Lead-rich carboxylate-substituted titanium–lead oxo clusters

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Abstract The carboxylate-substituted mixed-metal oxo clusters Pb₆Ti₆O₉(acetate)(methacrylate)₁₇ and Pb₄Ti₈O₁₀(OPr)₁₈(acetate)₂ contain a higher number of lead atoms in the cluster core than previously reported compounds. The metal atoms in both clusters are arranged in three layers of different composition, which are connected through oxygen, propionate and/or carboxylate bridges.

Graphical abstract

Keywords Metal oxo clusters · Lead compounds · Titanium compounds

Introduction

Metal oxo clusters of the general composition M₄O₈(OH/OR)₃(OOCR')₄ are obtained when early transition metal alkoxides, M(OR)ₓ, are reacted with more than one molar equivalent of carboxylic acid [1]. The carboxylic acid not only provides carboxylate ligands but also the oxo groups through esterification with the alcohol eliminated during the substitution reaction. This protocol can be extended to mixed-metal oxo clusters by employing mixtures of metal alkoxides or, alternatively, a metal alkoxide and a metal salt.

A variety of titanium/metal oxo clusters has been obtained by this route. The structures of some of them are based on common structural motives, as has been discussed elsewhere in detail [2, 3]. Carboxylate-substituted Pb/Ti oxo clusters are in a sense unique as a variety of compounds with different Pb:Ti proportions are known. This allows gaining insight into how the structural features depend on the Ti/metal ratio. Carboxylate-substituted mixed-metal clusters generally have a richer structural chemistry than polynuclear compounds with a similar composition but without such ligands, because the bridging ligands provide more possibilities for connecting metals. Thus, contrary to the many examples of carboxylate-substituted Pb/Ti oxo clusters, only one unsubstituted cluster is known, viz. Pb₂Ti₂O(OPr)₁₀, the structure of which is based on a Pb₂Ti₂(μ₂-O) tetrahedron [4].

The (chain-like) structures of the carboxylate-substituted oxo clusters with a Pb:Ti ratio of 2:2–4, Pb₂Ti₁₈O(OPr)₈(OAc)₂ (Pb₂Ti₂) [5], Pb₂Ti₁₈O₂(OPr)₁₂ (OCCC₇H₁₅)₂ (Pb₂Ti₃) [6], and Pb₂Ti₄O₂(OEt)₁₄(OAc)₂ (Pb₂Ti₄) [7], are based on Ti₁(OR)ₓ(μ₄-OOCR')ₙ building blocks. The polynuclear compounds Pb₂Ti₄(OR)₁₆ (OOCR')₄ [6, 8] (without oxo groups, with different R and R') have similar structures to that of Pb₂Ti₄.

The structures of the clusters Pb₂Ti₁₈O₆(OBu)₆X₂ (OMc)₁₆(BuOH)₂ (Pb₂Ti₈, X = OAc or OMc (OMc = methacrylate)) and Pb₂Ti₁₈O₆(OPr)₆X(OMc)₁₄ (X = O or OMc) (Pb₂Ti₆) [9], with a higher Ti proportion, however, are derived from cyclic Ti₈O₈(OOCR)₁₆.
In the latter compound, each Ti atom is connected to both neighbouring Ti atoms through one \( \mu_2 \)-oxygen and two bridging OMe ligands each. The Ti\(_8\)O\(_8\) ring has crown ether-like properties. In Pb\(_2\)Ti\(_8\), two Pb(II) ions occupy the central cavity. Coordination of the oxygen atoms of the Ti\(_8\)O\(_8\) ring to Pb is supported by bridging carboxylate ligands. In Pb\(_2\)Ti\(_6\), the central Pb\(_2\) unit is coordinated by a semi-circular Ti\(_6\) fragment of the Ti\(_8\)O\(_8\)(OMe)\(_{16}\) metallacycle.

Common to the known carboxylate-substituted Pb/Ti oxo clusters is the metal ratio of Pb\(_2\)Ti\(_x\) (\( x = 2–4, 6, 8 \)), notwithstanding the different structures, the different metal:oxygen ratios and the different ligand shell composition. In this article we report two new Pb/Ti oxo clusters with a greater number of lead atoms, viz. Pb\(_6\)Ti\(_6\)O\(_9\)(OAc)(OMe)\(_{17}\) (Pb\(_6\)Ti\(_6\)) and Pb\(_4\)Ti\(_8\)O\(_{10}\)(OiPr)\(_{18}\)(OAc)\(_2\) (Pb\(_4\)Ti\(_8\)).

Results and discussion

Metal oxo clusters are very reproducibly obtained when all reaction parameters are meticulously kept, whereas seemingly minor variations may result in different clusters. For example, crystals of Pb\(_2\)Ti\(_8\) were formed within three weeks when Pb(OAc)\(_2\), Ti(Obu)\(_4\), and methacrylic acid were reacted in a 1:1:4 ratio at room temperature \[9\]. In contrast, colourless crystals of Pb\(_6\)Ti\(_6\) were obtained after four months when equimolar amounts of Pb(OAc)\(_2\) and Ti(OiPr)\(_4\) were first reacted at 70 °C in allylic alcohol, and two equivalents of methacrylic acid were added after cooling. The same reaction at room temperature resulted in the same cluster as Pb\(_2\)Ti\(_8\) with OAllyl instead of OBu ligands. Note that Pb\(_6\)Ti\(_6\) contains no residual OR ligands as in the other PbTi clusters.

The structure of Pb\(_6\)Ti\(_6\) (Fig. 1; Table 1) represents an interesting variation of the “Ti\(_8\)O\(_8\) ring” motif, as it is
based on a Ti₆O₆ ring as the central structural feature. While a great variety of Ti₆O₆(OOCR)₁₆ (= [TiO(OOCR)₂]₁₆) structures is known (with different carboxylate ligands), Ti₆O₆ rings are not known, although a [TiO(OOCR)₂]₆ ring system appears to be stereochemically possible. The central unit of Pb₆Ti₆ comes close to such a structure (Fig. 1, right). The six titanium atoms are alternatively bridged by one or two oxygen atoms (whereas there is only one bridging oxygen between neighbouring Ti atoms in Pb₂Ti₈). The μ₂-oxygen atoms O(7)–O(9) are located within the Ti₆ plane.

The six Pb atoms are arranged in two layers of three Pb atoms each above and below the Ti₆ plane (Fig. 1, right). The three metal planes are almost parallel to each other. Each Pb atom is coordinated to one oxygen atom of the Ti₂O₂ units. Hence, these oxygen [O(1)–O(6)] atoms are μ₃, connecting two Ti and one Pb atom. The Pb–O axes, however, have different orientations. While four [Pb(1), Pb(3), Pb(4) and Pb(6)] point away from the ring centre, the other two Pb atoms [Pb(2) and Pb(5)] are located above and below the centre of the Ti₆ ring. Pb(3), Pb(4), and Pb(6) show positional disorder, but this does not affect the ligands. While each Pb atom is connected to two Ti atoms through a μ₃-O, only the outer Pb atoms are additionally connected to the Ti layer by bridging ligands (see below). The Pb-μ₃-O bonds of the central lead atoms Pb(2) and Pb(5) are significantly longer [Pb(2)–O(2) 2.509(2) Å, Pb(5)–O(5) 2.519(2) Å] than that of the outer Pb atoms [2.244(3)–2.284(2) Å].

Pb²⁺ has a lone pair of electrons, which is often stereochemically active. This is indicated by truncated coordination polyhedra of the corresponding metals. In Pb₆Ti₆, the lone pairs of the outer Pb atoms [Pb(1), Pb(3), Pb(4), and Pb(6)] point away from the cluster centre. In contrast, the lone pairs of Pb(2) and Pb(5) point to the centre the Ti₆ ring and towards each other. The Pb(2)–Pb(5) distance of 4.5535(7) Å is relatively short for a Pb–Pb distance of non-bridged lead atoms. This placement of two lead atoms above and below the centre of the Ti₆ ring at a short distance is apparently very favourable. The sum of bond angles around the μ₃-oxygen atoms support this assumption: while O(2) and O(5) are clearly pyramidal [Σ M–O(2)–M 327.4(3)° and M–O(5)–M 330.6(3)°], indicating some pulling of the lead atoms towards the ring centre, the other μ₃-oxygen atoms are planar [350.6(4)–356.9(3)].

The positioning of Pb(2) and Pb(5) above and below the Ti₆ ring centre at a short Pb–Pb distance is probably the reason for the non-centrosymmetric positions of the other...
lead atoms and the ligand shell around the Ti$_6$ ring (Fig. 2). Only Ti(1) and Ti(4) have OMc bridges to both neighbouring Ti atoms, but there is no methacrylate bridge between Ti(2) and Ti(3), or Ti(5) and Ti(6). The central Ti$_6$ ring system and the attached Pb atoms are approximately C$_2$-symmetric, with the axis of rotation passing through O(3) and the centre of the Ti$_2$O$_2$ ring, formed by O(6), O(7), Ti(5), and Ti(6). The pairs of Ti atoms which are not connected by a OMc bridge have instead OMc bridges to the adjacent Pb layers. Ti(2) and Ti(3) are connected to one Pb$_3$ layer through a $\mu_3$-OMc ligand each and to the other by a $\mu_2$-OMc ligand. Thus, Ti(3) is connected to Pb(1) and Pb(2) of the top layer through a $\mu_3$-OMc ligand and to Pb(4) of the bottom layer through a $\mu_2$-OMc ligand. Conversely, Ti(2) is connected to Pb(4) and Pb(5) of the bottom layer and to Pb(1) of the top layer. On the other side of the Ti$_6$ ring, Ti(5) and Ti(6) are connected to one Pb atom of both adjacent Pb$_3$ layers (Pb(3) and Pb(6)) by two OMc bridges. The two Ti atoms with two OMc bridges to both neighbouring Ti atoms also connect to the Pb$_3$ layers by one OMc bridge each [Ti(1)/C1/C1 Pb(1) and Ti(4)/C1/C1 Pb(4)].

The remaining four carboxylate ligands connect the Pb atoms in the Pb$_3$ layers. One carboxylate group bridges all three Pb atoms. It is chelating the central Pb atom [Pb(2) or Pb(5)] and bridging to both other Pb atoms of the layer. In the top layer this carboxylate ligand is an acetate group, but a methacrylate ligand in the bottom layer. Each of the other two OMc ligands is again chelating the central Pb atom [Pb(2) or Pb(5)] and bridges only to one other Pb atom.

Pb$_6$Ti$_6$ co-crystallizes with an allylic alcohol molecule which weakly interacts with Pb(6), with a Pb–O distance of 3.12(2) Å.

In an (unsuccessful) attempt to synthesize Pb$_2$Ti$_2$ from Pb(OAc)$_2$ and Ti(OiPr)$_4$ according to the literature [5] colourless crystals of Pb$_4$Ti$_3$O$_{10}$(OiPr)$_{18}$(OAc)$_2$ (Pb$_4$Ti$_8$) (Fig. 3; Table 2) were obtained after one year. This is of course no viable synthesis method; the structure of Pb$_4$Ti$_8$ is nevertheless included in this paper to demonstrate the structural richness of Pb/Ti oxo clusters and to discuss some construction principles. Its cluster core can again formally be split in three layers of metals connected through oxygen atoms. The cluster core is approximately mirror-symmetric, with the mirror plane passing through Pb(1), Ti(3), Ti(6), and Pb(4) and perpendicular to the three metal layers. The overall symmetry of the cluster is lower than that of the cluster core due to the orientation of the peripheral isopropyl groups.

The bottom layer (Fig. 4) is formed by a Pb$_3$O$_3$ ring (Pb(1)–Pb(3) and O(1)–O(3)) which is capped by a rare $\mu_3$-O/Pb group (O(11)). The Pb$^{2+}$ lone pairs are trans to the O(11) and thus point away from the Pb$_3$O$_3$ ring centre. The bond distance of the $\mu_3$-O/Pb group to Pb(1) (the Pb atom on the imagined mirror plane) is much shorter than to Pb(2) and Pb(3) [Pb(1)–O(11) 2.295(4) Å, Pb(2)–O(11) 2.622(4) Å, Pb(3)–O(11) 2.620(4) Å]. The ring oxygen atoms O(1) and O(2) are also shifted towards Pb(1) [Pb(1)–O(1) 230.6(4)/Pb(2)–O(1) 239.8(4) Å and Pb(1)–O(2) 229.9(4)/Pb(3)–O(2) 239.6(4) Å]. The asymmetry of the Pb$_3$O$_3$(11) unit and the uneven distribution of the Pb–O bond lengths in the Pb$_3$O$_3$ ring is a consequence of the composition of the top layer, as will be discussed later. Three Ti atoms [Ti(1)–Ti(3)] are attached to the Pb$_3$O$_3$ ring through the ring oxygen atoms (Fig. 4). The Ti atoms are slightly above the plane of the Pb atoms, shifted towards the central layer. All Ti atoms of the bottom layer are additionally bonded to both neighbouring Pb atoms through $\mu_2$-O/Pb groups with relatively long Pb–O bond lengths [2.634(4)–2.870(4) Å]. Three terminal O/Pb groups (one on each Ti atom) complete the ligand sphere of Ti(1)–Ti(3).

The central layer (Fig. 4) consists of an open Ti$_3$O triangle [Ti(4)–Ti(6) and O(6)] which is connected to the bottom layer through the three oxygen atoms of the Pb$_3$O$_3$ unit. These oxygen [O(1)–O(3)] atoms are thus $\mu_4$, connecting two Ti and two Pb atoms. Ti(4)–O(1) and Ti(5)–O(2) are about 0.1 Å longer than Ti(6)–O(1) [Ti(4)–O(1)]
2.050(4) Å, Ti(5)–O(2) 2.053(4) Å, Ti(6)–O(3) 1.950(4) Å] thus compensating the shorter Pb(1)–O(1) and Pb(1)–O(2) bond distances in the bottom layer. The central oxygen atom O(6) of the Ti3O unit is nearly planar [sum of bond angles 356.5(5)], but its coordination is best described as T-shaped [Ti(4)–O(6)–Ti(5) 169.5(2), Ti(4)–O(6)–Ti(6) and Ti(5)–O(6)–Ti(6) 95.0(2)°]. Concomitantly, Ti(4)–O(6) and Ti(5)–O(6) are about 0.1 Å shorter than Ti(6)–O(6) [Ti(4)–O(6) 1.921(4) Å, Ti(5)–O(6) 1.917(4) Å, Ti(6)–O(6) 2.027(4) Å]. This is not only a consequence of the asymmetry of the bottom layer, but also of the unsymmetrical substitution of the Ti3O unit. A μ3-O connects Ti(4), Ti(6), and Pb(2), as well as Ti(5), Ti(6) and Pb(3) [O(4) and O(5), respectively]. There is no equivalent group connecting Ti(4) and Ti(5). Instead, Ti(4) and Ti(5) are bonded to the bottom layer [to Ti(1) and Ti(2)] through the two acetate bridges and two bridging OPr groups. Both have shorter Ti–O bond lengths to the Ti atoms of the central layer, Ti(4) and Ti(5). While Ti(4) and Ti(5) are octahedrally coordinated, Ti(3) has only a coordination number of 5 with a trigonal bipyramidal coordination geometry. This is quite unusual for Ti, as it prefers an octahedral coordination. The central Ti(6) of the Ti3O unit is coordinated to μ3-O atom which connects the central layer to Ti(3) of the bottom layer and Pb(4) of the top layer. There are no bridging OPr or carboxylate ligands within the central layer, and between the central and the top layer.

The top layer (Fig. 4) contains two Ti and one Pb atom, which are bridged by a μ3-OPr group [O(12)]. This OPr group is perpendicular to the Ti3Pb plane and mirrors the μ3-OPr group of the bottom layer. Pb(4), Ti(7), and Ti(8) are additionally connected through μ4-O(8), which also binds to Ti(6). The Ti–O bond lengths of Ti(7) and Ti(8) to O(8) are relatively long [Ti(7)–O(8) 2.118(4) Å, Ti(8)–O(8) 2.112(3) Å], whereas Ti(6)–O(8) is much shorter [1.955(4) Å]. In addition to O(7), which links all three metal atoms, there are μ2-oxygen atoms bridge Ti atoms of the top layer and the central layer [Ti(4)–O(9)–Ti(7) and Ti(5)–O(10)–Ti(8)]. Every metal of the top layer is connected to both neighbouring metals through a μ2-OPr group. The Ti–O bonds of Pb–Ti bridging alkoxo groups are about 0.1 Å shorter than those bridging Ti–Ti [Ti(7)–O(25) 1.946(4) Å, Ti(8)–O(26) 1.944(4) Å, Ti(7)–O(27) 2.045(4) Å, Ti(8)–O(27) 2.037(4) Å]. Two terminal OPr groups complete the octahedral coordination sphere of Ti(7) and Ti(8).

**Conclusions**

The structures of the previously reported Pb2Ti6 (x = 2, 4, 6, 8) oxo clusters are based on structural motifs typical of monometallic titanium oxo clusters (see “Introduction”). This is no longer the case when the number of Pb2+ ions is increased. The high tendency of the [TiO3] octahedra to connect with each other is also observed in Pb6Ti6 and Pb4Ti8. The same is true for the PbO polyhedra (with different coordination numbers), where the Pb2+ lone pair is stereochemically active. The preferred condensation of polyhedra of the same kind is probably due to the different ionic radii of Ti(IV) and Pb(II) and especially pronounced in Pb6Ti6. Six [TiO3] octahedra in Pb6Ti6 form a planar six-membered ring, which is capped by Pb3 units from above
and below. In Pb₄Ti₈, five [TiO₆] octahedra connect with each other in a three-dimensional arrangement (the center and top layer) to which one isolated Pb/O polyhedron is condensed. This PbTi₅ unit is attached to a Pb₂O₃ ring (the bottom layer), to which two isolated [TiO₆] octahedra and one [TiO₅] trigonal bipyramid [Ti(3)] are bonded.

**Experimental**

All experiments were carried out under Ar atmosphere using standard Schlenk techniques. Pb(OAc)₂·2H₂O was obtained from Merck and Ti(OiPr)₄ from ABCR. Water-free lead acetate was obtained by drying in vacuum at 130 °C over night. The drying process was monitored by IR spectroscopy.

**PbTi oxo clusters**

Pb₆Ti₆O₉(OAc)(OMc)₁₇ (Pb₆Ti₆)

Pb(OAc)₂ (651 mg, 2 mmol), 568 mg of Ti(OiPr)₄ (2 mmol), and 278 mg of dry allylic alcohol (4 mmol) were heated for 2 h at 70 °C. The clear solution was allowed to cool to room temperature and then 1.62 g of methacrylic acid (18.9 mmol) was added. A white precipitate was formed, which disappeared after 1 h. Colourless crystals of Pb₆Ti₆O₉(OAc)(OMc)₁₇ were obtained after four months. Yield: 39 mg (34% rel. Ti).

Pb₂Ti₁₀(OiPr)₁₈(OAc)₂ (Pb₄Ti₈)

It was attempted to synthesize Pb₂Ti₂O(OiPr)₈(OAc)₂ according to the literature [5]. Dry Pb(OAc)₂ (1.306 g, 4 mmol) and 3.41 g of Ti(OiPr)₄ (12 mmol) were stirred in 20 cm³ of dry n-hexane. After 3 days [because of the low solubility of Pb(OAc)₂] a clear solution was obtained. After two weeks the solution was concentrated to 15 cm³. Colourless crystals were obtained after 1 year, beside much white precipitate.

**X-ray crystallography**

Crystallographic data were collected on a Bruker AXS SMART APEX II four-circle diffractometer with 𝜅-geometry at 100 K using MoKα (𝜆 = 0.71073 Å) radiation. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was employed. The cell dimensions were refined with all unique reflections. SAINT PLUS software (Bruker Analytical X-ray Instruments, 2007) was used to integrate the frames. Symmetry was checked with the program PLATON.
The structures were solved by charge flipping (JANA2006). Refinement was performed by the full-matrix least-squares method based on \(F^2\) (SHELXL97 [10]) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Crystal data, data collection parameters and refinement details are listed in Table 3.

### Table 3 Crystal data, data collection parameters and refinement details

|                | Pb6Ti6          | Pb4Ti8          |
|----------------|-----------------|-----------------|
| Empirical formula | \(\text{C}_{73}\text{H}_{93}\text{O}_{46}\text{Pb}_6\text{Ti}_6\) | \(\text{C}_{58}\text{H}_{132}\text{O}_{32}\text{Pb}_4\text{Ti}_8\) |
| \(M_r\)        | 3237.0          | 2553.6          |
| Crystal system  | Monoclinic      | Monoclinic      |
| Space group     | \(P2_1/n\)      | \(P2_1/n\)      |
| \(a/\text{Å}\)  | 14.170(2)       | 14.459(1)       |
| \(b/\text{Å}\)  | 19.755(3)       | 26.347(2)       |
| \(c/\text{Å}\)  | 35.927(5)       | 23.735(2)       |
| \(\beta/\text{°}\)| 90.010(2)       | 90.086(4)       |
| \(V/\text{Å}^3\)| 10.057(2)       | 9042(1)         |
| \(Z\)           | 4               | 4               |
| \(D_1/\text{Mg m}^{-3}\)| 2.138           | 1.876           |
| Crystal size/mm | 0.32 × 0.24 × 0.12 | 0.41 × 0.32 × 0.28 |
| No. of ind., obs. refl. | 31,237, 31,237 | 24,486, 19,725 |
| Criterion for obs. refl. | \(I > 2\sigma(I)\) | \(I > 2\sigma(I)\) |
| \(\Theta_{\text{min}, \text{max}}/\text{°}\)| 1.86, 30.77 | 1.15, 29.28 |
| \(R[F^2 > 2\sigma(F)], R_w(F^2)\), \(S\)| 0.027, 0.033, 1.197 | 0.039, 0.060, 1.072 |
| Weighting scheme* | \(x = 0.0064, y = 37.333\) | \(x = 0, y = 113.913\) |
| \(\Delta \rho_{\text{max/e Å}^{-3}}\)| 1.51, −1.54 | 3.55, −2.29 |

* \(\omega = 1/\sigma^2(F_0^2) + (xP)^2 + yP)\), where \(P = (F_0^2 + 2 F_c^2)/3\)

The structures were solved by charge flipping (JANA2006). Refinement was performed by the full-matrix least-squares method based on \(F^2\) (SHELXL97 [10]) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Crystal data, data collection parameters and refinement details are listed in Table 3.

CCDC 1530015 (Pb6Ti6) and 1530016 (Pb4Ti8) contain supplementary crystallographic data. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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