bond lengths in $(tmed)CuCo(CO)_4$ and $(bpy)CuCo(CO)_4$.

The longer Cu–Co bond length in the 2,2′-bipyridine derivative as compared to that in the tetramethylethylenediamine derivative is reflected in a longer, and presumably weaker, Cu-bridging CO bond in the former species. This observation is consistent with the lower $\nu(CO)$ vibration seen in the solid-state infrared spectrum for the semibridging CO ligand ($1820\ cm^{-1}$) in $(tmed)CuCo(CO)_4$ as compared to the analogous vibration in $(bpy)CuCo(CO)_4$ at $1850\ cm^{-1}$. It is most interesting however that while $(bpy)CuCo(CO)_4$ exhibits a low-frequency $\nu(CO)$ mode at $1850\ cm^{-1}$ in both the solid state and THF solution, the $(tmed)CuCo(CO)_4$ derivative's bridging $\nu(CO)$ vibration shifts from $1820\ cm^{-1}$ in the solid state to $1860\ cm^{-1}$ in CH_2Cl_2 solution.

On the basis of the shift of the bridging $\nu(CO)$ in $(tmed)CuCo(CO)_4$ from $1820\ cm^{-1}$ in the solid state to $1860\ cm^{-1}$ in solution, it has been suggested that there is disruption of the semibridging CO ligand in solution as a result of solvent coordination to the copper center.[2,3] However, the solution-phase $\nu(CO)$ frequency for this derivative at $1860\ cm^{-1}$ is quite similar to that observed herein for the analogous $(bpy)CuCo(CO)_4$ complex, where a semibridging CO moiety is clearly present. Hence, we conclude that the bridging CO ligand in $(tmed)CuCo(CO)_4$ is less associated with the copper center in solution than in the solid state. Nevertheless, it is still bridging the two metal centers asymmetrically. The solution structure may be the result of a 90° rotation about the Cu–Co bond, leading to a more normal Cu(I) tetrahedral arrangement of ligands.[13]

It is apparent from a comparison of the space-filling models of the $(bpy)CuCo(CO)_4$ and $(tmed)CuCo(CO)_4$ derivatives (Figures 2 and 3) that there is no hindrance to solvent coordination at the copper center of either derivative. Yet in the bpy complex no shift in the bridging $\nu(CO)$ vibration is noted in going from the solid state to the very polar THF solution. The reason for this difference in behavior of the two bimetallic derivatives is not clear. On the other hand, use of the highly coordinating dppe ligand rapidly cleaves the Cu–Co bond in both derivatives at −78 °C in THF with concomitant formation of $Co(CO)_4^-$. For example, the infrared spectrum in the $\nu(CO)$ region of $(bpy)CuCo(CO)_4$ in THF is characterized by four bands at 2024 (s), 1947 (s), 1932 (2, sh), and 1850 (m) cm^{-1}. The formation of the $Co(CO)_4^-$ anion was judged by the appearance of its diagnostic $\nu(CO)$ band at $1886\ cm^{-1}$. The infrared spectra for this process are depicted in Figure 4. On the other hand, the infrared spectrum of $(bpy)CuCo(CO)_4$ was not altered in refluxing THF over a 24-h period. Both $(bpy)CuCo(CO)_4$ and $(tmed)CuCo(CO)_4$ are insoluble in, and unreactive toward, deoxygenated water. This was demonstrated by the lack of detection of $Co(CO)_4^-$ in water by infrared spectroscopy, with the complexes being recovered unaltered.

Acknowledgment. The financial support of this research by the National Science Foundation (Grant CHE 88-17873) and the Robert A. Welch Foundation is greatly appreciated.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, and crystal data and data collection parameters for $(bpy)CuCo(CO)_4$ (4 pages); a table of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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(13) This was suggested by an anonymous reviewer of this paper.

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Preparation of Six Lead(II) Dialkoxides, X-ray Crystal Structures of $[Pb(\mu,\eta^1\text{-}OCH_2CH_2OMe)_2]_\infty$ and $[Pb_3(\mu\text{-}O\text{-}t\text{-}Bu)_6]$, and Hydrolysis Studies

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Six lead(II) dialkoxides prepared by alcoholyses of $Pb[N(SiMe_3)_2]_2$ are described: $Pb(O\text{-}i\text{-}Pr)_2$ (**1**), $Pb(O\text{-}t\text{-}Bu)_2$ (**2**), $Pb(OCMe_2Et)_2$ (**3**), $Pb(OCEt_3)_2$ (**4**), $Pb(OCH_2CH_2OMe)_2$ (**5**), and $Pb(OCHMeCH_2NMe_2)_2$ (**6**). All except **1** and **5** have good solubility in organic solvents. The compounds sublime or distill in the range 95–170 °C at 10^{-4} Torr; only **5** decomposes during sublimation. Hydrolysis of **3** or **6** in THF gives $3PbO\cdot H_2O$, which is not converted to massicot or litharge (polymorphs of PbO) by refluxing the reaction slurry. However, the first-formed $3PbO\cdot H_2O$ is converted to litharge when **3** is hydrolyzed in the presence of 10 mol % of $LiOCMe_2Et$ and the resulting slurry is refluxed. Two compounds are completely structurally characterized: $[Pb(\mu,\eta^1\text{-}OCH_2CH_2OMe)_2]_\infty$ (**5**) and $[Pb_3(\mu\text{-}O\text{-}t\text{-}Bu)_6]$ (**2**). Compounds **5** and **1** are isostructural in the solid state. Crystal data for **5**: monoclinic, $C2/c$, $a = 11.411\ (8)$ Å, $b = 14.641\ (6)$ Å, $c = 6.278\ (3)$ Å, $\beta = 108.34\ (5)°$, $V = 995.6\ (9)$ Å^3, $T = 22$ °C, $Z = 4$, and $D_c = 2.384\ g\ cm^{-3}$. Of the 3794 intensities measured, 1026 unique reflections with $I > 3\sigma(I)$ yielded $R(F_o) = 0.0258$ and $R_w(F_o) = 0.0320$. Crystal data for **2**: trigonal (hexagonal axes), $R\bar{3}$, $a = b = 10.174\ (2)$ Å, $c = 29.491\ (9)$ Å, $V = 2643.6\ (11)$ Å^3, $T = 22$ °C, $Z = 3$, and $D_c = 1.998\ g\ cm^{-3}$. Of the 1566 intensities measured, 517 unique reflections with $I > 3\sigma(I)$ yielded $R(F_o) = 0.0504$ and $R_w(F_o) = 0.0592$.

Introduction

We are interested in lead(II) dialkoxides as potential precursors[1] for vapor- and solution-phase syntheses of lead-substituted oxide superconductors[2] and lead-containing oxide ceramics in general.[3] There are a few reports of the in situ generation of lead(II) alkoxides in preparations of oxide ceramics,[4–7] but in none of these

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Table I. Spectroscopic and Physical Data

compd	IR (KBr): ν, cm^{-1}	^{1}H NMR (C_6D_6): δ, ppm	$^{13}C\{^1H\}$ NMR (C_6D_6): δ, ppm	subl pt [bp], °C (yield, %)[a]	molecularity, n[b]
$Pb(O\text{-}i\text{-}Pr)_2$ (**1**)	2950 m, 2917 w, 2854 w, 2816 w, 1455 w, 1370 m, 1356 m, 1333 m, 1152 m, 1123 vs, 958 vs, 819 m, 527 vs, 508 s, 494 s	*c*	*c*	130 (66)	*c*
$Pb(O\text{-}t\text{-}Bu)_2$ (**2**)	2958 s, 2918 m, 2889 w, 2856 w, 1454 m, 1378 m, 1354 vs, 1225 m, 1182 vs, 829 vs, 753 m, 540 m, 448 w	1.43 (s, 18 H)	71.19 (*C*Me$_3$), 35.72 (Me)	95 (89)	2.6 (1)
$Pb(OCMe_2Et)_2$ (**3**)	2960 s, 2916 m, 1461 w, 1370 w, 1355 m, 1285 w, 1216 w, 1168 s, 1149 s, 1057 w, 940 vs, 880 s, 532 s, 503 m, 420 w	1.67 (q, ^3J = 7.5 Hz, 4 H), 1.36 (br s, 12 H), 1.06 (t, ^3J = 7.5 Hz, 6 H)	73.48 (*C*Me$_2$Et), 40.92 (*C*H$_2$), 32.72 (C*Me*$_2$Et), 9.46 (CH$_2$*C*H$_3$)	105 (88)	2.8 (2)
$[Pb(OCEt_3)_2]_4\cdot Et_3COH$ (**4**)	2963 vs, 2934 vs, 2874 s, 2847 m, 1461 m, 1322 w, 1146 vs, 1036 w, 965 s, 944 vs, 919 s, 567 w, 529 s, 511 m, 498 m	1.59 (q, ^3J = 7.4 Hz, 12 H), 1.01 (t, ^3J = 7.4 Hz, 18 H)	78.54 (*C*Et$_3$), 33.81 (*C*H$_2$), 8.38 (*C*H$_3$)	[165–170] (72)	2.3 (2)
$Pb(OCH_2CH_2OMe)_2$ (**5**)	2910 w, 2868 m, 2835 w, 2814 m, 2806 m, 2690 w, 1451 w, 1378 w, 1351 w, 1197 w, 1121 vs, 1094 m, 1073 vs, 1023 m, 898 m, 840 m, 557 w, 509 w	4.27 (t, ^3J = 4.3 Hz, 4 H), 3.36 (t, ^3J = 4.5 Hz, 4 H), 3.15 (s, 6 H)	*c*	*d*	*c*
$Pb[OCHMeCH_2NMe_2]_2$ (**6**)	2946 m, 2912 m, 2884 m, 2876 m, 2846 m, 2817 s, 2776 s, 2722 w, 1456 m, 1358 w, 1332 m, 1265 w, 1131 vs, 1097 m, 1074 s, 1038 m, 940 vs, 858 w, 833 s, 500 vs	4.68–4.56 (m, 2 H), 2.57 (pseudo-t, $^{2,3}J$ = 10.9 Hz, 2 H), 2.23 (dd, ^3J = 11.3 Hz, ^2J = 2.5 Hz, 2 H), 2.16 (s, 12 H), 1.41 (d, ^3J = 6.0 H, 6 H)	71.53 (*C*H$_2$), 67.14 (*C*H), 44.63 (N*Me*$_2$), 26.08 (CH*C*H$_3$)	[106] (80)	1.3 (1)

[a] Sublimations and distillations were performed at 10^{-4} Torr. Percent recoveries are given in parentheses. [b] Where n is set by $[Pb(OR)_2]_n$; molecular weights were determined cryoscopically in benzene; see Experimental Section for details. Errors in the last digit are given in parentheses. [c] Insufficient solubility. [d] Decomposed.

have the alkoxide intermediates been isolated or identified conclusively. Many solution-phase ceramic syntheses use lead(II) carboxylates, instead of alkoxides, as the organolead precursors.[3,7]

Lead(II) alkoxides are not a well-established family of compounds. Several years ago, Lappert and co-workers prepared the red, monomeric, *aryl*oxide complex $(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O)_2Pb$.[8] Other studies suggested that simple lead(II) dialkoxides are insoluble and/or unstable with respect to oxo-containing complexes.[9,10] Two reports on lead(II) alkoxides appeared while our work was in progress. A communication by Hubert-Pfalzgraf and co-workers described the synthesis and thermal decomposition of $Pb(O\text{-}t\text{-}Bu)_2$.[10] In a recent review, Veith discussed the trimeric structure of $Pb(O\text{-}t\text{-}Bu)_2$ but provided no crystallographic data.[11]

The preparation of soluble and volatile lead(II) alkoxides was the goal of the present study. We now report the synthesis and complete characterization of six such examples, including $Pb(O\text{-}t\text{-}Bu)_2$.[10] Most are quite stable, and their solubilities and/or volatilities can be attributed to the bulky or chelating nature of the ligands chosen. Full structural characterization is given for two of the compounds, $[Pb(\mu,\eta^1\text{-}OCH_2CH_2OMe)_2]_\infty$ and $[Pb_3(\mu\text{-}O\text{-}t\text{-}Bu)_6]$. To our knowledge, these are the first published crystallographic data on lead(II) dialkoxides, although Veith and co-workers solved the crystal structure of $[Pb_3(\mu\text{-}O\text{-}t\text{-}Bu)_6]$ before we did.[11] We have also studied the hydrolysis of representative examples and have obtained results that differ from previous studies employing in situ generated lead(II) alkoxides.

Results

Synthesis and Properties. The alkoxides were prepared according to eq 1, which was the method used by Lappert and co-workers for the synthesis of $(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2O)_2Pb$.[8]

$$Pb[N(SiMe_3)_2]_2 + 2ROH \longrightarrow \underset{\mathbf{1-6}}{1/n[Pb(OR)_2]_n} + 2HN(SiMe_3)_2 \quad (1)$$

$$\begin{array}{llll} R = & i\text{-}Pr & n = \infty & \mathbf{1},\ 53\% \\ & t\text{-}Bu & 2.6 \text{ or } 3 & \mathbf{2},\ 86\% \\ & CMe_2Et & 2.8 \text{ or } 3 & \mathbf{3},\ 65\% \\ & CEt_3 & 2.3 & \mathbf{4},\ 72\% \\ & CH_2CH_2OMe & \infty & \mathbf{5},\ 91\% \\ & CHMeCH_2NMe_2 & 1.3 & \mathbf{6},\ 80\% \end{array}$$

Purification was routinely completed either by crystallization (**1–3**, **5**) or vacuum distillation (**4**, **6**). All of **1–6** were characterized by elemental analyses (C, H, N, Pb), and IR, ^{1}H NMR, and ^{13}C NMR spectroscopy (see Table I). The molecularities, n, given in eq 1 were determined in solution, in the solid state, or both as described in more detail below. In contrast to Lappert's red monomer, all of the compounds are colorless solids.

The lead(II) dialkoxides were found to be reasonably volatile compounds (see Table I) that sublimed or distilled in the range 95–170 °C at 10^{-4} Torr (66–89% recoveries). Only the least volatile eq 1 product, the methoxyethoxide **5**, decomposed extensively during sublimation. The integrity of the sublimed or distilled compounds was at least established by ^{1}H NMR spectroscopy and lead analysis for each case (see Experimental Section). Under the sublimation conditions used in this study, the most volatile compound, the *tert*-butoxide **2**, *did not* decompose to $Pb_4(\mu_4\text{-}O)(\mu\text{-}O\text{-}t\text{-}Bu)_6$, as was earlier found.[10] We *did* observe that sublimation of *crude* **1** and **3** gave lead-rich materials, presumably containing $Pb_x(O)_y(OR)_z$ species. However, *pure* **1** and

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Table II. Crystallographic Data for $[Pb_3(\mu\text{-O-}t\text{-Bu})_6]$ (**2**) and $[Pb(\mu,\eta^1\text{-OCH}_2CH_2OMe)_2]_\infty$ (**5**)

	2	**5**
chem formula	$C_{24}H_{54}O_6Pb_3$	$C_6H_{14}O_4Pb$
a, Å	10.174 (2)	11.411 (8)
b, Å	10.174 (2)	14.641 (6)
c, Å	29.491 (9)	6.278 (3)
α, deg	90	90
β, deg	90	108.34 (5)
γ, deg	120	90
V, Å^3	2643.6 (11)	995.6 (9)
Z	3	4
fw	1060.2	357.4
space group	$R\bar{3}$ (No. 148)	$C2/c$ (No. 15)
T, °C	22	22
λ, Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.998	2.384
μ, cm^{-1}	144.30	170.45
transm coeff	0.2788–1.0000	0.221–1.00
$R(F_o)^a$	0.0504	0.0258
$R_w(F_o)^b$	0.0592^c	0.0320^d

$^a R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w(F_o) = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$; $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$. $^c g = 0.0012$. $^d g = 0.0010$.

Table III. Atomic Positional Parameters and U(eq) for $[Pb(\mu,\eta^1\text{-OCH}_2CH_2OMe)_2]_\infty$ (**5**)

	x	y	z	U(eq), Å^2
Pb	0	746 (1)	2500	32 (1)
O(1)	1063 (4)	−338 (3)	4816 (7)	43 (1)
O(2)	2653 (4)	−1540 (4)	7964 (9)	61 (2)
C(1)	1767 (8)	−1003 (6)	4204 (12)	56 (3)
C(2)	2933 (7)	−1181 (6)	6084 (15)	68 (3)
C(3)	3653 (7)	−1683 (7)	9824 (15)	85 (4)

3 obtained by crystallization were sublimed without decomposition.

Although **2**–**4**, and **6** were very soluble in common organic solvents, **1** and **5** were not. The isopropoxide **1** was soluble in hot 2-propanol, and the methoxyethoxide **5** was sparingly soluble in benzene and THF. The low solubilities of **1** and **5** can be attributed to polymeric solid-state structures (see below). The molecularities of the more soluble compounds were determined cryoscopically in benzene (see Table I and the Experimental Section). In cold benzene the molecularity of the *tert*-butoxide **2** was 2.6, the molecularity of the *tert*-pentoxide **3** was 2.8, the molecularity of the *tert*-heptoxide **4** was 2.3, and the molecularity of the (dimethylamino)isopropoxide **6** was 1.3. Hubert-Pfalzgraf and co-workers determined a dimeric complexity for **2** in benzene by the Signer method,[10] which compares well with our measurements obtained with colder solutions. For comparison, **2** and **3** adopt trimeric structures in the solid state (see below).

The NMR data for **2**–**6** were found to be quite simple and, in most cases, deceptively so (see Table I). Only a single set of ligand resonances was observed in the ^{13}C and ^1H NMR spectra for each compound. For the *tert*-butoxide **2**, the data were consistent with the solid-state structure (see below) and indicated that the dimer–trimer equilibrium that probably exists in solution is rapid. The ^1H NMR resonances for **3** and **4** were gradually broadened upon cooling the corresponding samples to −80 °C in toluene-d_8, but decoalescence was not observed. Thus, for **3**, **4**, and the sparingly soluble methoxyethoxide **5**, symmetrical or rapidly fluxional oligomeric solution-phase structures were inferred. For the (dimethylamino)isopropoxide **6**, which is primarily a solution-phase monomer (see above), a single set of ligand resonances was expected. If **6** is involved in a monomer–dimer (or other) equilibrium, the data require it to be rapid.

Solid-State Structures. Needle-shaped crystals of the methoxyethoxide **5** suitable for X-ray crystallography were grown from methoxyethanol solution, and the structure was determined as described in Table II and the Experimental Section. Atomic positional parameters are given in Table III, and a listing of bond distances and angles in Table IV. Views of the one-dimensional chain structure of **5**, $[Pb(\mu,\eta^1\text{-OCH}_2CH_2OMe)_2]_\infty$, are shown in Figures 1 and 2.

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[Pb(\mu,\eta^1\text{-OCH}_2CH_2OMe)_2]_\infty$ (**5**)

Pb–O(1)	2.234 (4)	O(2)–C(2)	1.42 (1)
Pb–O(1A)	2.440 (5)	O(2)–C(3)	1.37 (1)
Pb–O(1B)	2.440 (5)	C(1)–C(2)	1.50 (1)
Pb–O(1C)	2.234 (4)	Pb–PbA	3.824 (1)
O(1)–C(1)	1.39 (1)		
O(1)–Pb–O(1A)	70.3 (2)	Pb–O(1)–PbA	109.7 (2)
O(1)–Pb–O(1B)	89.4 (1)	C(1)–O(1)–PbA	118.4 (4)
O(1A)–Pb–O(1B)	151.7 (2)	C(2)–O(2)–C(3)	114.9 (6)
O(1)–Pb–O(1C)	89.5 (2)	O(1)–C(1)–C(2)	110.5 (6)
Pb–O(1)–C(1)	120.4 (4)	O(2)–C(2)–C(1)	110.1 (7)

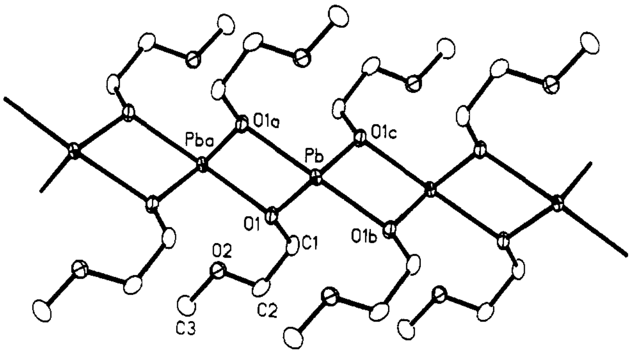

Figure 1. View of a segment from the chain structure of $[Pb(\mu,\eta^1\text{-OCH}_2CH_2OMe)_2]_\infty$ (**5**), providing the atom-numbering scheme.

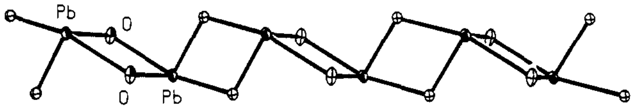

Figure 2. View of the $[Pb(\mu\text{-O})_2]_\infty$ central skeleton from the structure of $[Pb(\mu,\eta^1\text{-OCH}_2CH_2OMe)_2]_\infty$ (**5**).

All alkoxide ligands in the chains are crystallographically equivalent and bridge two, 4-coordinate lead atoms. No terminal ligands are present. Crystallographic 2-fold axes pass through the lead atoms, and crystallographic inversion centers lie in the middle of the $Pb\text{–}(\mu\text{-O})_2\text{–}Pb$ planes. The potentially bidentate alkoxide ligands do not chelate through ether oxygens; instead they adopt dangling conformations.

The sawhorse configuration about lead, which is visible in Figure 2, conforms to a trigonal bipyramid having a stereochemically active lone pair in an equatorial position. The trigonal bipyramid is significantly distorted. Both the $O_{ap}\text{–}Pb\text{–}O_{ap}$ and the $O_{eq}\text{–}Pb\text{–}O_{eq}$ angles (151.7 (2) and 89.5 (2)°, respectively) are compressed below ideal values, confirming the equatorial lone pair.

The apical Pb–O distance (2.44 (1) Å) is longer than the equatorial Pb–O distance (2.23 (1) Å). Because each alkoxide participates in one apical and one equatorial bond, the resulting bridges are asymmetric. The apical and equatorial bonds may be classified as dative and covalent bonds, respectively, according to the distinction recently proposed by Haaland.[12] The dative bonds are weaker (longer) than the covalent bonds and having a lesser spatial requirement are found to occupy apical rather than equatorial positions. We may also observe that the dative bonds do not disrupt the coordination geometry that would obtain were the dative bonds completely absent: disregarding the apical ligands, the central $O_{eq}\text{–}Pb\text{–}O_{eq}$ unit possesses the C_{2v} configuration expected for a diamagnetic $Pb(OR)_2$ monomer such as Lappert's $(2,6\text{-}t\text{-Bu}_2\text{-4-MeC}_6H_2O)_2Pb$.[8]

The coordination geometries about the lead atoms in **5** and in orthorhombic lead monoxide (massicot)[13] are strikingly similar. As in **5**, the oxide environment about the lead atoms in massicot approximates a trigonal bipyramid, with a lone pair in an equatorial position. As in **5**, the $Pb\text{–}O_{ap}$ distances are long, 2.49 (1)

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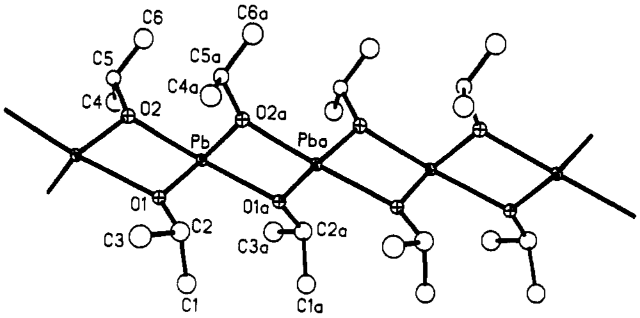


Figure 3. View of a segment from the chain structure of $[Pb(\mu\text{-O-}i\text{-Pr})_2]_\infty$ (**1**).

Table V. Atomic Positional Parameters and U(eq) for $[Pb_3(\mu\text{-O-}t\text{-Bu})_6]$ (**2**)

	x	y	z	U(eq), Å^2
Pb(1)	0	0	0	52 (1)
Pb(2)	0	0	1160 (1)	66 (1)
O(1)	1539 (19)	1632 (18)	668 (4)	90 (9)
C(1)	2777 (39)	3023 (35)	761 (9)	104 (18)
C(2)	2487 (46)	3859 (46)	1077 (12)	206 (34)
C(3)	3315 (50)	3983 (46)	340 (10)	240 (34)
C(4)	4044 (39)	2873 (59)	888 (15)	260 (42)

Å, and the Pb–O$_{eq}$ distances are short, 2.21 (2) and 2.22 (2) Å. The O$_{ap}$–Pb–O$_{ap}$ (147.5°) and the O$_{eq}$–Pb–O$_{eq}$ (90.4°) angles are similar to the corresponding angles in **5**. The structure of massicot also contains lead–oxygen chains, although the constitution of the chains is not the same as those in **5**. Structural analogies between oxides and alkoxides of the same element are often apparent.[14]

Apart from the examples described in the present study, to our knowledge only two other alkoxides (siloxides) of lead(II) have been structurally characterized: $Pb_4(\mu_4\text{-O})(\mu\text{-OSiPh}_3)_6$[15] and $Pb_6(\mu_3\text{-O})_4(\mu_3\text{-O-}i\text{-Pr})_4$.[9] In the former, the Pb–O distances involving the siloxide ligands range from 2.28 (1) to 2.49 (1) Å.[15] In the latter, the Pb–O distances involving the isopropoxide ligands range from 2.46 (4) to 2.56 (4) Å.[9]

We also succeeded in solving the structure of the isopropoxide **1**, as described in the Experimental Section, and **1** is isostructural to **5** (see Figure 3). However, the crystallographic determination was blemished by several strong residual electron density peaks (>4.35 e Å^{-3}) in the vicinity of the lead atom. Consequently, we are not able to report accurate atomic coordinates, bond distances, or bond angles for **1**, and we offer no further discussion of the structure.

As mentioned above, a recent review indicated that the solid-state structure of the *tert*-butoxide **2**, $[Pb_3(\mu\text{-O-}t\text{-Bu})_6]$, was previously solved by Veith's group.[11] We were unaware of Veith's results before our determination was completed.[15] Because Veith's determination has not been published, we include our data here.

Crystalline **2** was obtained from hexane solution as hexagonal plates. The structure was determined as described in Table II and the Experimental Section. Atomic positional parameters are given in Table V, and a listing of bond distances and angles in Table VI. The trimeric structure of **2** is shown in Figure 4.

The trimer is constructed of two 3-coordinate terminal lead atoms, a central 6-coordinate lead atom, and six bridging alkoxide ligands. The precise symmetry of the trimer is S_6, but the absence of dihedral symmetry planes is due to a small torsion angle about the O(1)–C(1) bond. If the methyl groups are disregarded, the remaining core is D_{3d}.

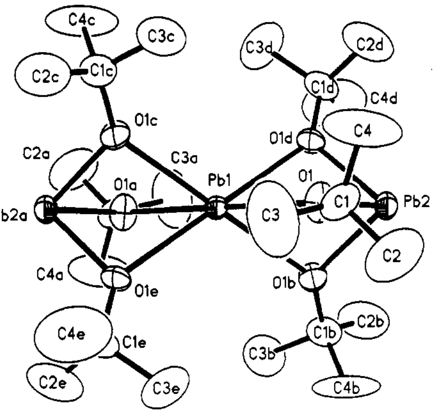
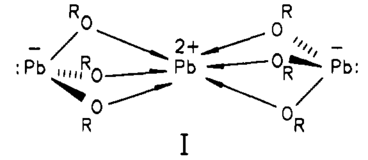


Figure 4. View of the trimeric unit from the crystal structure of $[Pb_3(\mu\text{-O-}t\text{-Bu})_6]$ (**2**), providing the atom-numbering scheme.

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for $[Pb_3(\mu\text{-O-}t\text{-Bu})_6]$ (**2**)

Pb(1)–Pb(2)	3.420 (2)	C(1)–C(2)	1.39 (6)
Pb(1)–O(1)	2.55 (1)	C(1)–C(3)	1.51 (4)
Pb(2)–O(1)	2.17 (1)	C(1)–C(4)	1.42 (7)
O(1)–C(1)	1.37 (3)		
O(1)–Pb(1)–O(1B)	66.6 (4)	Pb(1)–O(1)–C(1)	141 (1)
O(1)–Pb(2)–O(1B)	80.3 (4)	Pb(2)–O(1)–C(1)	126 (1)
Pb(1)–O(1)–Pb(2)	92.6 (5)		

As in **5**, the alkoxide ligand bridges asymmetrically; the Pb–O separation involving the central lead atom is 2.55 (1) Å, and the Pb–O separation involving the terminal lead atom is 2.17 (1) Å. These Pb–O distances are very similar to those in **5** (see above, and consequently the Pb–O bonds involving the central lead atom may be classified as dative bonds, and the Pb–O bonds involving the terminal lead atom may be classified as covalent bonds.[12] Such a description requires a formal uninegative charge on each terminal lead atom and a formal dipositive charge on the central lead atom, as depicted in I. The terminal lead atom has a trigonal-pyramidal configuration and an axial lone pair. The central lead atom has a trigonally distorted octahedral geometry; a *stereochemically active* lone pair is *not* apparent.



I

We also attempted to solve the structure of the *tert*-pentoxide **3**, as described in the Experimental Section. The similarity between the unit cell parameters of **2** (see Table II) and **3** (see the Experimental Section) suggested that **2** and **3** are isomorphous in the solid state. However, we were unable to find a satisfactory solution, presumably because of poor crystal quality or severe disorder relating to various conformations about the O–C bonds. We *were* able to locate the lead atoms in difference maps; their positions correspond to a linear, trimeric arrangement as in **2**. Attempts to obtain better quality crystals were not successful.

Hydrolysis Studies. The soluble lead(II) dialkoxides described herein should prove useful for sol–gel-processing applications. Consequently, a preliminary characterization of their hydrolytic behavior was desired. We carried out a series of simple hydrolysis experiments with **3** and **6**, which were chosen because of their high solubilities and ease of preparation and manipulation. Compound **2** could have been chosen by the same criteria.

THF solutions of **3** and **6** were hydrolyzed according to the conditions in Table VII, which resulted in immediate precipitation in all cases. The precipitates were characterized by X-ray powder diffraction (XRD) and elemental analyses (C, H, N, Pb). Three lead oxide phases were observed to form, the hydrate $3PbO{\cdot}H_2O$, orthorhombic PbO (massicot), and tetragonal PbO (litharge), either individually or as binary mixtures of massicot and litharge. The light, powdery products were difficult to collect quantitatively; thus, the yields reported in Table VII should be considered imprecise lower limits. Except for run 5, the hydrolyses likely resulted in complete precipitation of lead from solution.

The lead analyses on the dried powders in Table VII were lower than theory by 0.5–2.4%. On an absolute basis these values are

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(14) Chisholm, M. H. *J. Solid State Chem.* **1985**, *57*, 120.

(15) We were first informed of Veith's result by a reviewer, whom we thank.

Table VII. Hydrolysis of Lead(II) Dialkoxides (0.1 M in THF)

run	compd (g, mmol)	*T*, °C	time, h	product (g, mmol, % yield)[a]	anal. (C, H, N, Pb): % found (% calcd)
1[b]	**3** (0.40, 1.05)	66	3	$3PbO{\cdot}H_2O$[c] (0.21, 0.30, 86)	1.14, 0.35, 0.00, 88.3 (0, 0.29, 0, 90.4)
2[d]	**3** (0.40, 1.05)	66	14	$3PbO{\cdot}H_2O$ (0.20, 0.29, 83)	1.05, 0.35, 0.00, 88.6 (0, 0.29, 0, 90.4)
3[b,e]	**3** (0.40, 1.05)	66	2.5	mixture of 36% $3PbO{\cdot}H_2O$ and 64% litharge[f] (0.18, 0.80, 76)[g]	0.76, 0.25, 0.00, 89.2 (0, 0.19, 0, 91.3)
4[b,e]	**3** (0.40, 1.05)	66	18	PbO, litharge (0.20, 0.90, 85)	0.29, 0.00, 0.00, 91.2 (0, 0, 0, 92.8)
5	**6** (0.28, 0.68)	25	0.5	$3PbO{\cdot}H_2O$ (0.08, 0.12, 51)	1.17, 0.28, 0.03, 88.0 (0, 0.29, 0, 90.4)
6[b]	**6** (0.27, 0.66)	66	15	$3PbO{\cdot}H_2O$ (0.11, 0.16, 73)	1.71, 0.37, 0.00, 88.7 (0, 0.29, 0, 90.4)
7[h]	**6** (0.65, 1.58)	80	0.5	$3PbO{\cdot}H_2O$ (0.27, 0.39, 75)	0.47, 0.17, 0.00, 89.9 (0, 0.29, 0, 90.4)

[a] Yields given are lower than actual yields because of difficulties in collecting small quantities of the light powders. [b] Water was added at 25 °C. [c] $3PbO{\cdot}H_2O$; JCPDS file 22-1134. [d] Water was added to refluxing solution. [e] Conducted in the presence of 10 mol % $LiOCMe_2Et$. [f] PbO, litharge; JCPDS file 5-0561. [g] Relative amounts were established by comparison to an XRD calibration curve. [h] The alkoxide solution (15 mL) was added *to* water (15 mL) at 80 °C.

outside the normally acceptable range, but lead comprises a very large weight percent of the samples and such *relative* errors are fairly typical of our analytical technique. However, the carbon analyses indicated the presence of residual organics in the dried but unheated powders (0–2% C), which lowered slightly the observed values for lead. Additionally, the powders may have been hydrated slightly by traces of residual water.

Hydrolyses of *pure tert*-pentoxide **3** or (dimethylamino)isopropoxide **6** gave $3PbO{\cdot}H_2O$ under all conditions studied (see Table VII). The hydrate $3PbO{\cdot}H_2O$ is thermodynamically less stable than massicot and litharge.[16] Thus, $3PbO{\cdot}H_2O$ is a metastable, kinetically preferred product.

Hydrolyses of the *tert*-pentoxide **3** were also carried out in the presence of 10 mol % $LiOCMe_2Et$. $3PbO{\cdot}H_2O$ was precipitated at room temperature but was ultimately converted to litharge by refluxing the reaction slurries (see runs 3 and 4 in Table VII). Massicot was detected as an intermediate phase in some runs conducted in the presence of $LiOCMe_2Et$. Litharge is more stable than massicot at temperatures below 488 °C,[16] and is thus the expected thermodynamic product. We conclude that the conversion of the metastable $3PbO{\cdot}H_2O$ was catalyzed by the hydrolytically generated alkali-metal hydroxide.

Discussion. Our study demonstrates that lead(II) dialkoxides are generally stable, isolable compounds. With appropriate alkoxide substituents, they are also soluble and volatile. However, oxo–alkoxides such as $Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}O\text{-}i\text{-}Pr)_4$[9] and $Pb_4(\mu_4\text{-}O)(\mu\text{-}O\text{-}t\text{-}Bu)_6$[10] have been obtained elsewhere from rational attempts to prepare lead(II) dialkoxides. We suspect that the dialkoxide products are fairly sensitive to reaction conditions. For example, syntheses starting from lead(II) acetate (instead of $Pb[N(SiMe_3)_2]_2$ have given only oxo–alkoxides.[9,10] Lead(II) carboxylates are known to undergo transesterification-like condensation reactions with alkoxides to form μ-oxo groups.[1a,3c,7] Thus, lead(II) dialkoxides formed in the presence of lead(II) acetate may be consumed by steps such as eq 2, which ultimately result in oxo–alkoxides.

$$Pb(OR)_2 + Pb(OAc)_2 \longrightarrow (RO)Pb(u\text{-}O)Pb(OAc) + ROAc \qquad (2)$$

According to our results with **1** and **3**, the thermal stability of lead(II) dialkoxides appears to be purity dependent. Thus, dialkoxide decomposition in reaction mixtures may also be promoted by side products, adventitious water, other impurities, higher temperatures,[10] or concentration effects.[10] Fortunately, we are routinely able to isolate good yields of dialkoxides according to eq 1 by maintaining reaction temperatures of ca. 25 °C and rigorously dry and deoxygenated solvents and atmospheres.

As expected, bulkier alkoxide ligands generally decreased the degrees of aggregation of the lead(II) dialkoxides. Thus, **5** and **1**, which have the smaller methoxyethoxide and isopropoxide ligands, exhibit one-dimensional polymeric structures in the solid state (see Figures 1–3), whereas the *tert*-butoxide **2** is a solid-state trimer (see Figure 4). Bulky alkoxides typically lower metal coordination numbers by destabilizing alkoxide bridges, and smaller oligomer sizes generally result.[17] However, the lead atom coordination numbers of **5** and **1** are 4, whereas the coordination number of the central lead atom in **2** is 6. This comparatively high coordination number is possible because all six bonds about the central lead atom in **2** are dative bonds and, as such, have spatial requirements significantly smaller than those for normal covalent bonds.[12] The terminal lead atoms in **2** are 3-coordinate; so the average lead atom coordination numbers in **1**, **2**, and **5** are the same.

Veith has found several alkoxide trimers that are isostructural to **2** or very nearly so. These examples, $M(\mu\text{-}O\text{-}t\text{-}Bu)_3M'(\mu\text{-}O\text{-}t\text{-}Bu)_3M$, where M is from Ge, Sn, or Pb and M′ is from Mg, Ca, Sr, Ba, or Pb, are summarized in Veith's recent review.[11] Compound **2** appears to be the only presently known homometallic example. The structure of the tetramer $[Al(O\text{-}i\text{-}Pr)_3]_4$ is somewhat related in that it possesses a 6-coordinate central aluminum atom and three 4-coordinate terminal aluminum atoms.[18]

The stereochemically *inactive* lone pair on the central lead(II) atom is one of the most interesting features of **2**. The crystal structure did not reveal any peculiarities, such as excessive thermal motion or a distorted thermal ellipsoid for Pb(1), that could mask a stereochemically active lone pair (see Table V). Sterochemically inactive lone pairs on 6-coordinate lead(II) are common in nonmolecular solids, such as PbI_2, $CsPbCl_3$, and PbE, where E = S, Se, and Te.[19] However, molecular compounds of lead(II) having stereochemically inactive lone pairs are exceedingly rare.[19] One example of the latter is $Ge(\mu\text{-}O\text{-}t\text{-}Bu)_3Pb(\mu\text{-}O\text{-}t\text{-}Bu)_3Ge$;[11] another is **2**. Decaphenylplumbocene *may* have an inactive lone pair, but this has not been confirmed by single-crystal X-ray diffraction.[20] We are not aware of other examples.

Previous studies of the hydrolysis of in situ generated "$Pb(O\text{-}i\text{-}Pr)_2$" have been described by Yamaguchi et al.[5] and Narita et al.[6] On the basis of our present work with $Pb(O\text{-}i\text{-}Pr)_2$ (**1**), this compound is insufficiently soluble to actually be the substance under study in the previous reports. Considering that $Pb(O\text{-}i\text{-}Pr)_2$ was generated by reaction of lead(II) acetate and sodium isopropoxide,[5,6] it is likely[9,10] that the substances undergoing hydrolysis were oxo–alkoxides of the type $Pb_x(\mu\text{-}O)_y(O\text{-}i\text{-}Pr)_z$ or double alkoxides of the type $Na_xPb_y(OR)_{x+2y}$, which are expected to have solubilities greater than that of **1**.[1a] Consequently, our hydrolysis studies are the first to employ isolated, well-characterized lead(II) dialkoxides. We find that hydrolyses of *pure* lead(II) dialkoxides give exclusively $3PbO{\cdot}H_2O$; however, $3PbO{\cdot}H_2O$ may be converted to the thermodynamically preferred litharge when hydrolyses are performed in the presence of catalytic amounts of lithium alkoxide.

The previous studies conducted with in situ "$Pb(O\text{-}i\text{-}Pr)_2$" were generally consistent with our studies conducted with catalytic amounts of lithium alkoxide. Hydrolyses at low temperatures gave $3PbO{\cdot}H_2O$,[6] hydrolyses at higher temperatures gave predominantly litharge,[5,6] and hydrolyses under intermediate conditions gave mixtures of massicot and litharge.[5,6] The observed product dis-

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(17) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic: New York, 1978; pp 42–44.

(18) Reference 17, pp 80 and 124–128.

(19) Ng, S.-W.; Zuckerman, J. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 297.

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tributions were previously attributed to (1) pH effects due to the presence of sodium isopropoxide,[5] (2) hydrolysis rates,[6] or (3) seeding effects.[6] Our studies suggest a simple alternative explanation. The hydrate $3PbO{\cdot}H_2O$ is the kinetic product, and its conversion to massicot and then to litharge is catalyzed by sodium hydroxide generated from residual sodium isopropoxide. Because $3PbO{\cdot}H_2O$ is less stable than massicot and litharge, it may function as a more reactive component in ceramic oxide preparations.

We have made some preliminary investigations into the thermolysis behavior of our lead(II) dialkoxides to determine if they may serve as direct lead(II) oxide precursors. Thermal decomposition of **5** at 250 °C under a N_2 stream gave a mixture of metallic lead and massicot. However, under the same conditions **3** distilled from the furnace without decomposition. In a separate experiment, **3** was transported by N_2 into the furnace in the vapor phase, where decomposition occurred at 400–450 °C. Mixtures of metallic lead and massicot were deposited, as in the static decomposition of **5**. Efforts to optimize the lead(II) oxide yields in such procedures and to characterize the decomposition mechanism(s) are in progress and will be described separately.

Conclusions. Lead(II) dialkoxides are stable, generally accessible compounds. Under certain conditions, their hydrolyses are controlled by kinetic factors. The good solubilities and volatilities of several of the lead(II) dialkoxides described herein make them potentially useful precursors for ceramic oxide preparations.

Experimental Section

General Methods. All reactions were carried out under dry N_2 by using standard inert-atmosphere techniques. $Pb[N(SiMe_3)_2]_2$ was prepared by a literature procedure.[21] The alcohol reagents were purchased from Aldrich and distilled or used as received. All were stored over type 4-Å molecular sieves before use. Hexane, benzene, and THF were distilled from sodium benzophenone ketyl.

Melting points were measured under N_2. C, H, and N analyses were performed by Oneida Research Services, Whitesboro, NY. Lead analyses were performed in our laboratory by EDTA titration using xylenol orange as the indicator.[22] The isopropoxide determination was an oxidometric method.[23] Molecular weights were determined cryoscopically in benzene. NMR spectra were recorded at a field corresponding to 300 MHz for ^1H.

Preparation of $Pb(O\text{-}i\text{-}Pr)_2$ (1). 2-Propanol (2.0 g, 2.5 mL, 33 mmol) was added to a solution of $Pb[N(SiMe_3)_2]_2$ (5.0 g, 9.5 mmol) in hexane (15 mL), resulting in an exothermic reaction and the precipitation of a white solid. The mixture was refluxed for 15 min, and volatiles were then removed in vacuo. The residual white solid was dissolved in boiling 2-propanol (ca. 80 mL) and kept at room temperature for 15 h whereupon colorless crystals formed. The crystals were collected by filtration, washed with 4 mL of 2-propanol, and dried to give **1** (1.62 g, 5.0 mmol, 53%) as a white crystalline solid, mp 180–185 °C dec. Anal. Calcd for $C_6H_{14}O_2Pb$: O-*i*-Pr, 36.32; C, 22.15; H, 4.34; Pb, 63.68. Found: O-*i*-Pr, 36.57; C, 22.17; H, 4.45; Pb, 63.87.

Compound **1** is insoluble in hexane, benzene, and THF. **1** (0.78 g, 2.40 mmol) sublimed (10^{-4} Torr, 130 °C bath) to yield crystalline **1** (0.51 g, 1.57 mmol, 66%). Anal. Calcd for sublimed **1**, $C_6H_{14}O_2Pb$: Pb, 63.68. Found: Pb, 63.78.

Preparation of $Pb(O\text{-}t\text{-}Bu)_2$ (2). *tert*-Butyl alcohol (1.2 g, 1.5 mL, 16 mmol) was added to a solution of $Pb[N(SiMe_3)_2]_2$ (3.18 g, 6.0 mmol) in hexane (15 mL) resulting in an exothermic reaction. The solution was stirred for 15 min, and the volume was then reduced to 3–4 mL. Some material crystallized and was redissolved by warming the mixture (ca. 50 °C, 2 min). The solution was transferred to a hot water bath (ca. 50 °C) in a Dewar flask and was allowed to cool slowly for 8–10 h whereupon colorless, hexagonal, plate-type crystals formed. The mother liquor was removed by cannulation, and the crystals were washed with 1 mL of cold hexane and dried to give **2** (1.10 g, 3.11 mmol, 52%), mp 229–231 °C dec. Anal. Calcd for $C_8H_{18}O_2Pb$: C, 27.19; H, 5.13; Pb, 58.62. Found: C, 27.19, 27.08; H, 4.98, 4.91; Pb, 58.02, 58.65.

The mother liquor was dried in vacuo and sublimed (10^{-4} Torr, 95 °C) to yield additional **2** (0.73 g, 2.1 mmol, 34%), resulting in a total yield of 86%. Compound **2** is soluble in hexane, benzene, toluene, and THF. In a separate experiment, crystalline **2** (0.65 g, 1.8 mmol) was sublimed to give pure **2** as a white solid (0.58 g, 1.6 mmol, 89%), mp 227–228 °C. Anal. of sublimed **2**. Calcd for sublimed **2**, $C_8H_{18}O_2Pb$: C, 27.19; H, 5.13; Pb, 58.62. Found: C, 27.16; H, 4.86; Pb, 56.68. MW determinations on $[Pb(O\text{-}t\text{-}Bu)_2]_n$ found $n = 2.55$ (12) (average of measurements on four solutions with concentrations of 315–420 mg/20.0 mL).

Preparation of $Pb(OCMe_2Et)_2$ (3). $EtMe_2COH$ (4.0 g, 5.0 mL, 46 mmol) was added to $Pb[N(SiMe_3)_2]_2$ (4.75 g, 9.0 mmol) in hexane (25 mL), and the mixture was stirred for 15 min. The solution was concentrated to 6–7 mL and kept at −20 °C for 3 h whereupon colorless crystals formed. The mother liquor was removed by cannulation, and the crystals were washed with 1 mL of cold hexane and dried (yield 2.23 g, 5.9 mmol, 65%), mp 162–163 °C. Anal. Calcd for $C_{10}H_{22}O_2Pb$: C, 31.48; H, 5.81; Pb, 54.31. Found: C, 31.32; H, 5.44; Pb, 54.01.

Compound **3** is soluble in hexane, pentane, benzene, THF, and $EtMe_2COH$. **3** (0.50 g, 1.3 mmol) sublimed (10^{-4} Torr, 105 °C bath) to yield crystalline **3** (0.44 g, 1.2 mmol, 88%). Anal. Calcd for sublimed **3**, $C_{10}H_{22}O_2Pb$: 54.31. Found: Pb, 53.92. MW determinations on $[Pb(OCMe_2Et)_2]_n$ found $n = 2.8$ (2) (average of measurements on two solutions with concentrations 338 mg/20.0 mL and 396 mg/20.0 mL.

Preparation of $Pb(OCEt_3)_2$ (4). Et_3COH (2.9 g, 3.5 mL, 25 mmol) was added to $Pb[N(SiMe_3)_2]_2$ (5.00 g, 9.47 mmol) in hexane (20 mL), giving an exothermic reaction. The reaction mixture was stirred for 1 h, and then volatiles were removed in vacuo to give **4** as a viscous liquid, which solidified in ca. 30 min to a crystalline material (3.56 g, 8.13 mmol, 86%). Anal. Calcd for $C_{14}H_{30}O_2Pb$: Pb, 47.35. Found: Pb, 47.58.

Compound **4** is soluble in hexane, benzene, THF, and Et_3COH. **4** (2.80 g, 6.4 mmol) distilled unchanged on a short-path stillhead (10^{-4} Torr, 165–170 °C bath) as a viscous liquid, which solidified to a crystalline compound (2.02 g, 4.6 mmol, 72%), mp 37–38 °C. Anal. of distilled **4**. Calcd for $C_{14}H_{30}O_2Pb$: C, 38.42; H, 6.91; Pb, 47.35. Found: C, 38.82; H, 7.54; Pb, 47.24. MW determinations on $[Pb(OCEt_3)_2]_n$ found $n = 2.3$ (2) (average of measurements on two solutions with concentrations 329 mg/20.0 mL and 356 mg/20.0 mL).

Preparation of $Pb(OCH_2CH_2OMe)_2$ (5). 2-Methoxyethanol (0.62 g, 640 μL, 8.1 mmol) was added to $Pb[N(SiMe_3)_2]_2$ (2.10 g, 4.0 mmol) in hexane (30 mL), giving an exothermic reaction and the precipitation of a white solid. The mixture was stirred for 2 h, and **5** was collected by filtration, washed with hexane (2 × 5 mL), and dried (1.30 g, 3.6 mmol, 91%), mp 205–207 °C dec. Anal. Calcd for $C_6H_{14}O_4Pb$: C, 20.16; H, 3.95; Pb, 57.97. Found: C, 19.90; H, 3.58; Pb, 58.0.

Compound **5** is sparingly soluble in benzene and THF and soluble in 2-methoxyethanol. **5** was crystallized from 2-methoxyethanol solution as fine needles. **5** sublimed (10^{-4} Torr, 160 °C bath) with decomposition.

Preparation of $Pb[OCHMeCH_2NMe_2]_2$ (6). 1-(Dimethylamino)-2-propanol (0.82 g, 980 μL, 8.0 mmol) was added to a solution of $Pb[N(SiMe_3)_2]_2$ (2.04 g, 3.86 mmol) in hexane (25 mL), resulting in an exothermic reaction. The solution was stirred for 2 h, and volatiles were then removed in vacuo to give **6** as a colorless viscous liquid (1.56 g, 3.80 mmol, 98% crude yield).

Compound **6** is very soluble in hexane, benzene, and THF, and all crystallization attempts from solution failed. However, **6** (1.56 g, 3.80 mmol) was distilled (10^{-4} Torr, 106 °C at head) in good yield (1.25 g, 3.04 mmol, 80%), giving a colorless viscous liquid that solidified into crystalline **6**, mp 56–57 °C. Anal. Calcd for $C_{10}H_{24}N_2O_2Pb$: C, 29.18; H, 6.80; N, 5.88; Pb, 50.34. Found: C, 29.39; H, 6.84; N, 6.21; Pb, 49.87. MW determinations on $[Pb(OCHMeCH_2NMe_2)_2]_n$ found $n = 1.3$ (1) (average of determinations on two solutions with concentrations 270 mg/20.0 mL and 300 mg/20.0 mL).

General Procedure for the Hydrolysis of Lead(II) Alkoxides. Compounds **3** and **6** were used in the hydrolytic studies. Data obtained under various hydrolysis conditions are summarized in Table VII. Solutions of lead(II) alkoxides (ca. 0.1 M) were prepared in THF. The solutions were then hydrolyzed by addition of deionized water (ca. 4 molar equiv based on lead(II) alkoxide) over 1–2 min, except for run 7 (Table VII) where the alkoxide solution was added to water. In each case, precipitation began upon addition of the first drop of water. The mixtures were stirred at a given temperature for a given period, and then the precipitates were collected by filtration, washed with THF (5–10 mL), and dried. Products were characterized by XRD and elemental analyses (C, H, N, Pb).

General Crystallographic Procedures. Data were collected on a Seimens R3m diffractometer at ambient temperature using Mo Kα radiation ($\lambda = 0.71073$ Å). Crystallographic calculations were done on a microVAX II computer using the Siemens SHELXTL PLUS program package. Neutral-atom scattering factors were used.[24] Refinements for

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5 and **2** are described in the supplementary material. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions (d_{C-H} = 0.96 Å) and included in the final structure factor calculation by using a riding model.

Crystallographic Analysis of $[Pb(\mu,\eta^1\text{-}OCH_2CH_2OMe)_2]_\infty$ (5). A colorless needle (0.10 × 0.23 × 1.00 mm) obtained from methoxyethanol solution was mounted in a capillary for diffraction analysis. All attempts to cleave such needles to provide a sample with the proper dimensions were destructive. Crystal data are listed in Table II. The structure was determined by direct methods in the space group *Cc* (No. 9) and subsequently transformed into space group *C*2/*c* (No. 15). The reduction in the *R* index and some esd's for bond distances and angles confirmed the final choice of space group. Temperature factors (*U*) for hydrogen atoms were assigned a common value and refined to 0.08 (1) Å^2. The final residuals for 53 variables refined against the 1026 data for which $I > 3\sigma(I)$ were R = 0.0258 and R_w = 0.0320.

Crystallographic Analysis of $[Pb_3(\mu\text{-}O\text{-}t\text{-}Bu)_6]$ (2). A colorless prism (0.30 × 0.30 × 0.40 mm) was obtained from a synthetic reaction mixture and mounted in a glass capillary for diffraction analysis. Crystal data are listed in Table II. The hexagonal axial setting (R_{obv}) of the trigonal unit cell was chosen. Photographic evidence and systematic absences indicated the possible space groups were *R*3 (No. 146), $R\bar{3}$ (No. 148), R32 (No. 155), R3*m* (No. 160), or $R\bar{3}m$ (No. 166). Successful refinement confirmed the space group to be $R\bar{3}$ (No. 148). Temperature factors (*U*) for hydrogen atoms were fixed at 0.21 Å^2. The final residuals for 52 variables refined against the 517 data for which $I > 3\sigma(I)$ were R = 0.0504 and R_w = 0.0592.

Attempted Crystallographic Analysis of $[Pb(\mu,\eta^1\text{-}O\text{-}i\text{-}Pr)_2]_\infty$ (1). After the screening of more than 12 crystals, a marginally suitable sample was selected for diffraction studies. A monoclinic unit cell was determined: a = 17.86 (2) Å, b = 7.77 (1) Å, c = 6.585 (7) Å, β = 99.60 (1)°, and V = 901 (2) Å^2. Data collection and refinement in space group $P2_1/c$ by the general procedures described above (T = 22 °C, Z = 4, D_c = 2.295 g cm^{-3}; of the 1854 intensities measured, 1063 unique reflections with $I > 3\sigma(I)$ were used) led directly to the structure represented in Figure 3. However, the final difference map was not clean; several large residual peaks remained (largest difference peak 4.35 e Å^3).

Attempted Crystallographic Analysis of $Pb(OCMe_2Et)_2$ (3). After the screening of more than 12 crystals from different synthetic runs, no ideal sample was found. A marginally suitable crystal was selected for preliminary studies. Broadening of the ω-scan peak profile was observed for several of the 24 reflections used in unit cell determination. A rhombohedral cell with a hexagonal axial setting similar to that for **2** was obtained: $a = b$ = 10.774 (6) Å, c = 30.38 (2) Å, and V = 3054 (4) Å^3. A hemisphere of data ($+h,\pm k,\pm l$) were collected in the $\theta/2\theta$ mode, 1.2° scan width and 3.66–9.77° min^{-1}. Space group $R\bar{3}$ (No. 148) seemed to give the most convincing solution with lead atoms sitting on the origin, (0, 0, 0), and on the 3-fold axis, (0, 0, 0.1122), with a bridging oxygen atom in between. We were unable to locate the rest of the molecule, probably because of the severe disorder present and/or the questionable crystal quality.

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Registry No. **1**, 66149-40-4; **2** (coordinate entry), 129264-42-2; **2** (salt entry), 59335-87-4; **3**, 129264-44-4; **4**, 129264-46-6; **5**, 129264-43-3; **6**, 129264-45-5; $Pb[N(SiMe_3)_2]_2$, 55147-59-6; PbO, 1317-36-8.

Supplementary Material Available: Tables listing details of the crystallographic data collection, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters (9 pages); listings of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Preparation of Soluble and Volatile Zinc Dialkoxides. X-ray Crystal Structures of an (Amido)zinc Alkoxide and a Homoleptic Zinc Enolate: $\{Zn(\mu\text{-}OCEt_3)[N(SiMe_3)_2]\}_2$ and $Zn(1,4,7\text{-}\eta^3\text{-}OCH{=}CHNMeCH_2CH_2NMe_2)_2$

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Seven new zinc dialkoxides prepared by alcoholyses of $Zn[N(SiMe_3)_2]_2$ are reported: $Zn(OCEt_3)_2$ (**1**), $Zn(OCEt_2Me)_2$ (**2**), $Zn(OCH_2CH_2OMe)_2$ (**3**), $Zn(OCH_2CH_2OCH_2CH_2OMe)_2$ (**4**), $Zn(OCH_2CH_2NMe_2)_2$ (**5**), $Zn(OCHMeCH_2NMe_2)_2$ (**6**), and $Zn(OCH_2CH_2NMeCH_2CH_2NMe_2)_2$ (**7**). Each is soluble (**1**, **6**, and **7** in hydrocarbons), volatile (subliming at 170–225 °C/10^{-4} Torr), or both. Sublimation of **7** gives enolate $Zn(1,4,7\text{-}\eta^3\text{-}OCH{=}CHNMeCH_2CH_2NMe_2)_2$ (**8**) by thermal dehydrogenation. Two compounds are structurally characterized: mononuclear **8** and (amido)zinc alkoxide intermediate $\{Zn(\mu\text{-}OCEt_3)[N(SiMe_3)_2]\}_2$ (**9**). Crystal data for **8**: monoclinic, $P2_1/n$, a = 8.715 (5) Å, b = 16.525 (5) Å, c = 12.989 (4) Å, β = 106.95 (4)°, V = 1789.4 (12) Å^3, T = 22 °C, Z = 4, and D_c = 1.306 g cm^{-3}. Of the 4562 intensities measured, 2304 unique reflections with $I > 3\sigma(I)$ yielded $R(F_o)$ = 0.0383 and $R_w(F_o)$ = 0.0512. Crystal data for **9**: triclinic, $P\bar{1}$, a = 8.836 (5) Å, b = 10.611 (7) Å, c = 11.431 (8) Å, α = 93.40 (6)°, β = 105.88 (5)°, γ = 104.29 (5)°, V = 989.6 (11) Å^3, T = 22 °C, Z = 1, and D_c = 1.144 g cm^{-3}. Of the 3949 intensities measured, 2393 unique reflections with $I > 3\sigma(I)$ yielded $R(F_0)$ = 0.0375 and $R_w(F_0)$ = 0.0443.

Introduction

Zinc oxide materials are used in varistors,[1] electronic thin films,[2] and heterogeneous catalysts, particularly methanol-synthesis catalysts.[3] Solution-phase preparations of ZnO powders for varistors[4] and catalysts[5] and vapor-phase depositions of ZnO films[6] for electronic and optical applications have been recently described. Homoleptic alkoxides, $M_x(OR)_y$, are often useful precursors in such oxide syntheses;[7] however, presently available $Zn(OR)_2$

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