Synthesis and Characterization of the Heterometallic Aggregate $Pb_2Al_5(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu\text{-}OiPr)_9(OiPr)_3(\mu\text{-}OAc)_3$

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A novel heterometallic aggregate $Pb_2Al_5(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu\text{-}OiPr)_9(OiPr)_3(\mu\text{-}OAc)_3$ obtained from the interaction of $Pb(OAc)_2$ and $Al(O\text{–}iPr)_3$ is the first structurally characterized example based on lead and aluminum. This compound has been isolated in high yield and examined by ^{1}H-, ^{13}C-, and ^{27}Al NMR, and in the solid state by X-ray crystallography.

Introduction

The use of heterometallic alkoxides[1−3] as precursors for mixed metal oxides has increased significantly in recent times, with efforts directed towards understanding the relationship, with regard to both structure and properties, between the precursor and the final material.[4] Structural data, even for heterobimetallic alkoxides,[1] is still scarce. Lead and aluminum are important components of many such materials.[5]

The difficulty in preparing lead(II) alkoxides[6] has been overcome by using commonly accessible salts such as nitrate,[7] acetate,[8] halides, hydroxides, or β-diketonates.[9][10] In general metal acetates are the most common precursors associated with metal alkoxides. Structural features of the products[11] obtained by treating metal acetates with metal alkoxides show that the acetate ligand is bridging, or bridge-chelating, indicating the role of the carboxylate group in maintaining the stoichiometry during the various stages of the transformation that leads to mixed metal oxides.

This work reports on the synthesis and characterization of a heterobimetallic aggregate, $Pb_2Al_5(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu\text{-}OiPr)_9(OiPr)_3(\mu\text{-}OAc)_3$, based on lead and aluminum. This compound represents a unique example in which aluminum is present in three different coordination environments. The pentacoordination around the lead center observed in this system is rare in molecular compounds, and has been reported to be found in high-T_c superconductors.[12]

Results and Discussion

Reactions between metal alkoxides and metal acetates have generally been reported to give oxo products by the elimination of an ester.[11] Simple addition products[8] have also been reported in room-temperature reactions. However, under refluxing conditions the formation of oxo species is spontaneous. The product $Pb_2Al_5(O)_2(OiPr)_{12}(OAc)_3$ was obtained in a high and reproducible yield, which excludes formation by accidental hydrolysis.

In the IR spectrum of the compound the difference of 150 cm^{-1} in the $\nu(CO_2)$ absorption frequency of the asymmetric (1610 cm^{-1}) and symmetric (1460 cm^{-1}) bands is indicative of the acetate group acting as bidentate ligand. The absorptions observed at 1090 cm^{-1} and 1020 cm^{-1} account for the presence of terminal and bridging isopropoxy groups, respectively.

At ambient temperature ^{1}H- and ^{13}C-NMR spectra of the compound are not structurally informative. However, the ^{27}Al-NMR spectrum shows a broad peak ($\delta = 32-58$) centered at $\delta = 42.24$, which is at a position characterisitic of both octahedral and tetrahedral symmetries around the aluminum centers.[13]

The X-ray crystallography and molecular structure of the compound is given in Figure 1 and the core is shown in Figure 2.

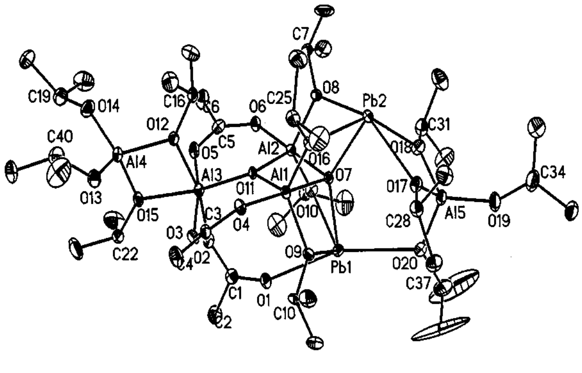

Figure 1. Molecular structure of $Pb_2Al_5(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu\text{-}OiPr)_9(OiPr)_3(\mu\text{-}OAc)_3$; thermal ellipsoids are represented with 25% probability; hydrogen atoms have been omitted for clarity

Selected bond dimensions are summarized in Table 1. The compound has a Pb_2Al_5 unit linked by acetato, isopropoxo, and oxo groups, making a complex and interesting structure. There are two tetrahedral aluminum atoms [Al(5), Al(4)] which differ environmentally, two trigonal bipyramidal aluminum centers [Al(2) and Al(1)], and one which is octrahedrally surrounded [Al(3)]. This constitutes the first example of a system containing the same metal atom in three different coordination environments. Both the lead atoms are pentacoordinate, having different geometries

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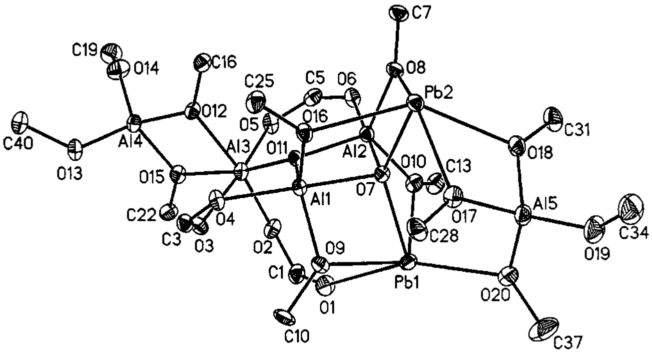

Figure 2. Plot of the core of $Pb_2Al_5(\mu_3\text{-}O)(\mu_4\text{-}O)(\mu\text{-}O\mathit{i}Pr)_9(O\mathit{i}Pr)_3(\mu\text{-}OAc)_3$

but each essentially that of a distorted teragonal pyramid with a lone pair.

Table 1. Selected bond dimensions for compound $Pb_2Al_5(O)_2(O\mathit{i}\text{-}Pr)_{12}(OAc)_3$

Bond lengths[Å]			
Pb(1)−O(7)	2.250(4)	Pb(1)−O(9)	2.440(4)
Pb(1)−O(10)	2.454(5)	Pb(1)−O(1)	2.535(5)
Pb(1)−O(20)	2.686(5)	Pb(2)−O(7)	2.234(4)
Pb(2)−O(17)	2.485(5)	Pb(2)−O(18)	2.476(5)
Pb(2)−O(8)	2.487(5)	Pb(2)−O(16)	2.491(4)
Al(1)−O(16)	1.790(5)	Al(1)−O(9)	1.808(5)
Al(1)−O(11)	1.822(5)	Al(1)−O(4)	1.878(5)
Al(1)−O(7)	1.920(5)	Al(2)−O(8)	1.788(5)
Al(2)−O(10)	1.797(5)	Al(2)−O(11)	1.806(4)
Al(2)−O(6)	1.869(5)	Al(2)−O(7)	1.909(5)
Al(3)−O(11)	1.825(5)	Al(3)−O(2)	1.857(5)
Al(3)−O(5)	1.920(5)	Al(3)−O(3)	1.926(5)
Al(3)−O(12)	1.942(5)	Al(3)−O(15)	1.960(5)
Al(4)−O(14)	1.694(6)	Al(4)−O(13)	1.717(5)
Al(4)−O(15)	1.784(5)	Al(4)−O(12)	1.787(5)
Al(5)−O(19)	1.694(6)	Al(5)−O(20)	1.747(6)
Al(5)−O(18)	1.757(5)	Al(5)−O(17)	1.763(5)
O(1)−C (1)	1.228(9)	O(2)−C(1)	1.295(9)

Bond angles [°]			
O(7)−Pb(1)−O(9)	65.1(2)	O(7)−Pb(1)−O(10)	65.2(2)
O(9)−Pb(1)−O(10)	116.5(2)	O(7)−Pb(1)−O(1)	102.6(2)
O(9)−Pb(1)−O(1)	73.2(2)	O(10)−Pb(1)−O(1)	81.7(2)
O(7)−Pb(1)−O(20)	95.3(2)	O(9)−Pb(1)−O(20)	108.0(2)
O(10)−Pb(1)−O(20)	113.5(2)	O(1)−Pb(1)−O(20)	160.4(2)
O(7)−Pb(2)−O(17)	82.75(2)	O(7)−Pb(2)−O(18)	83.4(2)
O(17)−Pb(2)−O(18)	61.9(15)	O(7)−Pb(2)−O(8)	64.82(2)
O(17)−Pb(2)−O(8)	142.2(2)	O(18)−Pb(2)−O(8)	94.2(2)
O(7)−Pb(2)−O(16)	65.73(2)	O(17)−Pb(2)−O(16)	92.12(2)
O(18)−Pb(2)−O(16)	142.4(2)	O(8)−Pb(2)−O(16)	91.6(2)
O(16)−Al(1)−O(4)	93.3(2)	O(9)−Al(1)−O(4)	95.1(2)
O(11)−Al(1)−O(4)	97.1(2)	O(16)−Al(1)−O(7)	87.8(2)
O(9)−Al(1)−O(7)	85.3(2)	O(11)−Al(1)−O(7)	81.44(2)
O(4)−Al(1)−O(7)	178.5(2)	O(8)−Al(2)−O(6)	92.6(2)
O(10)−Al(2)−O(6)	94.6(2)	O(11)−Al(2)−O(6)	97.5(2)
O(8)−Al(2)−O(7)	86.7(2)	O(10)−Al(2)−O(7)	86.5(2)
O(11)−Al(2)−O(7)	82.1(2)	O(6)−Al(2)−O(7)	178.9(2)
O(11)−Al(3)−O(2)	100.1(2)	O(11)−Al(3)−O(5)	96.0(2)
O(11)−Al(3)−O(3)	94.6(2)	O(5)−Al(3)−O(3)	169.3(2)
O(11)−Al(3)−O(15)	168.7(2)	O(5)−Al(3)−O(15)	85.7(2)
O(3)−Al(3)−O(15)	84.0(2)	O(12)−Al(3)−O(15)	74.9(2)
O((14)−Al(4)−O(15)	119.1(3)	O(14)−Al(4)−O(12)	112.9(3)
O(15)−Al(4)−O(12)	83.2(2)	O(19)−Al(5)−O(18)	118.1(3)
O(19)−Al(5)−O(17)	117.6(3)	O(18)−Al(5)−O(17)	92.1(2)

The coordination around Al(5) is completed by one terminal and three doubly bridging O*i*Pr groups. The angles subtended by O(20) are normal tetrahedral angles, while the acute angle [O(18)−Al(5)−O(17), 92.1°] due to the four-membered ring [−Pb(2)−O(17)−Al(5)−O(18)−] leads to a widening of the other two angles (average 117.8°). The second tetrahedral aluminum atom, Al(4), has two terminal and two μ-O*i*Pr groups. Four of the tetrahedral angles are almost normal. The larger deviations in case of the angles O(15)−Al(4)−O(12) [83.2(2)°] and O(14)−Al(4)−O(15) [119.1(3)°] are caused by two isopropoxy groups bridging to the octahedral Al(3). The former is quite comparable to the corresponding angle (83.1°) in $[Al(O\mathit{i}Pr)_3]_4$.[14]

Al(2) and Al(1) are pentacoordinate with similar environments. The coordination around Al(1) is completed by two μ-O*i*Pr groups bridging with Pb(1) and Pb(2), and two oxo groups μ_3-O(11) and μ_4-O(7) and one bidentate acetate group bridging to Al(3). Al(1) and Al(2) almost lie in the plane constituted by O(11), O(10), O(8) and O(9), O(11), O(16), respectively. Bond angles at the pentacoordinated Al atoms to the axial oxygen atoms are close to linear, e.g. O(6)−Al(2)−O(7) = 178.9°. Octahedral Al(3), along with the coordination by oxo functionality O(1), is linked by three bridging OAc groups, two aluminum atoms [Al(1) and Al(2)] and one lead atom [Pb(1)], and two μ-O*i*Pr groups with Al(4), allowing the metal center to reach its most common coordination number six. Due to the complexity of the structure the angles for the octahedron range from 74.9(2)−100.1(2)°.

Among the Al−O*i*Pr bond lengths the terminal Al−O distances (average 1.701 Å) of the tetrahedral Al(4) and Al(5) are the shortest. In the bridging distances the pattern is Al−O (tetrahedral) (average 1.767 Å) < Al−O (trigonal-bipyramidal (average 1.797 Å) < Al−O (octahedral) (average. 1.951 Å). These are well within the range already reported in the literature.[14−16] The aluminum−oxygen bond lengths due to the bridging acetate groups are almost equal, whereas that of the bridging Pb(1) is somewhat shorter (see Table 1) The coordination around Pb(1) is completed by three μ-O*i*Pr groups bridging Al(1), Al(2), and Al(5), and a bidentate acetate group bridging Al(3) and μ_4-O(7). Pb(2) is surrounded by four bridging oxygen atoms of isopropoxy groups, two with Al(5) and one each with Al(1) and Al(2) and μ_4-O(7). Thus Pb_2O_9 essentially constitutes a bitetragonal-pyramidal geometry. The tetragonal angles for Pb(1) range from 73.2(2)° [O(9)−Pb(1)−O(1)] to 113.5(2)° [O(10)−Pb(1)−O(20)], while for Pb(2) the range is 61.9(2)° [O(17)−Pb(2)−O(18)] to 94.2(2)° [O(18)−Pb(2)−O(8)]. This difference is obviously a consequence of the different degree of constraint imposed by the coordinating groups. For Pb(1) the lead−oxygen distances cover the unusually wide range from 2.250(4) to 2.686(5) Å. However, for Pb(2) the range [2.234(4)−2. 491(4) Å] is comparable to reported[8] values.

The coordination geometry of the μ_3-O(11) group is almost planar (Σangles = 357.6°) while that around μ_4-O(7) is distorted tetrahedrally with angles ranging from 94.0(2)−138.6(2)°. This distortion is not as severe as observed in the case of $Pb_2Ti_2(\mu_4\text{-}O)(\mu_3\text{-}O\mathit{i}Pr)_2(\mu\text{-}O\mathit{i}Pr)_4(O\text{-}\mathit{i}Pr)_4$[17] where the angles around μ_4-O range from 95.0(5) to 163.0(7)°.

For the two acetato moieties, bridging aluminum atoms, the C−O distances (average 1.259 Å) are almost similar. However, some asymmetry [C(1)−O(1) 1.228(9) Å, C(1)−O(2) 1.295(9) Å] is introduced for the third one attached to lead and aluminum atoms.

Conclusions

The first structurally characterized heterometallic aggregate based on lead and aluminum is found to have a high degree of asymmetry. It is the first reported occurence of the presence of the three identical metal centers (aluminum) in three different coordination environments. The asymmetry is also reflected by the fact that the pair of tetrahedral aluminum atoms and the tetragonal-pyramidal lead centers also differ in their coordinating groups.

Experimental Section

General: The reaction was performed under dry argon using standard Schlenck and glove-box techniques. Toluene and $CDCl_3$ were dried by standard procedures and stored over molecular sieves. Aluminum isopropoxide (Aldrich) was distilled prior to use. Anhydrous lead acetate was obtained by refluxing $Pb(OAc)_2 \bullet 3\ H_2O$ (BDH) with acetic anhydride (Qualigens). − IR: JASCO FT IR-5300; Nujol mulls between NaCl plates. − ^{1}H,^{13}C, and ^{27}Al NMR: JEOL-FX 90Q spectrometer ($CDCl_3$); $SiMe_4$ internal reference for ^{1}H- and ^{13}C-NMR spectra, $[Al(H_2O)_6]^{3+}$ external reference for ^{27}Al spectrum. Lead was estimated as lead chromate and aluminum as aluminum oxinate. O*i*Pr analysis was done by the method described by Bradley et al.[18]

Crystallography: The structure determination was performed by using a Siemens P4 diffractometer equipped with a CCD area detector and low-temperature device LTL. Mo-K_α radiation with λ = 0.71013 Å was used and the sample cooled to 193 K. Data reduction was performed with the program SAINT and absorption by SADABS. Computer calculations were carried out by using the SHELXS-97 (Sheldrick, **1990**) program package and the structure was solved by the heavy-atom method. The refinement was performed by SHELXL-97 (Sheldrick, **1997**) program with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined as a riding model. The carbon atoms of one isopropyl group shows large anisotropic motion.

Crystallographic Data: $C_{42}H_{92}Al_5O_{20}Pb_2$; molecular mass 1466.44; a = 13.1182(3), b = 23.6499(4), c = 20.l6104(3) Å; β = 96.885(1)°, V = 6348.1(2) Å^3, monoclinic system, space group $P2_1/n$, Z = 4, $d = 1.534\cdot10^{-9}$ g/cm^{-3}, μ = 5.427 mm^{-1}, 2θ = 2−49.42°, index range $-15 < h < 15$, $-22 < k < 27$, $-24 < l < 24$, max./min. transmission: 0.483/0.283, measured/unique/observed reflections: 29924/9671/7677 (R_{int} = 4.46%), no. of variables: 622, $R1$ = 0.0411, $wR2$ (all data) = 0.0970, weight (x/y) = 0.0442/12.2106, Goodness-of-fit = 1.090, $\Delta\rho$ = 1.411e/Å. The weighting scheme is $w^{-1} = \sigma^2 F_o^{\,2} + (xP)^2 + yP$ with $P = (F_o^{\,2} + 2\,F_o^{\,2})/3$. It should be noted that atoms C(38) and C(39) have large thermal parameters indicating rotational disorder. Calculations with split positions did not improve the result significantly. Additional data (except structure factor tables) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-104505. Copies may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@cam.ac.uk].

$Pb_2Al_5(O)_2(O\mathit{i}Pr)_{12}(OAc)_3$: A suspension of lead acetate (2.41 g, 7.41 mmol) in toluene (ca. 25 mL) was added dropwise to a solution of aluminum isopropoxide (3.02 g, 14.8 mmol) in toluene (ca. 30 mL) with stirring at room temp. (25°C). The reaction mixture was heated slowly by raising the bath temperature to 100°C. At this stage all the acetate had dissolved and the stirring was continued for 1 h while maintaining the bath temp. A very small quantity of solid suspension was filtered off and the solution concentrated to 20 mL and kept at −15°C to afford a white crystalline product (4.51 g, yield 83%). − $C_{42}H_{93}Al_5O_{20}Pb_2$ (1467.49): calcd. Pb 28.25, Al 9.19, O*i*Pr 48.29; found Pb 28.50, Al 8.91, O*i*Pr 48.19. − ^{1}H NMR (25°C): δ = 1.24, [d, CH_3 (O*i*Pr)], 4.42 (sept., CH), 2.00 [s, CH_3 (OAc)]. − ^{13}C NMR: δ = 174.72, 177.37, 179.50 [CO (OAc)], 64.11, 64.31 (CH), 27.31 and 27.69 [CH_3 (O*i*Pr and OAc)]. − Single crystals were grown from toluene at −15°C.

Acknowledgments

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