I5 bridge the edges of the Pb_3 triangle (Pb–μ-I 323.1–332.7(1) pm). These iodo ligands deviate by 57.8(4) (I5), −32.3(5) (I3) and −22.3(4) pm (I4) from the Pb_3 plane. The octahedral co-ordination of Pb1 and Pb2 is completed by two terminal I atoms (I6–I9) with Pb–I distances ranging from 304.2 to 313.4(1) pm. In contrast, only one terminal iodo ligand is bound to Pb3 (Pb3–I10 305.1(1) pm). We suggest that electrostatic forces inhibit the binding of a sixth ligand to Pb3. Therefore $[Pb_3I_{11}]^{5-}$, which would have the inverse structure to the $Cs_{11}O_3$ unit in caesium suboxides[6] and would be isostructural to the iodoantimonate anion in $[Cu(MeCN)_4]_2[Sb_3I_{11}]$,[7] is not formed. For cesium suboxides it has been shown that the unstable cation $[Cs_{11}O_3]^{5+}$ is stabilized by five electrons involved in metal–metal bonding.[6] In the $[Sb_3I_{11}]^{2-}$ anion all Sb atoms are co-ordinated by two μ_3, two μ as well as two terminal iodo ligands in a distorted octahedral fashion. The lower co-ordination number of Pb3 compared to Pb1 and Pb2 in **1** causes a shortening of the Pb3–I bonds by 10 pm in average (mean values Pb1–I 327.3, Pb2–I 327.0, Pb3–I 317.5 pm). The different co-ordination numbers of the Pb atoms and the combination of *trans* influences are obviously responsible for the asymmetry in bond lengths of the bridging iodo ligands. Five-co-ordinated Pb^{2+} ions in halogeno complexes have been observed in $[Ph_4P][PbCl_3]$, $[Pr_4N][PbI_3]$ or $[Mg(dmf)_6][PbI_3]_2$, where PbX_5 (X = Cl or I) square pyramids share common edges to form polymeric chains.[8]

In complex **2** two of the $[Pb_3I_{10}]^{4-}$ anions of **1** are linked by a PbI_2 unit (Fig. 2). This is in keeping with the observation that **2** preferentially crystallizes from reaction solutions richer in PbI_2. According to the crystal structure analysis (space group $P2_1/n$) both Pb_3 units in the $[Pb_7I_{22}]^{8-}$ anion define two parallel planes separated by 136.2(2) pm. Atom Pb4 occupies the inversion centre between the two Pb_3I_{11} groups. Through the linkage of two $[Pb_3I_{10}]^{4-}$ anions by PbI_2 or two (hypothetical) $[Pb_3I_{11}]^{5-}$ anions by an additional Pb^{2+} ion (Pb4), respectively, each Pb atom has distorted octahedral co-ordination. At the same time the degree of bridging of the iodo ligands increases: I10, which was terminal in **1**, becomes μ bridging in **2**, and I3, which was μ in **1**, is μ_3 bridging in **2**. As a result the distances and angles in **2** change compared to those in **1**. As expected, the shortest Pb–I distances are found to the terminal iodo ligands ($Pb–I_{term}$ 304.67–308.38(9) pm); in *trans* position to the terminal ligands the longest bonds are found to triply bridging ligands (Pb–μ_3-I 313.80–354.30(9) pm).

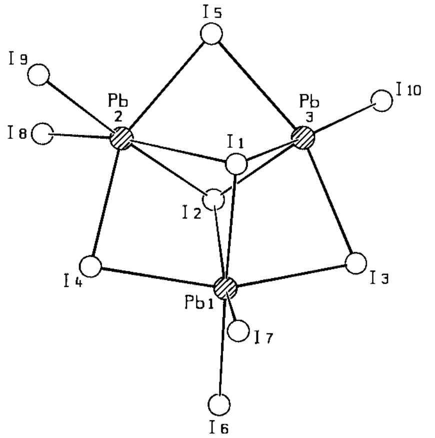

Fig. 1 Crystal structure of the $[Pb_3I_{10}]^{4-}$ anion in complex **1**. Selected distances (±0.1) and angles (±0.03): Pb1–I1 325.7; Pb1–I2 366.0; Pb1–I3 331.6; Pb1–I4 323.1; Pb1–I6 313.4; Pb1–I7 304.2; Pb2–I1 350.5; Pb2–I8 304.4; Pb3–I1 327.1; Pb3–I2 298.5; Pb3–I3 327.7 and Pb3–I10 305.1 pm; I1–Pb1–I2 79.12; I1–Pb1–I6 175.96; I3–Pb1–I4 154.27; I1–Pb3–I2 89.68; I1–Pb3–I10 168.06; I2–Pb3–I10 102.26; Pb1–I1–Pb2 81.33 and Pb1–I3–Pb3 81.29°.

In an alternative description, the anion of complex **2** contains a Pb_5I_{18} chain formed by five *trans* face sharing PbI_6 octahedra (Pb2, Pb3, Pb4, Pb3′, Pb2′). This structural principle is also observed in the pentanuclear iodobismuthate $[Ph_4P]_3$-$[Bi_5I_{18}]$[9] and in the polymeric chains of iodoplumbates [Cat]-$[PbI_3]$[2] with $Cat^+ = Me_4N^+$, Bu_4N^+, Ph_4P^+, Hpy^+, $Hpip^+$ (pip = piperidine), *etc.* Formally the anion of **2** is generated from the Pb_5I_{18} chain by addition of two PbI_2 groups (Pb1, I6, I7 and symmetry related atoms) which are bound by the iodo ligands I1–I4. Thus the bond angle Pb1–I3–Pb4 is 153.44(2)°, whereas all other Pb–I–Pb angles are in the range 74.83(2) to 86.24(2)°. In **2** the weakest Pb–I interaction is found between Pb1 and I3 with a distance of 354.30(9) pm.

Fig. 3 shows the result of the crystal structure determination of complex **3** which crystallizes in space group $P\bar{4}2c$, with D_2-symmetric $[Pb_{10}I_{28}]^{8-}$ anions. This anion is composed of Pb_3I_{10} subunits (one unit is highlighted in Fig. 3). As in **1** and **2**, these subunits feature Pb_3 triangles triply capped by two iodo ligands. In contrast, however, only two edges of the Pb_3 triangle (Pb1 ··· Pb3, Pb2 ··· Pb3) are bridged. Two Pb_3I_{10} units share a common Pb atom (Pb1) and three common I atoms (I1–I3). Two of the resulting Pb_5I_{17} groups are linked by six common I atoms to form $[Pb_{10}I_{28}]^{8-}$ anions in **3**. In this way the co-ordination number of some iodo ligands is increased compared to those in the basic $[Pb_3I_{10}]^{4-}$ structure: I1 is μ_4 bridging (Pb–I1 320.29–363.96(7) pm) and the former μ ligand I3 is now μ_3, being bound to Pb1, Pb3 and Pb3′.

The missing μ iodo ligand between Pb1 and Pb2 leads to elongation of the Pb1 ··· Pb2 distance (Pb1 ··· Pb2 494.33(4), Pb1 ··· Pb3 442.25(8), Pb2 ··· Pb3 419.45(6) pm). Whereas the (distorted) octahedral co-ordination of Pb2 is completed by interaction with the ligand I1′ of the neighboring Pb_3I_{10} unit, Pb1 remains in a square pyramidal environment. This again allows a rather short Pb1 ··· Pb1′ distance of 374.4(1) pm, which is the shortest Pb ··· Pb distance observed in iodoplumbates. It is however significantly longer than the Pb–Pb single bond in $Me_3Pb–PbMe_3$ (288 pm) or the Pb ··· Pb distance in metallic lead (349 pm),[10] and therefore a bonding Pb ··· Pb interaction is not indicated. As in **1** the shortest Pb–I distances involve I atoms in *trans* position to unoccupied co-ordination sites (Pb1–I3 296.2(1) pm). In crystals of **3** the $[Pb_{10}I_{28}]^{8-}$ anions occupy positions of a tetragonal body centered lattice, with the

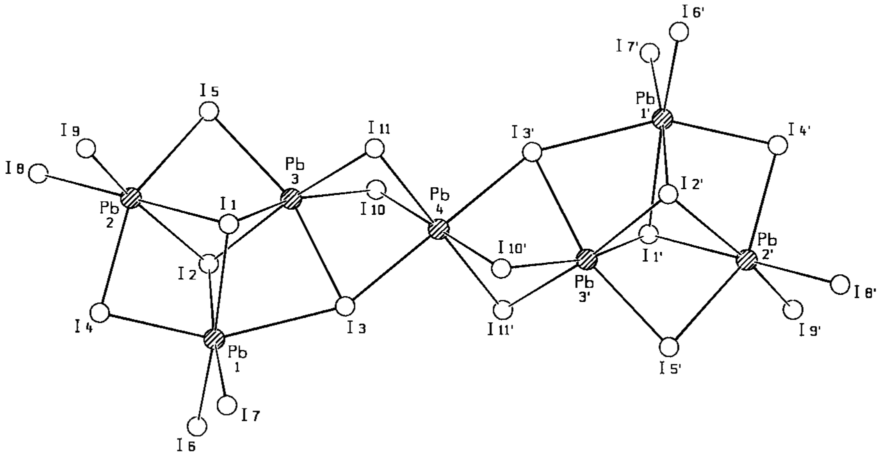

Fig. 2 Crystal structure of the $[Pb_7I_{22}]^{8-}$ anion in complex **2**. Selected distances (±0.09) and angles (±0.03): Pb1–I1 346.17; Pb1–I2 326.43; Pb1–I3 354.30; Pb1–I4 312.16; Pb1–I6 306.78; Pb1–I7 307.87; Pb2–I1 329.04; Pb2–I8 308.38; Pb3–I1 313.80; Pb3–I2 318.26; Pb3–I3 328.55; Pb3–I10 324.27; Pb4–I3 325.56 and Pb4–I10 320.89 pm; I1–Pb1–I2 80.62; I1–Pb1–I6; 167.10; I3–Pb1–I4 152.63; I1–Pb3–I2 87.07; I1–Pb3–I10 165.79; I2–Pb3–I10 98.51; I10–Pb4–I11 85.96; Pb1–I1–Pb2 79.89; Pb1–I3–Pb3 78.67; Pb1–I3–Pb4 153.44 and Pb3–I3–Pb4 74.83°.

Pb1 $\cdots$ Pb1′ direction alternatingly aligned along the crystallographic *a* and *b* axes.

Small yellow needles of $[Me_3N(CH_2)_5NMe_3]_2[Pb_3I_{10}]$ **4** crystallize after addition of diethyl ether to a solution of PbI_2, NaI and $[Me_3N(CH_2)_5NMe_3][PF_6]_2$ in DMF. According to the crystal structure determination, the anions of **4** (space group *C*2/*c*) form polymeric chains, oriented along the crystallographic [001] direction. As shown in Fig. 4, these chains contain Pb_3I_{11} links; the shared I4 atoms are situated on the inversion centers. Twofold rotation axes run along [010] through the atoms Pb2 and I2.

The basic building block of the anionic chains of complex **4** consists of a Pb_3I_{10} unit as in **1**. The triangle Pb1, Pb1′, Pb2 is almost equilateral (Pb1 $\cdots$ Pb2 432,1(1), Pb1 $\cdots$ Pb1′ 425.5(1) pm). The ligands I1 are triply bridging (Pb–μ_3-I 319.8–339.7(1) pm); I2 and I3 act as μ-bridging ligands (Pb–μ-I 325.7–329.6(1) pm; Pb–μ-I–Pb 80.39–82.88(4)°) within the Pb_3I_{10} units and I4 links two trinuclear fragments (Pb1–I4 321.96(6) pm; Pb–I4–Pb 180°). Owing to its position on the twofold axis, I2 is situated within the Pb_3 plane, while I3 deviates by 18.9(3) pm, which is significantly less than in **1**, **2** or **3**. The Pb_3 planes in the polymeric anion of **4** are parallel (inversion center on I4) with a difference in height of 505.0(4) pm. Compound **4** is structurally related to the recently published iodoplumbate $[Me_3N(CH_2)_2NMe_3]_2[Pb_3I_{10}]$[4] which also features a one-dimensional polymer based on the Pb_3I_{11} unit. These anions differ in the connectivity of the building blocks: using the labelling scheme of **4**, in $[Me_3N(CH_2)_2NMe_3]_2[Pb_3I_{10}]$ the atoms I4 and I6 link the Pb_3I_{10} units leading to zigzag chains.

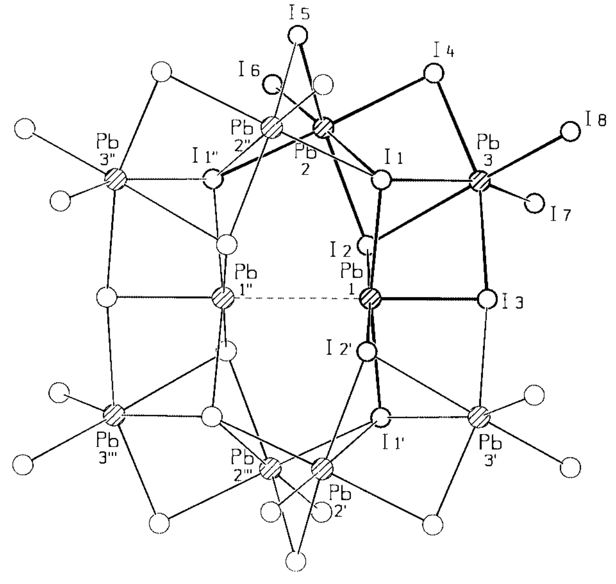

Fig. 3 Crystal structure of the $[Pb_{10}I_{28}]^{8-}$ anion in complex **3**. Selected distances (±0.1) and angles (±0.03): Pb1–I1 320.3; Pb1–I2 323.2; Pb1–I3 296.2; Pb2–I1 357.0; Pb2–I4 318.4; Pb3–I1 364.0; Pb3–I2 351.5; Pb3–I3 346.5; Pb3–I7 296.0 and Pb1 $\cdots$ Pb1″ 374.4 pm; I1–Pb1–I2 83.01; I1–Pb1–I1′ 170.24; I1–Pb3–I2 73.15; I1–Pb3–I7 162.33; I3–Pb3–I4 158.39; Pb1–I1–Pb2 93.59; Pb1–I3–Pb3 86.59 and Pb3–I3–Pb3–173.19°.

The complex $[Pr_3N(CH_2)_5NPr_3]_2[Pb_7I_{18}]$ **5** can be isolated as small, yellow platelets after addition of diethyl ether to a solution of PbI_2, NaI and $[Pr_3N(CH_2)_5NPr_3][PF_6]_2$ in DMF. Fig. 5 shows a fragment of the crystal structure (space group *P*2$_1$/*n*), which consists of a two-dimensional polymeric network spreading along [010] and [101] directions. The building blocks of this network are Pb_7I_{22} fragments as observed as discrete $[Pb_7I_{22}]^{8-}$ anions in **2**.

In complex **5** each of these fragments shares its eight terminal iodo ligands (I6–I9) with four neighboring anions, leading to doubly and triply bridging co-ordination of all I atoms. Since no terminal ligands are present, the co-ordination of the triply bridging atoms I1 and I2 (Pb–μ_3-I 323.7–334.3(1) pm) is more symmetrical than in **1**–**4**, where *trans* influences of the strong terminal Pb–I bonds lead to elongation of the Pb–μ_3-I distances. In contrast to I1 and I2, I3 co-ordinates to the Pb atoms with two short bonds and one long bond (Pb3–I3 322.1(1), Pb4–I3 324.9(1), Pb1–I3 356.1(1) pm, Pb1–I3–Pb4 152.38(3)°). The latter results in a weak *trans* influence on the Pb1–I4 bond (310.8(1) pm), which is the shortest Pb–I distance in **5**. All other I atoms (I5–I9) act as μ bridges with Pb–I distances ranging from 313.6 to 329.9(1) pm. As in **2** the Pb_3 planes (Pb $\cdots$ Pb 420.29–427.86(9), Pb3 $\cdots$ Pb4 392.69(6) pm) within one Pb_7I_{22} unit of **5** are related by inversion centers occupied by Pb4. They are parallel with a height difference of 69.8(4) pm. As in most of the iodoplumbates characterized so far (for exceptions see ref. 8), all Pb atoms in **5** are co-ordinated by six iodo ligands in a distorted octahedral fashion. Within the Pb_7I_{22} units, the PbI_6 octahedra share common faces, linking to neighboring units being achieved through common edges of PbI_6 octahedra. The two-dimensional anionic nets in **5** slightly deviate from planarity (deviation of Pb1 from the idealized plane 133 pm) and are stacked along $[10\bar{1}]$ with the diammonium cations located between the anionic layers (Fig. 6).

Conclusion

The crystal structures of complexes **1**–**5**, $[Me_3N(CH_2)_2NMe_3]_2[Pb_3I_{10}]$ and $[Me_3N(CH_2)_2NMe_3]_3[Pb_3I_9]_2$[4] can all be dis-

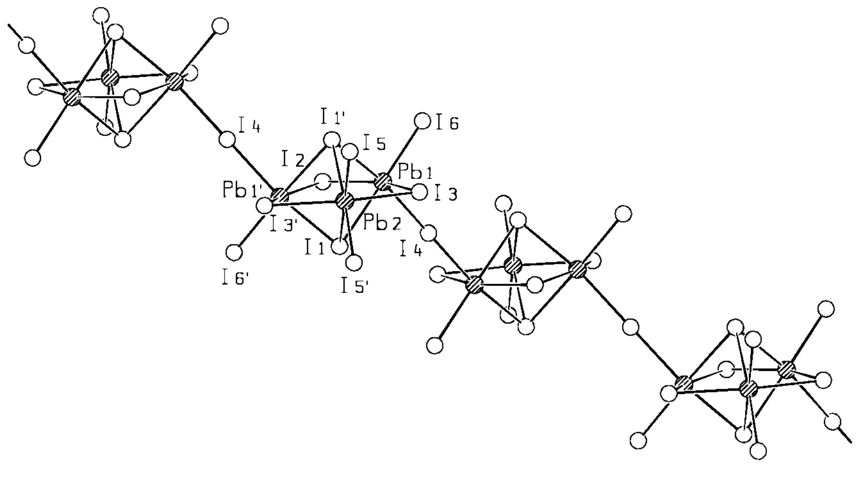

Fig. 4 Fragment of the polymeric anion structure of complex **4**. Selected distances and angles: Pb1–I1 336.6(1); Pb1–I2 329.6(1); Pb1–I3 327.3(1); Pb1–I4 321.96(6); Pb1–I6 307.9(2); Pb1–I1′ 319.8(1); Pb2–I1 339.7(1); Pb2–I3 325.7(1); Pb2–I5 306.2(2) and Pb1 $\cdots$ Pb2 432.1(1) pm; I1–Pb–I1′ 84.41(3); I1–Pb1–I2 80.48(3); I1–Pb1–I6 175.67(5); I2–Pb1–I3 158.39(4); I1–Pb2–I1′ 80.99(4); I1–Pb2–I5 171.86(4); Pb1–I3–Pb2 82.88(3) and Pb1–I4–Pb1″ 180°.

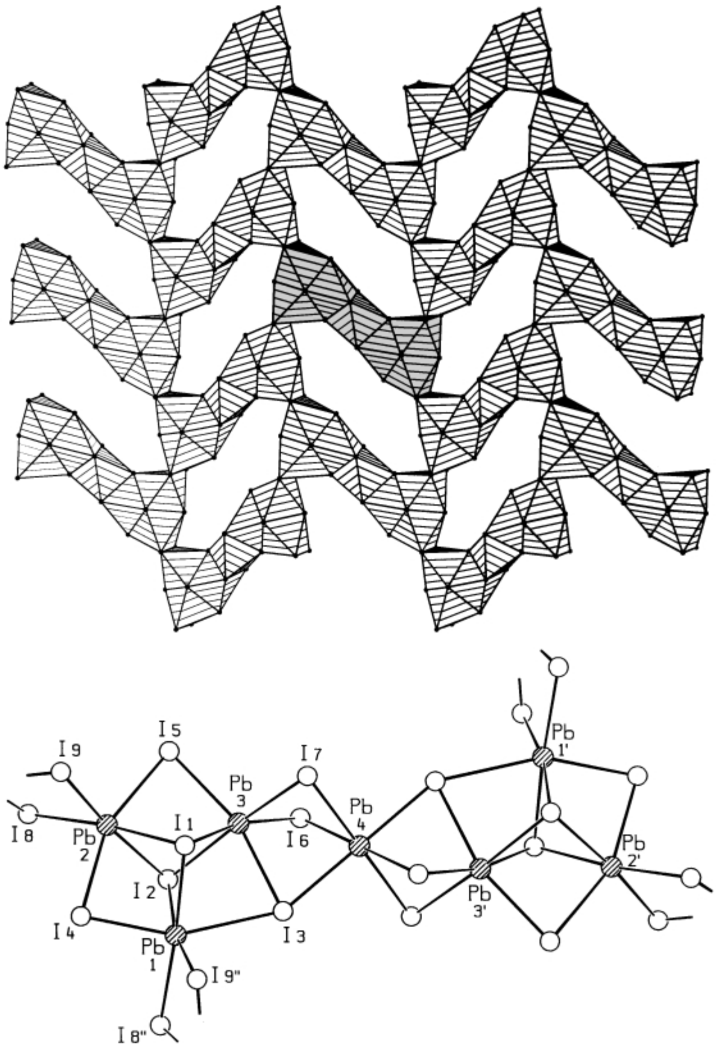

Fig. 5 Fragments of the polymeric anion structure of complex **5**. Selected distances (±0.1) and angles (±0.03): Pb1–I1 323.8; Pb1–I2 326.9; Pb1–I3 356.1; Pb2–I1 331.2; Pb2–I4 321.3; Pb2–I8 318.4; Pb3–I1 323.7; Pb3–I2 326.9; Pb3-I3 322.1; Pb3–I7 317.6; Pb4–I3 324.9; Pb1 ··· Pb2 420.3 and Pb3 ··· Pb4 392.7 pm; I1–Pb1–I2 84.16; I1–Pb1–I3 78.25; I1–Pb2–I4 78.85; I1–Pb2–I8 174.24; I3–Pb4–I7 88.71; Pb1–I1–Pb2 79.82; Pb1–I3–Pb3 78.06 and Pb1–I3–Pb4 152.38°.

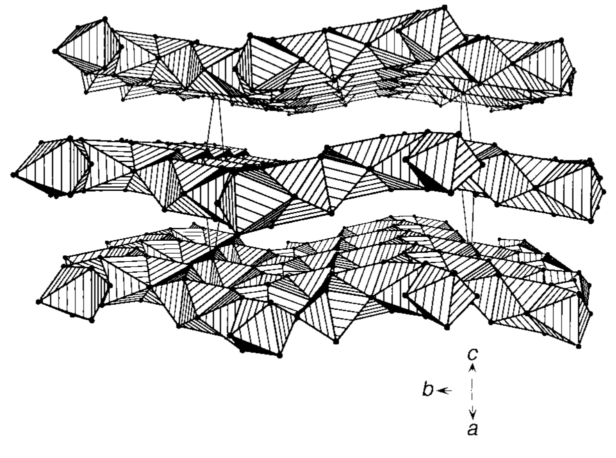

Fig. 6 View approximately along [101] on the iodoplumbate layers in complex **5**.

cussed in terms of $[Pb_3I_{10}]^{4-}$ subunits. This pattern supports the hypothesis that oligonuclear iodoplumbate complexes are present in solution. In the solid state the $[Pb_3I_{10}]^{4-}$ anions are organized to various oligomeric or polymeric structures, depending on size, shape and charge of the counter ions used for crystallization. The selective synthesis of **1**–**3** containing the same diammonium cation clearly demonstrates the sensitivity of the Pb^{2+}/I^-/cation system to small changes in crystallization conditions. This sensitivity is consistent with the lability of the Pb–I bond.

Experimental

Preparations

$[Bu_3N(CH_2)_4NBu_3]_2[Pb_3I_{10}]$ 1. The compounds PbI_2 (230 mg, 0.50 mmol), NaI (188 mg, 1.25 mmol) and $[Bu_3N(CH_2)_4NBu_3][PF_6]_2$ (358 mg, 0.50 mmol) were dissolved in DMF (5 ml). Diethyl ether (25 ml) was condensed into the clear yellow solution. Over the course of two weeks, yellow platelets of **1**·DMF·$0.5Et_2O$ crystallized together with colorless needles of NaI·3DMF, which can be removed by washing with ethanol (330 mg, 70%) (Found: C, 25.2; H, 4.7; N, 2.7. $C_{56}H_{124}I_{10}N_4Pb_3 \cdot C_3H_7NO$ requires C, 25.2; H, 4.7; N, 2.5%).

$[Bu_3N(CH_2)_4NBu_3]_4[Pb_7I_{22}]$ 2. The compounds PbI_2 (230 mg, 0.50 mmol), NaI (86 mg, 0.57 mmol) and $[Bu_3N(CH_2)_4NBu_3][PF_6]_2$ (205 mg, 0.29 mmol) were dissolved in DMF (5 ml). After addition of THF (10 ml) to the clear, yellow solution, diethyl ether (25 ml) was slowly added by condensation. Complex **2** crystallizes as yellow rods (320 mg, 75%) (Found: C, 22.4; H, 4.4; N, 2.1. $C_{112}H_{248}I_{22}N_8Pb_7$ requires C, 22.6; H, 4.2; N, 1.9%).

$[Bu_3N(CH_2)_4NBu_3]_4[Pb_{10}I_{28}]$ 3. The compounds PbI_2 (230 mg, 0.50 mmol), NaI (60 mg, 0.40 mmol) and $[Bu_3N(CH_2)_4$-

Table 1 Crystallographic data of complexes **1**–**5**

	1·DMF·0.5Et$_2$O	**2**	**3**	**4**	**5**
Formula	$C_{61}H_{136}I_{10}N_5O_{1.5}Pb_3$	$C_{122}H_{248}I_{22}N_8Pb_7$	$C_{112}H_{248}I_{28}N_8Pb_{10}$	$C_{22}H_{56}I_{10}N_4Pb_3$	$C_{46}H_{104}I_{18}N_4Pb_7$
M	2854.32	5949.31	7332.28	2267.28	4447.86
Crystal system	Triclinic	Monoclinic	Tetragonal	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{4}2c$ (no. 112)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a/pm	1533.91(9)	1673.0(2)	2291.16(9)	2088.9(2)	1191.4(1)
b/pm	1692.0(1)	2682.3(3)	2291.16(9)	1327.6(1)	2811.2(4)
c/pm	2067.4(1)	2049.6(2)	1852.03(7)	1842.3(2)	1536.8(2)
α/°	72.963(5)				
β/°	70.719(5)	105.87(1)		101.25(1)	110.248(9)
γ/°	74.467(4)				
U/10^6 pm^3	4754.8(5)	8847(2)	9722.1(7)	5011.1(8)	4829(1)
T/K	210(2)	200(2)	193(2)	193(2)	293(2)
Z	2	2	2	4	2
D_c/g cm^{-3}	1.994	2.233	2.505	3.005	3.059
μ(Mo-Kα)/cm^{-1}	85.8	105.1	131.1	162.3	179.4
2θ range/°	3–48	3–48	3–50	3–48	3–46
Reflections measured	19324	32340	39676	14017	10801
Unique reflections [R_{int}]	14940 [0.023]	13110 [0.039]	8541 [0.038]	3844 [0.050]	6723 [0.031]
Observed reflections, $I > 2\sigma(I)$	11658	9337	7772	3388	5261
Parameters	696	393	357	124	340
$R1$ (observed reflections)	0.047	0.040	0.028	0.056	0.032
$wR2$ (all reflections)	0.125	0.102	0.063	0.138	0.068
Flack parameter x	—	—	−0.005(4)	—	—

NBu$_3$][PF$_6$]$_2$ (143 mg, 0.20 mmol) were dissolved in DMF (4 ml). Layering the yellow solution with toluene or ethanol (20 ml) gave orange-red crystals of **3** (286 mg, 78%) (Found: C, 18.3; H, 3.3; N, 1.6. $C_{112}H_{248}I_{28}N_8Pb_{10}$ requires C, 18.3; H, 3.4; N, 1.5%).

[Me$_3$N(CH$_2$)$_5$NMe$_3$]$_2$[Pb$_3$I$_{10}$] 4. A suspension of PbI$_2$ (460 mg, 1.00 mmol), NaI (75 mg, 0.50 mmol) and [Me$_3$N(CH$_2$)$_5$-NMe$_3$][PF$_6$]$_2$ (239 mg, 0.50 mmol) in DMF (50 ml) was stirred at 100 °C for 2 h. After removing the undissolved solid by filtration, diethyl ether (50 ml) was slowly condensed into the yellow solution. After a few days small crystals of **4** formed as yellow, mainly twinned needles (58 mg, 10%) (Found: C, 11.8; H, 2.7; N, 2.5. $C_{22}H_{56}I_{10}N_4Pb_3$ requires C, 11.7; H, 2.5; N, 2.5%). According to the elemental analysis, the solid removed by filtration has the same composition (340 mg, 60%) (Found: C, 11.9; H, 2.9; N, 2.4%).

[Pr$_3$N(CH$_2$)$_5$NPr$_3$]$_2$[Pb$_7$I$_{18}$] 5. The compounds PbI$_2$ (230 mg, 0.50 mmol), NaI (38 mg, 0.25 mmol) and [Pr$_3$N(CH$_2$)$_5$-NPr$_3$][PF$_6$]$_2$ (81 mg, 0.25 mmol) were dissolved in DMF (5 ml). Diethyl ether (10 ml) was slowly condensed into the clear yellow solution. After several days bundles of small yellow platelets of **5** crystallized (45 mg, 16%) (Found: C, 12.6; H, 2.3; N, 1.3. $C_{46}H_{104}I_{18}N_4Pb_7$ requires C, 12.4; H, 2.4; N, 1.3%).

Crystal structure analyses of complexes 1–5

The data collections were performed on STOE STADI IV four circle diffractometers (**1**, **5**) and STOE IPDS imaging plate diffractometers (**2**, **3**, **4**) using Mo-Kα radiation. All intensities were corrected for Lorentz-polarization effects. An empirical absorption correction was applied for **1**, numerical absorption corrections for **2**–**5**. The structures were solved by direct methods (SHELXS 86[11]) and refined by full-matrix least squares based on F^2 using all measured unique reflections (SHELXL 97[11]). Anisotropic displacement parameters were used for Pb, I, N and in **1**, **3** and **5** also for the C atoms. Hydrogen atoms were included in calculated positions. Other important crystallographic data are summarized in Table 1. Graphical presentations were drawn using SCHAKAL 92[12] and DIAMOND 2.[13]

CCDC reference number 186/1527.

See http://www.rsc.org/suppdata/dt/1999/2731/ for crystallographic files in .cif format.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Professor D. Fenske for his support.

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Paper 9/02640A