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Synthesis and crystal structures of iodoplumbate chains, ribbons and rods with new structural types

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One-dimensional infinite iodoplumbates with new structural types have been prepared by crystallization from solutions containing PbI_2 and NaI with large counter ions. Whereas $[(PhCH_2)_4P]_2[Pb_3I_8]$ **1** contains Pb^{II} with octahedral and square pyramidal coordination, in $[Me_3N(CH_2)_6NMe_3][PbI_3]_2$ **2**, $[Na(dmf)_3]_4[Pb_6I_{16}]$ **3**, $[Na_4(dmf)_{14}][PbI_3]_4$ **4**, $[PrN(C_2H_4)_3NPr][Pb_2I_6]$ **5** and $[Bu_3N(CH_2)_2NBu_3]_2[Pb_{10}I_{24}]$ **6** all Pb atoms are six-coordinated. The great structural variety of these compounds is achieved by condensation of PbI_6 octahedra in several different ways. Face-sharing octahedra are observed in **2** and **4**, edge-sharing octahedra characterize the anionic substructure of **6**. In the iodoplumbates **3** and **5** PbI_6 octahedra share common faces, edges and vertices at the same time. The Pb–I distances ranging from 293.5 to 364.5 pm can be explained on the basis of different degrees of bridging of the iodo ligands and the *trans* influence of ligands in *trans* position. The composition and structure of the iodoplumbate anions are mainly determined by the size, shape and charge of the counter ions used for crystallization.

Introduction

Oxometalates with various structures have been reported, which are constructed by condensation of MO_6, MO_5 and MO_4 polyhedra.[1] In a similar way condensation of EI_6 octahedra with E = Sb, Bi, Sn or Pb leads to discrete or polymeric iodoantimonate, iodobismuthate,[2] iodostannate[3] or iodoplumbate[4–10] anions. Their stability and chemical reactivity are different from those of the oxometalates since the bonding interactions of M^{2+} or M^{3+} with I^- ions are significantly weaker than those between M^{4+}, M^{5+} or M^{6+} and O^{2-}.

Iodoplumbates with a great variety of different compositions and structures can be obtained by reaction of PbI_2 with NaI in polar organic solvents and crystallization with large counter ions. Their structures range from isolated anions with nuclearities of 2 up to 18 in $[Ph_4P]_2[Pb_2I_6]$[4] and $[Bu_4N]_8[Pb_{18}I_{44}]$[5] to infinite chains as in $[Me_4N][PbI_3]$[6] or $[Me_3N(CH_2)_2NMe_3]_2[Pb_3I_{10}]$[7] and two- or three-dimensional polymeric networks, *e.g.* $[Pr_3N(CH_2)_5NPr_3]_2[Pb_7I_{18}]$[8] and $[MeNH_3][PbI_3]$.[9] Whereas lead atoms with coordination numbers 4 or 5 are observed in only a few iodoplumbate structures,[4,8] most structures contain Pb^{II} in (distorted) octahedral coordination of iodo ligands. Their structural diversity is the result of various combinations of face-, edge- and vertex-sharing of PbI_6 octahedra.

In this paper we report on the synthesis and crystal structures of iodoplumbate chains, ribbons and rods with new structural types, $[(PhCH_2)_4P]_2[Pb_3I_8]$ **1**, $[Me_3N(CH_2)_6NMe_3][PbI_3]_2$ **2**, $[Na(dmf)_3]_4[Pb_6I_{16}]$ **3**, $[Na_4(dmf)_{14}][PbI_3]_4$ **4**, $[PrN(C_2H_4)_3NPr][Pb_2I_6]$ **5** and $[Bu_3N(CH_2)_2NBu_3]_2[Pb_{10}I_{24}]$ **6**.

Results and discussion

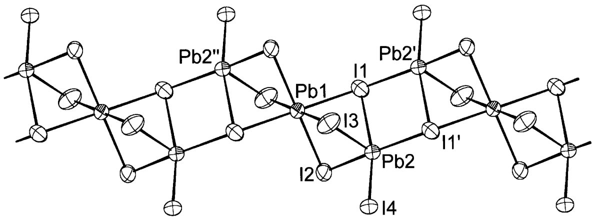

Fig. 1 Fragment of the polymeric anion structure of $[(PhCH_2)_4P]_2[Pb_3I_8]$ **1** (70% ellipsoids). Distances and selected angles: Pb1–μ-I 323.13(8)–324.5(1); Pb2–I1 360.4(1); Pb2–I1′ 334.75(9); Pb2–I2 314.68(9); Pb2–I3 299.7(1); Pb2–I4 294.7(1) and Pb1 · · · Pb2 414.3(1) pm; I1–Pb1–I2 81.31(2); I1–Pb2–I2 77.01(2); I1–Pb2–I4 167.28(2); I1′–Pb2–I2 170.87(2); Pb1–I1–Pb2 74.40(2); Pb1–I1–Pb2′ 133.29(2); Pb2–I1–Pb2′ 80.39(2) and Pb1–I2–Pb2 80.83(2)°.

Fig. 1 shows the structure of the Pb–I framework of $[(PhCH_2)_4P]_2[Pb_3I_8]$ **1** (space group $P\bar{1}$). Infinite iodoplumbate chains stretching along [100] are formed by face sharing of PbI_6 octahedra with PbI_5 square pyramids and edge sharing of square pyramids. Pb1 (inversion center) is octahedrally surrounded by six iodo ligands (Pb1–μ-I 323.1–324.5(1) pm), which are bridging to Pb2 and Pb2″. Pb2 is coordinated by five iodo ligands occupying the vertices of a distorted square pyramid (I–Pb–I 77.01–99.61; 167.28; 170.87(2)°). I1, in *trans* position to the terminal ligand I4 (Pb2–I4 294.7(1) pm), is only weakly bonded to Pb2 (Pb2–I1 360.4(1) pm). The position opposite of I3 (Pb2–I3 299.7(1) pm) is vacant; the nearest neighbours in this direction are two carbon atoms of a phenyl group of a $(PhCH_2)_4P^+$ cation. However, the Pb · · · C distances of 335.0 and 357.5(7) pm are too long for significant bonding interactions between the π-electron system and Pb^{2+}. For comparison, the Pb–C bonds in the arene complex $[Pb(\eta^6\text{-}C_6H_6)(AlCl_4)_2]\cdot C_6H_6$[11] are significantly shorter (Pb–C 308–313(4) pm). A similar iodoplumbate chain with all Pb^{II} six-coordinated is found in $[Hhmta]_2[Pb_3I_8(hmta)_2]$ (hmta = hexamethylenetetramine), where hmta ligands occupy the positions vacant in **1**.[12] The Pb–I bond lengths in **1** and $[Hhmta]_2[Pb_3I_8(hmta)_2]$ are quite similar with exception of the bond Pb2–I3, which is 27 pm longer in $[Hhmta]_2[Pb_3I_8(hmta)_2]$ due to the hmta ligand in *trans* position.[13] Iodoplumbates with five-coordinated Pb^{2+} ions have been observed in $[Pr_4N][PbI_3]$, $[Fe(dmf)_6][PbI_3]_2$[4] and $[Bu_3N(CH_2)_4NBu_3]_2[Pb_3I_{10}]$.[8]

The most common iodoplumbate solid state structure is the infinite $[PbI_3]^-$ chain consisting of *trans* face-sharing PbI_6 octahedra.[6] A related iodoplumbate chain is observed in $[Me_3N(CH_2)_6NMe_3][PbI_3]_2$ **2** (space group *P*2/*c*), which can be obtained by crystallization from solutions of PbI_2, NaI and $[Me_3N(CH_2)_6NMe_3][PF_6]_2$ in acetone. The Pb atoms are again octahedrally coordinated, the PbI_6 octahedra share common

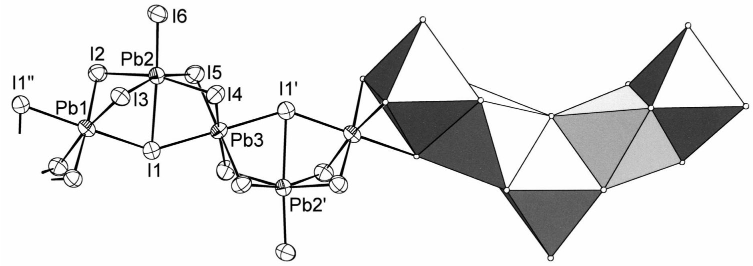

Fig. 2 Fragment of the polymeric anion structure of $[Me_3N(CH_2)_6NMe_3][PbI_3]_2$ **2** (70% ellipsoids). Selected distances and angles: Pb1–I1 334.3(1); Pb1–I2 318.9(2); Pb1–I3 324.1(2); Pb2–I1 360.3(2); Pb2–I2 326.9(2); Pb2–I3 318.0(2); Pb2–I6 301.0(2) and Pb1 · · · Pb2 408.1(1) pm; I1–Pb1–I1 173.87(7); I1–Pb1–I2 86.32(4); I1–Pb2–I2 80.99(4); I1–Pb2–I3 82.35(4); I1–Pb2–I6 175.49(5); I2–Pb2–I6 98.01(5); Pb1 · · · Pb2 · · · Pb3 101.68(2); Pb2 · · · Pb3 · · · Pb2′ 173.34(4); Pb1–I1–Pb2 71.86(3); Pb1–I1–Pb3 144.26(5) and Pb1–I2–Pb2 78.36(4)°.

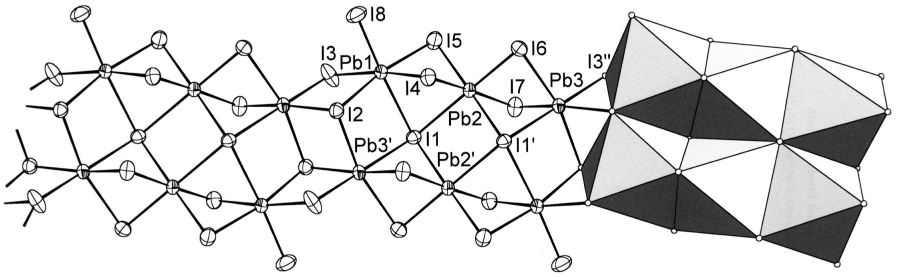

Fig. 3 Fragment of the polymeric anion structure of $[Na(dmf)_3]_4[Pb_6I_{16}]$ **3** (70% ellipsoids). Selected distances and angles: Pb1–I1 344.05(8); Pb1–I2 324.40(9); Pb1–I3 327.24(9); Pb1–I4 318.50(8); Pb1–I8 293.53(8); Pb2–I1 343.27(8); Pb2–I4 308.71(8); Pb1 · · · Pb2 410.39(8) and Pb1 · · · Pb3′ 470.30(8) pm; I1–Pb1–I2 88.90(2); I1–Pb1–I8 176.67(2); I2–Pb1–I4 87.50(2); I4–Pb1–I8 96.12(2); Pb1 · · · Pb2 · · · Pb3 177.96(1); Pb2 · · · Pb1 · · · Pb3′ 90.92(1); Pb1–I1–Pb2 73.32(2); Pb1–I1–Pb2′ 130.65(2) and Pb1–I4–Pb2 81.72(2)°.

faces, alternatingly *trans* faces (*e.g.* row of octahedra around Pb2, Pb3, Pb2′) and faces with one common I atom (I1, octahedra around Pb1, Pb2, Pb3). The resulting wave-shaped chain is orientated along [100] with its amplitude in [001] direction (Fig. 2). Pb1 and Pb3 occupy positions on twofold rotation axes, Pb2 is on a general position. In addition there is approximately a non-crystallographic mirror plane defined by the Pb atoms and by I1 and I6. I6 and all symmetry related atoms in each iodoplumbate chain are shifted from this hypothetic mirror plane to the same direction by 41.7 pm.[14]

As a consequence of the connectivity of PbI_6 octahedra in complex **2** the iodo ligands are acting as μ_3 (I1) and μ bridges (I2–I5) and as terminal ligands (I6). Pb–μ-I distances are in the range of 318.0–331.7(2) pm, average 322.8 pm, in accordance with corresponding lengths in chains of *trans* face-sharing PbI_6 octahedra.[6] The longest Pb–I distance is observed for the triply bridging ligand I1 (Pb2–I1 360.3(2) pm) due to its higher connectivity and the *trans* influence of the terminal ligand I6 (Pb2–I6 301.0(2) pm) in *trans* position to I1.[13] For comparison, in solid PbI_2, which crystallizes in the CdI_2 structural type with layers of edge-sharing PbI_6 octahedra, the Pb–I bond length of the μ_3-I atoms is 322.7 pm, the Pb–I–Pb angle 89.8°.[15]

Bent M_3X_{12} fragments corresponding to the octahedra around Pb1, Pb2 and Pb3 in complex **2** have been found in $[Me_3NH]_3[As_3I_{12}]$ and $[Et_3NH]_3[As_3Br_{12}]$ as isolated anions.[16] These halogenoarsenate anions can be regarded as AsX_6 (X = I or Br) octahedra, in which two triangular X_3 faces with one common vertex are capped by AsX_3 units. Isolated $[M_3X_{12}]^{3-}$ anions consisting of three *trans* face-sharing octahedra corresponding to the fragment of PbI_6 octahedra around Pb2, Pb3 and Pb2′ in **2** are observed in $[Bu_4N]_3[Bi_3I_{12}]$ and $[Et_4N]_3[As_3Br_{12}]$.[17]

PbI_2 reacts with NaI and Bu_4NPF_6 in acetone to form $[Bu_4N]_8[Pb_{18}I_{44}]$.[5] However, if dmf is used as a solvent, layering with diethyl ether yields crystals of $[Na(dmf)_3]_4[Pb_6I_{16}]$ **3**. Unusual is the presence of solvated Na^+ as counter ion, whereas Bu_4N^+ is not included in the crystal, but important for the formation of **3**. Using similar reaction and crystallization conditions without Bu_4N^+, **3** is not observed, but $[PbI_2(dmf)]$,[10] $[Na_4(dmf)_{14}][PbI_3]_4$ **4** or $[Na(dmf)_3]I$[18] are formed instead, depending on the molar ratio of the starting compounds. Obviously the purpose of Bu_4N^+ is to stabilize an intermediate in the formation of **3**.

The cations of **3** consist of infinite linear chains of *trans* face-sharing $Na(dmf)_6{}^+$ octahedra with bridging dmf ligands (Na–μ-O 236.6–243.5(7) pm, Na · · · Na 311.6(3) and 314.2(3) pm, Na · · · Na · · · Na 173.5(1) and 180°), which have been observed in $[Na(dmf)_3]I$ (Na · · · Na 327(1) pm).[18]

Both the cationic chain and the iodoplumbate ribbon of complex **3** (space group $P\bar{1}$) are orientated along the crystallographic *a* axis. The polymeric $[Pb_6I_{16}]^{4-}$ anions (Fig. 3) contain Pb_6I_{20} building blocks consisting of a 2 × 3 array of face-, edge- and vertex-sharing PbI_6 octahedra. All six Pb atoms in each block are positioned in a plane within ±3.5(5) pm. The Pb · · · Pb distances are 410.39 and 410.60(8) pm for face-sharing PbI_6 octahedra (Pb1 · · · Pb2, Pb2 · · · Pb3), 470.30(8) and 456.80(10) pm for edge-sharing octahedra (Pb1 · · · Pb3′, Pb2 · · · Pb2′). In a crude approximation, the I atoms occupy two plains (deviation ±52 pm) 190 pm above and below the Pb_6 plain, respectively.

Neighbouring Pb_6I_{20} units are linked by four common I atoms (I2, I3 and equivalent atoms), thus forming infinite ribbons with a height difference of the Pb_6 plains of 99 pm. In this arrangement of linked PbI_6 octahedra there are inversion centers in the middle of each Pb_6I_{20} block and between the linked Pb_6I_{20} units. The Pb–I bond lengths vary according to the degree of bridging of the ligands: one out of eight crystallographically independent iodo ligands (I1) is μ_4 bridging with Pb–I distances ranging from 326.06 to 347.54(9) pm. The shortest bond is observed for the terminal iodo ligand I8 (Pb1–I8 293.53(8) pm). The Pb–I distances of the μ and μ_3 bridging atoms are intermediate (μ_3-I–Pb 313.89–339.71(8); μ-I–Pb 301.97–327.24(9) pm).

In an alternative description the anion of complex **3** can be regarded as a double chain structurally related to the anions of $[Me_3N(CH_2)_3NMe_3]_2[Pb_3I_{10}]$[7] or $[H_3NC_3H_6NH_3]_2[Pb_3I_{10}]$[19] in which Pb^{2+} and I^- ions build single chains corresponding to the upper half of the anion of **3** (Fig. 3). Isolated M_3I_{12} fragments of the structure of **3** consisting of three face-sharing

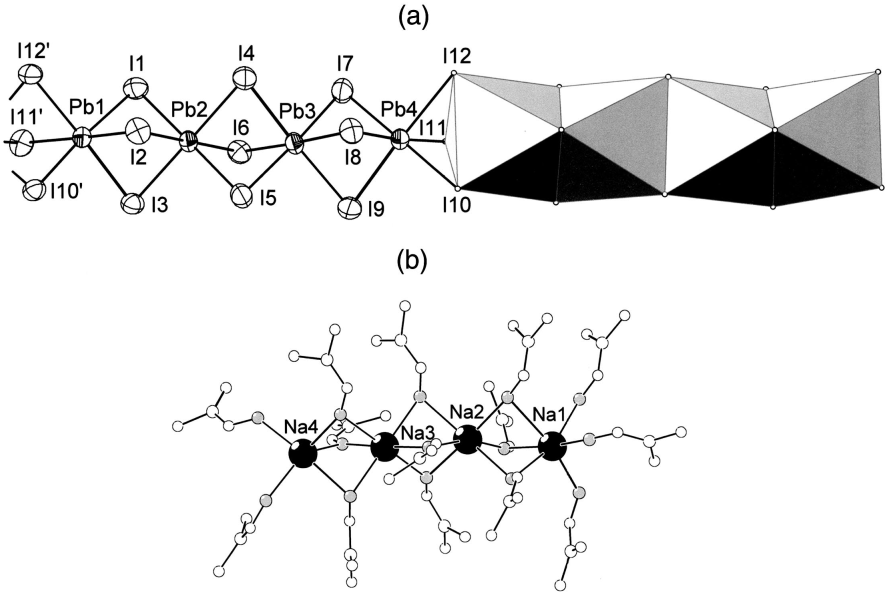

Fig. 4 Crystal structure of $[Na_4(dmf)_{14}][PbI_3]_4$ **4**. (a) Fragment of the polymeric anion (70% ellipsoids). Selected distances and angles: Pb1–I1 324.7(1); Pb1–I2 319.7(1); Pb2–I1 321.1(1); Pb2–I2 323.5(1); Pb1 · · · Pb2 399.5(1) and Pb2 · · · Pb3 398.3(1) pm; I1–Pb1–I2 87.92(3); I1–Pb1–I 84.1(2) and Pb1–I1–Pb2 76.44(2)°. (b) The cation. Selected distances and angles: Na1 · · · Na2 321.0(7); Na2 · · · Na3 313.1(7); Na3 · · · Na4 308.4(7); Na1–O1 227.8(9); Na1–O5 240.1(9); Na2–O5 234.8(10) and Na4–O14 224(1) pm; Na1 · · · Na2 · · · Na3 170.1(2); O1–Na1–O5 93.7(4) and Na1–O5–Na2 85.1(3)°.

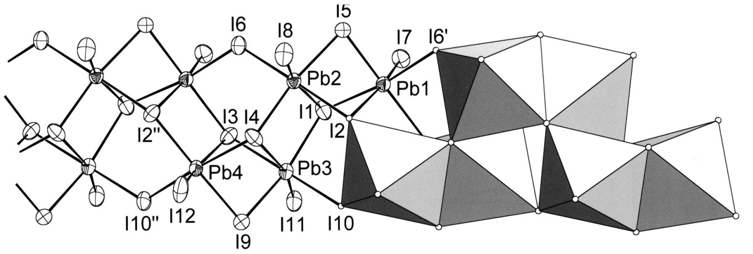

Fig. 5 Fragment of the polymeric anion structure of $[PrN(C_2H_4)_3NPr][Pb_2I_6]$ **5** (50% ellipsoids). Selected distances and angles: Pb1–I1 336.2(1); Pb1–I2 348.2(1); Pb1–I5 315.7(1); Pb1–I6′ 317.6(1); Pb1–I7 298.8(1); Pb2–I1 352.5(1); Pb2–I2 330.6(1); Pb2–I5 322.2(1); Pb2–I6 318.3(1); Pb1 · · · Pb2 428.45(9) and Pb1 · · · Pb4′ 453.92(9) pm; I1–Pb1–I2 82.20(3); I1–Pb1–I5 85.66(3); I1–Pb1–I6′ 171.65(4); I2–Pb1–I6′ 100.67(4); I2–Pb1–I7 168.02(4); Pb2 · · · Pb1 · · · Pb4′ 88.77(2); Pb1–I1–Pb2 76.90(3); Pb1–I1–Pb3 124.90(5); Pb2–I1–Pb3 84.21(3) and Pb1″–I6–Pb2 121.14(4)°.

octahedra (Pb1, Pb2, Pb3) are observed in the iodobismuthate $[Bu_4N]_3[Bi_3I_{12}]$.[17]

The anion of $[Na_4(dmf)_{14}][PbI_3]_4$ **4** consists of chains of *trans* face-sharing PbI_6 octahedra (Fig. 4a) as observed in several iodoplumbates, *e.g.* $[Me_4N][PbI_3]$.[6] Pb–I distances (318.3–330.2(1) pm) and Pb–I–Pb angles (81.98–98.13(3) and 175.28–179.48(3)°) on average are in agreement with the data of $[Me_4N][PbI_3]$ (Pb–I 322 pm; I–Pb–I 86.3, 93.7 and 180°). In **4** the infinite $[Na(dmf)_3]^+$ chain of **3** or $[Na(dmf)_3]I$[18] is split into tetranuclear fragments by additional terminal dmf ligands in order to compensate the difference between the Pb · · · Pb distance (398.3 pm) in the polymeric anion and the Na · · · Na distance (308.4–321.0(7) pm) in the cation. Three NaO_6 octahedra (Na1, Na2, Na3) and one NaO_5 trigonal bipyramid (Na4) share common triangular faces and form $[Na_4(dmf)_{14}]^{4+}$ cations (Fig. 4b). Four Na^+ ions are linked by nine μ bridging dmf ligands (Na–μ-O 227.0(9)–265.5(11) pm; Na–O–Na 80.7–85.1(3)°) to a linear arrangement, slightly tilted towards the anionic chain. The coordination spheres of Na1 and Na4 are completed by three and two terminal dmf ligands (Na–O 223.9(11)–233.9(9) pm). Crystallization from solutions richer in NaI yields crystals of $[Na(dmf)_3]I$;[18] solutions poorer in NaI lead to crystallization of $[PbI_2(dmf)]$.[10]

The reaction of PbI_2 with NaI and $[PrN(C_2H_4)_3NPr][PF_6]_2$ in acetone yields small yellow crystals of $[PrN(C_2H_4)_3NPr][Pb_2I_6]$ **5**. The anionic chains of **5**, which crystallizes in space group $P2_12_12$, contain Pb_2I_9 bioctahedra as building blocks (Fig. 5). These bioctahedra are arranged in two parallel rows (first row: Pb1, Pb2, I1, I2, I4–I8, I3′, I6′. Second row: Pb3, Pb4, I1, I3, I4, I9–I12, I2″, I10″) orientated along the crystallographic *c* axis. Within each row the bioctahedra are linked by μ-iodo ligands I6 and I10, respectively. I1 and I2, which are bridging ligands in the Pb_2I_9 bioctahedra of the first row, additionally bind to a bioctahedron of the second row and become triply bridging; the coordination mode of I3 and I4 is analogous to that of I1 and I2. Thus **5** features distorted PbI_6 octahedra sharing common faces (Pb1/Pb2; Pb3/Pb4), common edges (Pb2/Pb3; Pb1/Pb4′) and common vertices (Pb1/Pb2′; Pb3/Pb4′).

Compared to other iodoplumbates, the distortion of the PbI_6 octahedra is more developed and is again due to the different coordination modes of iodo ligands and their *trans* influence. The terminal ligands I7, I8, I11 and I12 form the strongest Pb–I bonds (296.8–303.7(1) pm); the longest, rather weak interactions are observed for triply bridging iodo ligands (I1–I4) in *trans* position to terminal bonds (Pb1–I2 348.2; Pb2–I1 352.5; Pb3–I4 364.5; Pb4–I3 346.5(1) pm; average μ_3-I-Pb 335.4 pm). The average μ-I-Pb bond length is 319.5 pm (315.7–322.4(1) pm). The angles I–Pb–I are in the ranges 76.04 to 101.67(4) and 163.30 to 178.46(4)°. Whereas the Pb-μ-I-Pb angles for I5 and I9 (Pb1–I5–Pb2 84.38; Pb3–I9–Pb4 86.52(3)°) are in the typical range of 80–90°,[4–10] the angles Pb2–I6–Pb1′ 121.14(4)° and Pb3–I10–Pb4′ 123.50(4)° are quite unusual. Although all lead atoms in **5** (Pb1–Pb4) are in similar chemical environments, there is no crystallographic symmetry operation transforming two PbI_6 octahedra into each other. Pb_2I_9 bioctahedra sharing originally terminal iodo ligands to form a

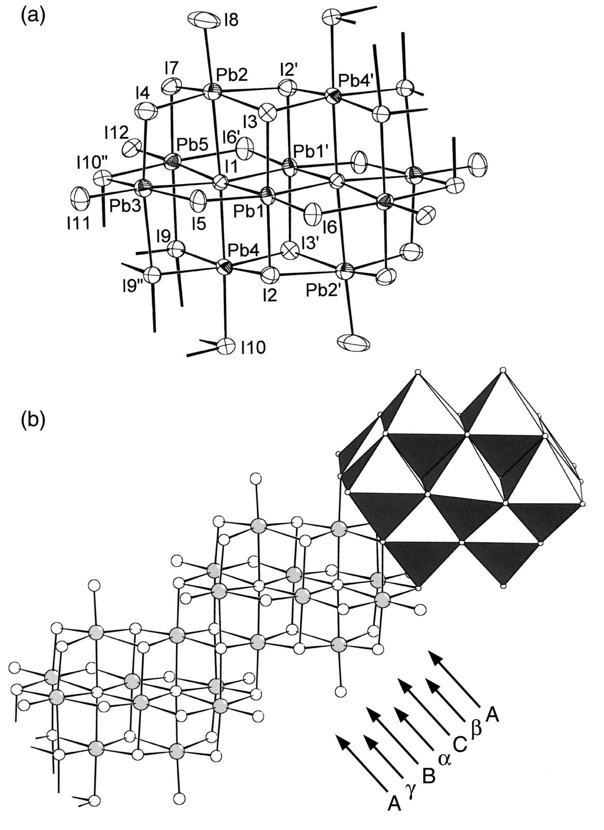

Fig. 6 Fragments of the polymeric anion structure of $[Bu_3N(CH_2)_2NBu_3]_2[Pb_{10}I_{24}]$ **6** (50% ellipsoids). The section drawn as polyhedra corresponds to the structure of $[V_{10}O_{28}]^{6-}$. Selected distances and angles: Pb1–I1 341.30(7); Pb1–I2 323.14(9); Pb1–I5 306.04(9); Pb1–I1′ 337.54(8); Pb2–I1 363.88(8); Pb3–I1 355.39(8); Pb3–I5 323.09(9); Pb3–I11 292.9(1); Pb1 ··· Pb2 496.73(7) and Pb1 ··· Pb3 487.56(8) pm; I1–Pb1–I2 85.07(2); I1–Pb1–I5 87.26(2); I5–Pb1–I1′ 170.50(2); I1–Pb3–I5 82.36(2); I1–Pb3–I11 175.42(3); I5–Pb3–I11 97.29(2); Pb2 ··· Pb1 ··· Pb4 91.78(1) and Pb3 ··· Pb1 ··· Pb1′ 88.70(1)°.

two-dimensional network have been found in $[Me_3N(CH_2)_2NMe_3]_2[Pb_2I_7]I$.[20]

The iodoplumbate $[Bu_3N(CH_2)_2NBu_3]_2[Pb_{10}I_{24}]$ **6** (space group $P\bar{1}$) can be obtained by solvothermal synthesis starting from PbI_2, NaI and $[Bu_3N(CH_2)_2NBu_3][PF_6]_2$ in acetone. The structure of the polymeric anion can be described as a cylinder-shaped section of the NaCl lattice. $Pb_{10}I_{28}$ units composed of 10 edge-sharing PbI_6 octahedra in the same arrangement as the VO_6 octahedra in the decavanadate $Ca_3[V_{10}O_{28}]{\cdot}27H_2O$[21] share four common I atoms (I9, I10, I9′, I10′) with each neighbouring unit. Fig. 6 shows the $Pb_{10}I_{28}$ fragment of **6**, its condensation to infinite rods and the stacking of layers alternatingly consisting of Pb or I atoms, respectively. The stacking order is *AγBαCβ,A...* (*A*, *B*, *C*: layers of I. *α*, *β*, *γ*: layers of Pb), as known for the NaCl structure with cubic close packing of Cl^- or Na^+ ions. If layer *A* consists of atoms I9–I12 and I9″–I12″, *B* contains the atoms I1, I2, I4, I5, I7, I3′, I6′, I8′ and *C* the symmetry related atoms I3, I6, I8, I1′, I2′, I4′, I5′ and I7′. The lead atoms occupy all octahedral sites generated by the iodide sublattice. Atoms Pb1, Pb2, Pb1′ and Pb2′ define layer *α* (congruent with layer *A*), Pb3′–Pb5′ form *β* and Pb3–Pb5 layer *γ*. The stacking direction in the anion of **6** is parallel to the crystallographic *a* axis. The separations between the iodide layers are 370 (layers *B*, *C*, atom I8 excluded) and 377 pm (layers *A*, *B* and *C*, *A*) compared to 374 pm in the layer structure of PbI_2 (CdI_2 type; 324 pm separation for iodide layers without lead occupation).[15]

Although the discrete anion of $[Bu_4N]_8[Pb_{18}I_{44}]$[5] has already been interpreted as a section of the NaCl structure **6** is one of the rare examples of complexes featuring a μ_6-coordinating halogeno ligand (Pb–I1 336.90–363.88(8) pm; Pb–I1–Pb 81.62–95.28 and 172.86–176.62(2)°). The other I atoms in **6** are μ_4 (I9), μ_3 (I2, I3, I10), μ (I4–I7) bridging or terminal (I8, I11, I12) ligands. As expected, the Pb–I bond lengths vary with degree of bridging, average values being μ_6-I–Pb 347.7, μ_4-I–Pb 340.2, μ_3-I–Pb 326.8, μ-I–Pb 312.1 and I_{term}–Pb 291.7 pm. The Pb–I–Pb angles of all bridging iodo ligands are in the ranges 81.62–102.28 and 172.86–176.62°, consistent with the description as a NaCl structure fragment, which requires 90 and 180° angles.

Conclusion

The syntheses and crystal structures of compounds **1**–**6** show the importance of the counter ions and their influence on the substructures of the iodoplumbate anions. Iodoplumbates with the same composition $A_x[Pb_yI_z]$ and different structures are formed (*e.g.* compounds **2**, **4** and **5** or **1** and **3**), depending on the conditions of reaction and crystallization. The factors determining the anionic substructures are the concentration and molar ratio of the starting materials, nature of the solvent and, most important, size, shape and charge of the counter ions. Obviously by crystallization of one iodoplumbate salt chemical equilibria in solution are shifted with the consequence that one solid product is formed selectively.

Compound **1** is one of the rare examples of iodoplumbates containing Pb^{2+} with a coordination number lower than six. As in $[Ph_4P]_2[Pb_2I_6]$,[4] $[Fe(dmf)_6][PbI_3]_2$[4] and $[Bu_3N(CH_2)_4NBu_3]_4[Pb_{10}I_{28}]$[8] the coordination polyhedra of Pb^{2+} can be regarded as incomplete octahedra, I–Pb–I angles being close to 90 and 180°. In the large group of iodoplumbates with Pb^{2+} in (distorted) octahedral environment the polymeric chains of *trans* face-sharing PbI_6 octahedra as observed in $[Me_4N][PbI_3]$[6] or in **4** are very common. In $[BuN(CH_2CH_2)_3NBu]_3[Pb_5I_{16}]$[22] and in **2** coordination octahedra share adjacent faces. Whereas in $[MeNH_3][PbI_3]$ PbI_6 octahedra have common vertices and form a perovskite-type structure, edge sharing is found in $[PbI_2(dmf)]$, $[Ph_4P]_4[Pb_{15}I_{34}(dmf)_6]$[10] and $[H_3N(C_6H_4)NH_3][Pb_2I_6]$[23] as ribbon-shaped sections of PbI_2 layers and in $[Bu_4N]_8[Pb_{18}I_{44}]$[5] and **6**, which are related to the NaCl structure. **3** and **5** belong to a series of iodoplumbates in which two or more of these condensation patterns are present at the same time. Some of them are one-dimensional polymers, *e.g.* $[Me_3N(CH_2)_2NMe_3]_2[Pb_3I_{10}]$[7] (vertex sharing of cyclic Pb_3I_{11} trioctahedra); examples for two-dimensional networks are $[Me_3N(CH_2)_2NMe_3]_2[Pb_2I_7]I$[20] (vertex sharing of Pb_2I_9 bi-octahedra), $[Pr_3N(CH_2)_2NPr_3][Pb(dmf)_6][Pb_5I_{14}]$[20] (vertex and face sharing) and $[Me_3N(CH_2)_3NMe_3]_3[Pb_3I_9]_2$[7] (vertex, edge and face sharing).

Experimental

Preparations

$[(PhCH_2)_4P]_2[Pb_3I_8]$ 1. PbI_2 (100 mg, 0.22 mmol), NaI (16 mg, 0.11 mmol) and $(PhCH_2)_4PPF_6$ (119 mg, 0.22 mmol) were dissolved in acetone (50 ml). After filtration diethyl ether (50 ml) was condensed into the yellow solution. Over the course of two weeks yellow crystals of **1** were formed (30 mg, 23%).

$[Me_3N(CH_2)_6NMe_3][PbI_3]_2$ 2. A mixture of PbI_2 (270 mg, 0.59 mmol), NaI (90 mg, 0.60 mmol) and $[Me_3N(CH_2)_6NMe_3][PF_6]_2$ (75 mg, 0.15 mmol) in 10 ml of acetone was refluxed for 4 h. The resulting yellow product was isolated by filtration, washed with diethyl ether and dried *in vacuo*. (190 mg, 92%. Found: C 10.4, H 2.4, N 2.1. $C_6H_{15}I_3NPb$ requires C 10.5, H 2.2, N 2.0%). Small, mainly twinned crystals (yellow rods) of complex **3** were obtained by heating a sealed ampoule containing PbI_2 (90 mg, 0.20 mmol), NaI (30 mg, 0.20 mmol), $[Me_3N(CH_2)_6NMe_3][PF_6]_2$ (25 mg, 0.05 mmol) and 2 ml of acetone to 120 °C and cooling to room temperature within 20 h.

Table 1 Crystallographic data of complexes **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{56}H_{56}I_8P_2Pb_3$	$C_{12}H_{30}I_6N_2Pb_2$	$C_{36}H_{84}I_{16}N_{12}Na_4$- $O_{12}Pb_6$	$C_{42}H_{98}I_{12}N_{14}Na_4$- $O_{14}Pb_4$	$C_{12}H_{26}I_6N_2Pb_2$	$C_{52}H_{116}I_{24}N_4Pb_{10}$
M	2427.72	1378.16	4242.66	3466.86	1370.60	5914.99
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2/c$ (no. 13)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_12_12$ (no. 18)	$P\bar{1}$ (no. 2)
a/pm	933.4(2)	1267.6(2)	1249.5(2)	1594.0(1)	2966.2(4)	1125.03(9)
b/pm	1355.9(3)	994.04(9)	1362.3(2)	1654.8(1)	2071.1(3)	1647.9(1)
c/pm	1428.6(4)	2298.4(3)	1423.1(2)	1907.9(2)	902.9(1)	1860.1(2)
α/°	78.06(2)		80.47(1)	95.36(1)		102.05(1)
β/°	71.54(2)	100.03(2)	84.66(1)	104.678(9)		96.65(1)
γ/°	73.02(2)		89.15(1)	93.97(1)		98.144(9)
$U/10^6$ pm^3	1627.2(5)	2851.8(9)	2378.6(6)	4824.4(7)	5547(2)	3300.7(5)
T/K	200(2)	298(2)	173(2)	213(2)	298(2)	298(2)
Z	1	4	1	2	8	1
μ/cm^{-1}	116.2	182.9	158.3	58.75	188.0	183.37
Reflections measured	5644	25484	15922	35815	50976	33736
Unique reflections [R_{int}]	5257 [0.015]	4466 [0.067]	7886 [0.037]	15252 [0.047]	9773 [0.078]	10919 [0.052]
Observed reflections, $I > 2\sigma(I)$	4490	3627	5624	9267	8129	8203
Parameters	314	201	391	531	258	406
*R*1 (observed reflections)	0.026	0.051	0.029	0.042	0.040	0.041
*wR*2 (all reflections)	0.071	0.141	0.066	0.098	0.096	0.115
Flack parameter *x*	—	—	—	—	0.006(5)	—

$[Na(dmf)_3]_4[Pb_6I_{16}]$ 3 and $[Na_4(dmf)_{14}][PbI_3]_4$ 4. PbI_2 (230 mg, 0.50 mmol), NaI (37.5 mg, 0.25 mmol) and Bu_4NPF_6 (194 mg, 0.50 mmol) were dissolved in dmf (5 ml). Diethyl ether (25 ml) was condensed into the clear yellow solution. After thin fibres of $[PbI_2(dmf)]$ had formed, compound **3** crystallized (110 mg, 41%).

Reaction of PbI_2 (230 mg, 0.50 mmol) with NaI (75 mg, 0.50 mmol) in dmf (5 ml) in the absence of Bu_4NPF_6 and crystallization by addition of diethyl ether (25 ml) yielded yellow rods of complex **4** (320 mg, 74%. Found: C 14.6, H 2.8, N 5.6. $C_{21}H_{49}I_6N_7Na_2O_7Pb_2$ requires C 14.6, H 2.9, N 5.7%). So far we did not succeed in the synthesis of **3** in the absence of Bu_4NPF_6.

$[PrN(C_2H_4)_3NPr][Pb_2I_6]$ 5. A mixture of PbI_2 (270 mg, 0.59 mmol), NaI (90 mg, 0.60 mmol) and $[PrN(C_2H_4)_3NPr][PF_6]_2$ (150 mg, 0.31 mmol) in 10 ml of acetone was refluxed for 4 h. The resulting yellow product was isolated by filtration, washed with acetone and dried *in vacuo* (345 mg, 86%. Found: C 10.8, H 2.1, N 2.2. $C_6H_{13}I_3NPb$ requires C 10.5, H 1.9, N 2.0%). Single crystals of complex **5** were obtained by heating a sealed ampoule containing the starting materials to 120 °C and cooling to room temperature within 20 h.

$[Bu_3N(CH_2)_2NBu_3]_2[Pb_{10}I_{24}]$ 6. A sealed ampoule containing PbI_2 (92 mg, 0.20 mmol), NaI (10 mg, 0.067 mmol), $[Bu_3N(CH_2)_2NBu_3][PF_6]_2$ (69 mg, 0.10 mmol) and 1 ml of acetone was heated at 105 °C for two weeks. After cooling to room temperature the ampoule contained light yellow rods of complex **6** (82 mg, 71%. Found: C 11.2, H 2.3, N 1.0. $C_{26}H_{58}I_{12}N_2Pb_5$ requires C 10.6, H 2.0, N 1.0%). If the reaction is performed with 15 mg (0.10 mmol) NaI, $[Bu_3N(CH_2)_2NBu_3][PbI_4]$ is formed as intensely yellow crystals.

Crystal structure analyses of complexes 1–6

The data collections were performed on a STOE STADI IV four circle diffractometer (complex **1**) and on STOE IPDS imaging plate diffractometers (**2**–**6**) using Mo-Kα (**1**–**3**, **5**, **6**; $\lambda = 0.71073$ nm) or Ag-Kα radiation (**4**; $\lambda = 0.56087$ nm). All intensities were corrected for Lorentz and polarization effects. Empirical absorption correction was applied for **1**, numerical absorption corrections for **2**–**6**. The structures were solved by direct methods (SHELXS 97[24]) and refined by full-matrix least squares based on F^2 using all measured unique reflections (SHELXL 97[24]). Anisotropic displacement parameters were used for all non-hydrogen atoms in **1**–**3** and **6**, for Pb, I, Na and O atoms in **4** and only for Pb and I atoms in **5**. Hydrogen atoms were included in calculated positions. Other important crystallographic data are summarized in Table 1. Graphical presentations were drawn using DIAMOND 2.[25]

CCDC reference numbers 153703–153708.

See http://www.rsc.org/suppdata/dt/b0/b009488i/ for crystallographic data in CIF or other electronic format.

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