

## Synthesis, Characterization, and Reactivity of Lead(II) Glycolate Complexes

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### Introduction

There is currently considerable interest in the preparation of soluble metal-organic complexes that might be suitable as precursors for the formation of perovskite phase metal oxide materials.<sup>1-3</sup> The sol-gel method of hydrolysis and condensation of metal alkoxide precursors is an attractive route to formation of such materials due to low processing temperatures and the potential for control over stoichiometry at the molecular level.<sup>4-7</sup> However, one potential disadvantage of this method is that different metal-organic precursors can react with each other *prior to or during* hydrolysis to form mixtures of compounds with *incorrect* stoichiometries.<sup>8</sup>

As a method to circumvent such problems, we<sup>9-12</sup> and others<sup>7,13,14</sup> have been investigating the reactions of metal-organic compounds in which stoichiometry is controlled at the molecular level by formation of "single-component" molecular precursors. In this work, we report the synthesis and characterization of two lead(II)  $\alpha$ -hydroxy carboxylate complexes,  $[\text{Pb}(\text{O}_2\text{CCR}_2\text{OH})_2]$  ( $\text{R} = \text{H}, \text{Me}$ ), and their reactivity toward Ti and Sn alkoxide compounds. These species were prepared because they contain a site of latent reactivity, the hydroxyl group, which may react with other metal-organic moieties, such as metal alkoxide compounds, to form heterobimetallic species of fixed stoichiometry. While a number of metal  $\alpha$ -hydroxy carboxylates have been prepared,<sup>15</sup> there are relatively few examples of glycolate derivatives of divalent metals.<sup>16,17</sup>

### Experimental Section

i. **General Procedures.** All manipulations were carried out under an atmosphere of dry (molecular sieves) dinitrogen using standard Schlenk techniques.<sup>18</sup> All hydrocarbon and etheral solvents were dried and distilled from sodium benzophenone ketyl and stored over 4-Å molecular sieves. Glycolic acid and  $\beta$ -diketones were purchased from Aldrich Chemical Co. and used without further purification. The compounds  $(\text{RO})_2\text{M}(\beta\text{-diketonate})_2$  ( $\text{M} = \text{Ti}, \text{Sn}$ ) were prepared by methods previously described in the literature.<sup>19-22</sup> Elemental analyses were performed either by Oneida Research Services, New York, or by Ms. R. Ju, Department of Chemistry, University of New Mexico. NMR data were recorded on a Bruker AC-250P NMR spectrometer by using the protio impurities of the deuterated solvents as references for  $^1\text{H}$  NMR and the  $^{13}\text{C}$  resonance of the solvents as reference for  $^{13}\text{C}$  NMR spectroscopy. Temperatures were calibrated with either ethylene glycol or methanol. Infrared data were recorded on a Perkin-Elmer Model 1620 FTIR spectrophotometer. Thermogravimetric data were obtained with a Perkin-Elmer Model 7700 series instrument.

ii. **Syntheses.** A representative example of the synthesis of the lead(II) glycolate compounds is given below.

**Preparation of  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$ .** Lead carbonate (5.34 g, 0.02 mol) was suspended in water (20 mL), and glycolic acid (3.04 g, 0.04 mol) was added. The mixture effervesced and some undissolved material remained, so the solution was refluxed until all the solid had dissolved. Heating was discontinued and the solution left to cool overnight. Clear, colorless crystals were obtained which were found to be analytically pure. Yield: 95%.

**Characterization Data.**  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$ .  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 300 K, 250 MHz): 4.02 ppm (s,  $\text{O}_2\text{CCH}_2\text{OH}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$  with benzene- $d_6$  internal reference, 300 K, 62.9 MHz): 181.2 (s,  $\text{O}_2\text{CCH}_2\text{OH}$ ), 62.1 ppm (s,  $\text{O}_2\text{CCH}_2\text{OH}$ ).  $^{207}\text{Pb}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ , 300 K, 52.3 MHz): -1964 ppm (s). IR (KBr pellet): 3050 (s), 2870 (s), 2740 (s), 2634 (s), 2546 (s), 1560 (s), 1472 (s), 1427 (s), 1370 (s)  $\text{cm}^{-1}$ . IR ( $\text{D}_2\text{O}$  exchange, KBr pellet): 2925 (m), 2325 (s), 1560 (s), 1430 (s)  $\text{cm}^{-1}$ . Anal. Calc for  $\text{C}_4\text{H}_6\text{O}_6\text{Pb}$ : C, 13.4; H, 1.7. Found: C, 13.4; H, 1.5.

$[\text{Pb}(\text{O}_2\text{C}(\text{CH}_3)_2\text{OH})_2]$ .  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 300 K, 250 MHz): 1.22 ppm (s,  $\text{O}_2\text{C}(\text{CH}_3)_2\text{OH}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$  with benzene- $d_6$  internal reference, 300 K, 62.9 MHz): 185.7 (s,  $\text{O}_2\text{C}(\text{CH}_3)_2\text{OH}$ ), 75.55 (s,  $\text{O}_2\text{C}(\text{CH}_3)_2\text{OH}$ ), 27.65 ppm (s,  $\text{O}_2\text{C}(\text{CH}_3)_2\text{OH}$ ).  $^{207}\text{Pb}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ , 300 K, 52.3 MHz): -1875 ppm (s) ( $\Delta\nu_{1/2} = 150$  Hz). IR (KBr pellet): 3300 (s), 2980 (s), 2930 (s), 1573 (vs), 1477 (s), 1364 (vs)  $\text{cm}^{-1}$ . Anal. Calc for  $\text{C}_8\text{H}_{14}\text{O}_6\text{Pb}$ : C, 23.2; H, 3.4. Found: C, 23.1; H 3.4.

**Reaction of  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$  with  $(\text{dpm})_2\text{Ti}(\text{O}-i\text{-Pr})_2$ .**  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$  (0.23 g, 0.5 mmol) was suspended in refluxing MeOH (30 mL), a MeOH (20 mL) solution of  $(\text{dpm})_2\text{Ti}(\text{O}-i\text{-Pr})_2$  (0.37 g, 0.69 mmol) was added dropwise over a 2-h period, and the solution was refluxed for a further 1 h after the addition was complete. A white precipitate formed during and after the addition. The solution was then filtered and the product dried in vacuo. The extremely low solubility of the product hampered characterization by the usual spectroscopic techniques. Anal. Calc for  $\text{C}_{26}\text{H}_{43}\text{O}_{10}\text{TiPb}$ : C, 40.52; H, 5.62. Found: C, 44.26; H, 6.29. The presence of  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$  in the product accounts for the excess C and H (40.52% C, 5.86% H). These observations are consistent with the Ti content (7.3%) and the higher lead content (51.8%) than anticipated, as determined by X-ray fluorescence spectroscopy. Numerous attempts to remove  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$  by washing were unfruitful.

iii. **Single-Crystal X-ray Diffraction Data.** Crystal data for  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$ : colorless, transparent crystals (0.136 × 0.240 × 0.260 mm) grown from water at 23 °C;  $\text{C}_4\text{H}_6\text{O}_6\text{Pb}$ , orthorhombic,  $Pbca$ ,  $a = 7.1803$  (11) Å,  $b = 10.346$  (2) Å,  $c = 17.712$  (4) Å,  $V = 1315.8$  (5) Å<sup>3</sup>,  $Z = 8$ ,  $D(\text{calc}) = 3.607$  g  $\text{cm}^{-3}$ ,  $T = 293$  K. Of 5036 data that were collected on a Siemens R3m/V instrument, using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and employing a graphite monochromator, and that were corrected for adsorption ( $2^\circ < 2\theta < 50^\circ$ ) (SHELXTL), 1160 were independent and 940 with  $F_o > 4.0\sigma(F_o)$  were observed. At convergence with all non-hydrogen atoms anisotropic except for carbons and O(4) and all hydrogen atoms idealized except H(3) and H(6), which were fixed

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Table I. Crystallographic Data for  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$ 

chem formula: $\text{C}_4\text{H}_6\text{O}_6\text{Pb}$	space group: <i>Pbca</i>
fw 357.3	$T = 20^\circ\text{C}$
$a = 7.1803$ (11) Å	$\lambda = 0.71073$ Å
$b = 10.346$ (2) Å	$\rho_{\text{obsd}} = 3.607$ g cm <sup>-3</sup>
$c = 17.712$ (4) Å	$\mu = 2.582$ cm <sup>-1</sup>
$V = 1315.8$ (5) Å <sup>3</sup>	$R(F_o) = 4.70\%$
$Z = 8$	$R_w(F_o) = 5.22\%$

Table II. Atomic Coordinates and Positional Parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq), Å <sup>2</sup>
Pb	3056 (1)	3933 (1)	5806 (1)	13 (1)
O(1)	2870 (13)	6124 (8)	6241 (6)	17 (3)
O(2)	3752 (14)	7704 (9)	6992 (6)	20 (3)
O(3)	4512 (16)	4298 (10)	7046 (6)	29 (3)
C(1)	3781 (19)	6526 (13)	6804 (7)	12 (3)
C(2)	4937 (23)	5595 (12)	7238 (8)	21 (4)
O(4)	6361 (13)	4840 (9)	5534 (6)	20 (3)
O(5)	9348 (15)	4735 (10)	5888 (6)	27 (3)
O(6)	5875 (15)	2319 (10)	5677 (7)	31 (3)
C(3)	7720 (21)	4235 (15)	5785 (6)	12 (3)
C(4)	7593 (21)	2814 (12)	5966 (7)	12 (2)

<sup>a</sup> Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table III. Bond Lengths (Å)

Pb—O(1)	2.397 (9)	Pb—O(3)	2.460 (10)
Pb—O(4)	2.597 (10)	Pb—O(6)	2.633 (10)
Pb—O(4') <sup>a</sup>	2.724 (10)	Pb—O(2a)	2.778 (10)
O(2)—C(1)	1.263 (16)	Pb—O(5a)	2.793 (10)
O(3)—C(2)	1.418 (16)	O(1)—C(1)	1.264 (16)
O(4)—C(3)	1.242 (18)	C(1)—C(2)	1.485 (19)
O(5)—C(3)	1.291 (18)	O(4)—Pb'	2.724 (10)
O(6)—C(4)	1.430 (18)	C(3)—C(4)	1.507 (20)

<sup>a</sup> Primed atoms generated from parent atom by the transformation  $1-x, 1-y, 1-z$ .

Table IV. Bond Angles (deg)

O(1)—Pb—O(3)	65.9 (3)	O(1)—Pb—O(4)	76.7 (3)
O(3)—Pb—O(4)	73.9 (3)	O(1)—Pb—O(6)	132.1 (3)
O(3)—Pb—O(6)	81.3 (4)	O(4)—Pb—O(6)	60.7 (3)
O(1)—Pb—O(4') <sup>a</sup>	81.2 (3)	O(3)—Pb—O(4')	129.8 (3)
O(4)—Pb—O(4')	61.9 (4)	O(6)—Pb—O(4')	95.8 (3)
Pb—O(1)—C(1)	122.4 (8)	O(1)—C(1)—C(2)	118.9 (11)
Pb—O(3)—C(2)	116.8 (8)	O(3)—C(2)—C(1)	111.7 (12)
O(1)—C(1)—O(2)	121.1 (12)	Pb—O(4)—C(3)	118.0 (9)
O(2)—C(1)—C(2)	119.9 (11)	C(3)—O(4)—Pb'	115.2 (8)
Pb—O(4)—Pb'	118.1 (4)	Pb—O(6)—C(4)	113.9 (8)
O(4)—C(3)—C(4)	121.3 (13)	O(4)—C(3)—O(5)	124.1 (14)
O(6)—C(4)—C(3)	109.0 (11)	O(5)—C(3)—C(4)	114.6 (13)

<sup>a</sup> See footnote a, Table III.

in their positions identified in the difference map,  $R_F = 4.70\%$ ,  $R_{wF} = 5.22\%$ ,  $\Delta(\rho) = 4.07$  e Å<sup>-3</sup>, and  $N_o/N_v = 10.3$ . The large residual electron density is common in structures with a large contribution from heavy atoms and is most likely due to (i) a severe absorption correction and (ii) a Fourier series termination effect. Crystal data are given in Table I, atomic coordinates in Table II, and relevant bond lengths and angles in Tables III and IV, respectively. Two views of the molecular structure are shown in Figures 1 and 2, and the crystal structure is shown in Figure 3.

## Results and Discussion

The complexes,  $[\text{Pb}(\text{O}_2\text{CCR}_2\text{OH})_2]$  ( $R = \text{H}, \text{Me}$ ), were prepared by the reaction of an aqueous solution of lead(II) carbonate with a slight excess of the corresponding  $\alpha$ -hydroxy carboxylic acid. After the effervescence had subsided, the dissolution of the metal salt was complete. The products were recrystallized from water ( $R = \text{H}$ ) and 95% ethanol ( $R = \text{Me}$ ) solutions to give colorless crystalline solids that gave satisfactory analytical and spectroscopic data. As an example,  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$ , isolated by recrystallization from water, gave a satisfactory analysis and exhibited only a single type of glycolate ligand in

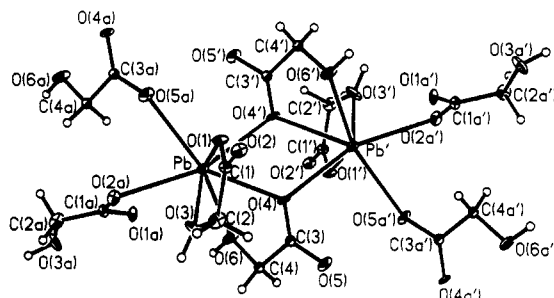


Figure 1. ORTEP plot of the molecular structure of  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$  showing the coordination environment about lead.

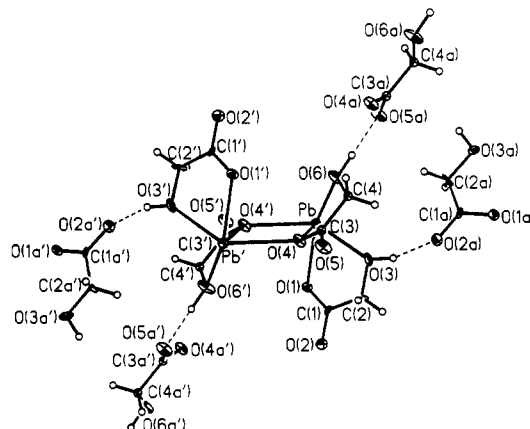


Figure 2. ORTEP plot of the molecular structure of  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$  emphasizing the hydrogen-bonding structure. Note: some of the oxygen atoms (O(2a) and O(5a)) coordinated to lead have been omitted from this view.

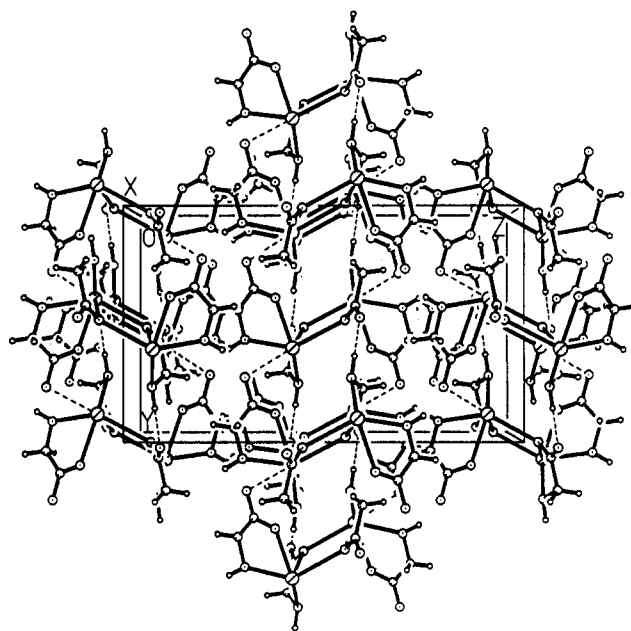


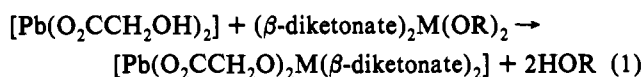
Figure 3. Crystal structure of  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$  showing the intermolecular hydrogen bonding and acetate bridging.

aqueous solution by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and a single sharp resonance ( $\Delta\nu_{1/2} = 69.8$  Hz) was observed by <sup>207</sup>Pb NMR spectroscopy at  $-1964$  ppm, 640 ppm upfield of the resonance of lead(II) acetate in D<sub>2</sub>O. However, these species exhibited some interesting features in their solid-state FTIR spectra. The derivative  $[\text{Pb}(\text{O}_2\text{CCMe}_2\text{OH})_2]$  exhibited  $\nu(\text{O}-\text{H})$  at  $3310$  cm<sup>-1</sup>, and the highest  $\nu(\text{C}-\text{O})$  bands were centered at  $1570$  cm<sup>-1</sup>, probably resulting from coordination of the carboxylate oxygen to the metal center. However,  $[\text{Pb}(\text{O}_2\text{CCH}_2\text{OH})_2]$  exhibited a  $\nu(\text{O}-\text{H})$  band at a significantly lower position of  $3050$  cm<sup>-1</sup>. This

assignment was confirmed by recrystallization from D<sub>2</sub>O, where the glycolate  $\nu(\text{O}-\text{D})$  was observed at 2325 cm<sup>-1</sup>. This is consistent with a strong hydrogen bond analogous to those observed between coordinated alcohols and alkoxide ligands in metal alkoxide complexes.<sup>12,23</sup>

To investigate the coordination geometry of lead in [Pb(O<sub>2</sub>CCH<sub>2</sub>OH)<sub>2</sub>] further, a solid-state single-crystal X-ray diffraction study was carried out. ORTEP plots of the molecular structure are shown in Figures 1 and 2, and the crystal structure is shown in Figure 3. The relevant bond lengths and angles are presented in Tables III and IV. Each lead atom is approximately eight-coordinate, being coordinated to four oxygen atoms at relatively short distances (<2.65 Å) (O(1), O(3), O(4), O(6)) and to three oxygen atoms at significantly longer distances (O(4'), O(2a), O(5a)), and each lead probably retains a stereochemically active lone pair, as shown in Figure 1. The glycolate ligands chelate to the lead atoms via the hydroxyl oxygen and one carboxylate oxygen atom. A different view of the molecule showing only the shortest Pb-O distances and emphasizing the hydrogen-bonding structure is shown in Figure 2. On the basis of the coordination mode of the carboxylate ligands, two distinct types of glycolate ligand coordination can be identified. In one type of glycolate ligand, one carboxylate oxygen coordinates to a lead atom (e.g. O(1)) and the other carboxylate oxygen atom (e.g. O(2)) is hydrogen-bonded to a glycolate hydroxyl group of an adjacent molecule (e.g. O(2a) to O(3)) and is also bonded to a lead atom of an adjacent molecule; see Figure 2. In the other type of glycolate ligand, one carboxylate atom bridges two lead atoms (e.g. O(4)), while the remaining carboxylate oxygen (e.g. O(5)) hydrogen-bonds to a glycolate hydroxyl group of an adjacent molecule (e.g. O(5a) to O(6)) and is also bonded to a lead atom of an adjacent molecule; see Figure 2. As a result, a three-dimensional polymeric structure is formed consisting of carboxylate oxygen bridged lead dimers connected by bridging acetate ligands and hydrogen bonds, which probably accounts for the low solubility of this material in aprotic solvents. The chelated nature of the glycolate ligand is a particularly important structural feature of this complex in this context because this is likely to raise the acidity of the hydroxylic proton and enhance its reactivity toward metal alkoxide species.

In order to investigate whether the hydroxyl protons are accessible for further reaction in this system, [Pb(O<sub>2</sub>CCH<sub>2</sub>OH)<sub>2</sub>] was reacted with a number of compounds with general formula (β-diketonate)<sub>2</sub>M(OR)<sub>2</sub> (M = Ti, β-diketonate = acetylacetonate (acac), dipivaloylmethanate (dpm); M = Sn, β-diketonate = acac, R = *i*-Pr).<sup>19-22</sup> The rationale for the choice of these reagents is that the alcohol elimination reaction is expected to fix the Pb to M stoichiometry at 1:1 according to eq 1. The β-diketonate ligands



could then be removed in subsequent thermolysis or hydrolysis steps. The reaction of eq 1 was carried out in pyridine and methanol and resulted in the slow precipitation of a white powder. The eliminated alcohol was identified by gas chromatography by comparison to a standard sample of 2-propanol in pyridine. For a typical example (β-diketonate = dpm, M = Ti), elemental analysis data showed higher carbon and hydrogen contents than expected for [Pb(O<sub>2</sub>CCH<sub>2</sub>O)<sub>2</sub>M(β-diketonate)<sub>2</sub>], which was believed to be derived from incorporation of [Pb(O<sub>2</sub>CCH<sub>2</sub>OH)<sub>2</sub>]

into the precipitate. Repeated washing of the precipitate did not remove the unreacted [Pb(O<sub>2</sub>CCH<sub>2</sub>OH)<sub>2</sub>], but the presence of Ti was confirmed by XRF. Thermogravimetric analysis of the white solid revealed an onset of weight loss at 200 °C which was complete by 400 °C and corresponded to formation of PbTiO<sub>3</sub> (calculated weight loss = 39%; observed weight loss = 40%). In a separate experiment, a bulk sample of the white powder formed from the reaction of eq 1 was heated to 400 °C for 1 h. X-ray powder diffraction data revealed the presence of the crystalline perovskite phase PbTiO<sub>3</sub> together with PbO.<sup>24</sup> It is likely that the origin of the PbO is lead glycolate that may have precipitated during the reaction with (dpm)<sub>2</sub>Ti(O-*i*-Pr)<sub>2</sub>. Isolation of the precipitate by filtration would remove any unreacted (dpm)<sub>2</sub>Ti(O-*i*-Pr)<sub>2</sub> and result in the formation of a lead-rich material after thermolysis. This is consistent with the characterization data obtained for the crude material isolated from this reaction.

A comparison of the formation of the crystalline perovskite phase PbTiO<sub>3</sub> from sol-gel and coprecipitation methods has previously been reported.<sup>25</sup> The sol-gel method, using lead acetate and Ti(OCH<sub>2</sub>CH<sub>2</sub>OMe)<sub>4</sub> as precursors, resulted in the formation of crystalline PbTiO<sub>3</sub> after heating to 425 °C for 600 min. The product of coprecipitation of lead(II) nitrate and titanium(IV) chloride forms crystalline PbTiO<sub>3</sub> after heating to 375 °C for 600 min. A more recent report<sup>26</sup> has shown that crystalline PbTiO<sub>3</sub> can be formed by heating the product of the reaction between lead acetate and titanium ethoxide in an O<sub>2</sub> atmosphere for 1 h at 250 °C. On the basis of the TGA data presented, it seems likely that these conditions induce an exothermic reaction, perhaps resulting in locally higher temperatures.

## Conclusions

Two lead(II) glycolate complexes have been prepared, and one example was characterized in the solid state by single-crystal X-ray diffraction. [Pb(O<sub>2</sub>CCH<sub>2</sub>OH)<sub>2</sub>] exhibited a solid-state structure in which the lead atom was eight-coordinate and the glycolate ligands chelated the metal centers via one carboxylate oxygen atom and the hydroxyl oxygen atom. Dimeric, carboxylate oxygen bridged lead centers formed a three-dimensional network via bridging acetate groups and intermolecular hydrogen-bonding between the glycolate hydroxyl groups and carboxylate oxygen atoms. These species reacted with (RO)<sub>2</sub>M(β-diketonate)<sub>2</sub> (M = Ti, Sn) to liberate alcohol and form a mixed-metal precipitate which was too insoluble to allow unambiguous characterization. However, thermolysis of this solid at 400 °C for 1 h in air resulted in formation of the crystalline perovskite phase PbTiO<sub>3</sub> but was contaminated with PbO. This relatively low temperature and short time for crystallization may result from the molecular scale homogeneity of the mixed-metal intermediate. Further experiments are in progress to prepare other divalent metal glycolate complexes containing alkyl groups to enhance solubility and aid characterization of the intermediates.

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**Supplementary Material Available:** Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom locations, and a refinement summary (8 pages). Ordering information is given on any current masthead page.

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