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Influence of Lead(II) Lone Pairs on the Serpentine Structures for Heterometallic Alkoxides

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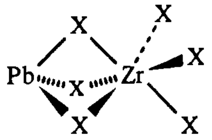
Heterometallic alkoxides,[1] $M_aM'_b(OR)_m$, most often adopt closed polyhedral structures, in part to give suitably high coordination numbers to all metals. In general, the ratio $m/(a + b)$ is typically low (because one or more of M and M′ are low valent) so that μ_2- and μ_3-OR functionalities are required, and a closed polyhedron best accommodates such demands. Thus the metals of $KZr_2(O^iPr)_9$[2] and $[BaZr_2(O^iPr)_{10}]_2$[3] form triangles, those of $K_2Zr_2(O^tBu)_{10}$[4] form a diamond, and those of $K_4Zr_2O(O^iPr)_{10}$[2] form an octahedron. We report here the very different outcome of combining Zr(IV) with the *soft* divalent metal Pb(II). These results demonstrate that rational synthetic control of two different stoichiometries can be effected in heterometallic alkoxide chemistry.

Given the existence of $PbZr(O^tBu)_6$,[5] we were interested in establishing the effect of decreasing alkoxide steric bulk. We therefore sought a species of formula $PbZr(O^iPr)_6$.[6] Insoluble, polymeric $Pb(O^iPr)_2$,[7] slurried in Et_2O, is dissolved by addition of $Zr(O^iPr)_4$. The ^1H NMR of the resulting solid, dissolved in C_6D_6, did not resemble the two equal-intensity alkoxide environments predicted for the 3-fold-symmetric structure of I.[8] Making use of solubility differences, it is possible to separate the solid product into two distinct compounds as shown in eq 1. This represents aggregation of heterometallic alkoxides in an unprecedented manner: instead of aggregation of a $PbZr(O^iPr)_6$ repeat unit, two aggregates of *different* (and complementary) chemical formulas are preferred: 4:2 and 2:4. Moreover, although each product has a potentially triangular simplest formula, no complete $PbZr_2$ or Pb_2Zr triangles are found in either structure. In addition, neither six-metal molecule adopts an octahedral structure. Instead, each assumes a serpentine motif.[9]



I (X = O^iPr)

$$6Pb(O^iPr)_2 + 6Zr(O^iPr)_4 \rightarrow Pb_4Zr_2(O^iPr)_{16} + Pb_2Zr_4(O^iPr)_{20} \quad (1)$$

The structure of $Pb_4Zr_2(O^iPr)_{16}$ (Figure 1)[10,11] contains a central $(^iPrO)Pb(\mu\text{-}O^iPr)_2Pb(O^iPr)$ unit (analogous to that of $Sn_2(O^tBu)_4$[12]) bonded to two $Pb(\mu\text{-}O^iPr)_3Zr(O^iPr)_3$[5] units. The latter is precisely the simple unit, I, we anticipated forming at the outset of this work. The entire molecule is rigorously centrosymmetric with the six metals approximately planar, and thus *each* terminal O^iPr of the $(^iPrO)Pb(\mu\text{-}O^iPr)_2Pb(O^iPr)$ unit binds to a distinct $PbZr(O^iPr)_6$ unit. This increases the coordination number of Pb2 to 4, and the resulting geometry of this Pb is "sawhorse" or pseudo trigonal bipyramidal,[13] with O8 and O16 axial and an (unseen) Pb lone pair equatorial. The O8–Pb2 bridge between these two units is the longest (2.43(2) Å) of the Pb–O bonds (2.23(2)–2.39(2) Å) in the molecule. However, it is clear that this molecule, once isolated, does not

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[1] Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969.

[2] Vaartstra, B. A.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 8593.

[3] Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 3068.

[4] Teff, D. J.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 6289.

[5] Vaartstra, B. A. *Mater. Res. Soc. Symp. Proc.* **1993**, *282*, 689. An additional goal of our study is to examine the influence of alkoxide steric profile on compound identity.

[6] For a literature review, see: Mehrotra, R. C.; Singh, A.; Sogani, S. *Chem. Rev.* **1994**, *94*, 1643.

[7] Goel, S. C.; Chiang, M. Y.; Buhro, W. E. *Inorg. Chem.* **1990**, *29*, 4640. In contrast, "$Pb(O^tBu)_2$" is the linear trimer $Pb(\mu\text{-}O^tBu)_3Pb(\mu\text{-}O^tBu)_3Pb$, with metal coordination numbers 3, 6, and 3.

[8] This structure has been suggested for $Pb(\mu\text{-}O^tBu)_3Zr(O^tBu)_3$.[5]

[9] Another rare case of a serpentine metal complex is $Mo_6O_{10}(O^iPr)_{12}$. See: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

[10] Crystallographic data (−174 °C): $a = 12.190(6)$ Å, $b = 14.701(7)$ Å, $c = 19.978(13)$ Å, $\beta = 105.57(3)°$ with $Z = 2$ in space group $P2_1/c$. $R(F) = 0.0647$ for 2656 reflections with $F > 2.33\sigma(F)$.

[11] $[Pb_4Zr_2(O^iPr)_{16}]$: ^1H NMR (toluene-d_8, 25 °C, 300 MHz) δ 5.02 (br, 16H), 1.39 (d, 96H, $^3J_{H-H} = 6$ Hz); ^1H NMR (−60 °C) δ 6.50 (br, 2H), 5.78 (br, 2H), 5.32 (br, 2H), 4.85 (br septet, 4H, $^3J_{H-H} = 6$ Hz), 4.69 (br septet, 6H, $^3J_{H-H} = 6$ Hz), 1.55–1.43 (br, 96H). Satisfactory C and H analyses were obtained.

[12] (a) Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1985**, 939. (b) Veith, H.; Hobein, P.; Rösler, R. *Z. Naturforsch.* **1989**, *44B*, 1067.

[13] A pseudo-trigonal-bipyramidal geometry for Pb(II) has been reported in a complex with deprotonated γ-cyclodextrin: Klüfers, P.; Schuhmacher, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1863.

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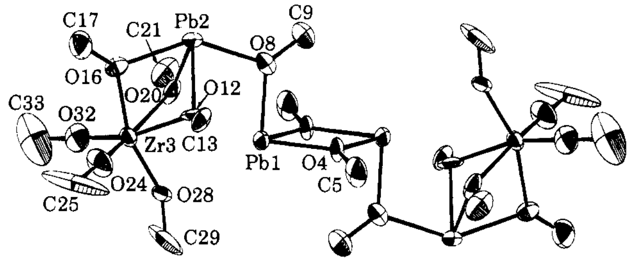

Figure 1. ORTEP drawing of $Pb_4Zr_2(O^iPr)_{16}$. Methyl groups have been omitted for clarity, and unlabeled atoms are related to those shown by a center of symmetry between Pb1 and Pb1′.

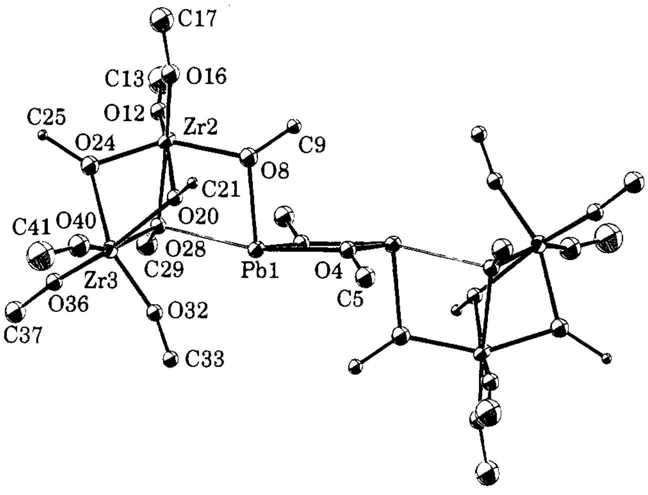

Figure 2. ORTEP drawing of $Pb_2Zr_4(O^iPr)_{20}$. Methyl groups have been omitted for clarity, and unlabeled atoms are related to those shown by a center of symmetry between Pb1 and Pb1′.

dissociate into $PbZr(O^iPr)_6$ and $Pb(O^iPr)_2$ in benzene, since the latter is an insoluble polymer.

The other stoichiometric product, $Pb_2Zr_4(O^iPr)_{20}$, is again rigorously centrosymmetric (Figure 2)[14,15] and can be subdivided mentally into a central $(^iPrO)Pb(\mu\text{-}O^iPr)_2Pb(O^iPr)$ unit, each of whose terminal O^iPr units bridges to a *different* $Zr_2(O^iPr)_8$ unit, thereby creating a $Zr_2(O^iPr)_9$ unit of face-shared bioctahedral structure. In this unit, terminal Zr−OR distances (1.89(2)−1.97(2) Å) are shorter than those of $Zr_2(\mu\text{-OR})$ (2.16(2)−2.27(2) Å), and the longest $Zr(\mu\text{-OR})$ distances are of those groups *trans* to terminal OR ligands. Nevertheless, the $Zr_2(O^iPr)_9$ unit is but little distorted from bioctahedral, and the $Pb_2(O^iPr)_4$ unit is again similar in structure to $Sn_2(O^tBu)_4$. The six metals are slightly distorted from planarity so that O28 approaches within bonding distance (2.72(2) Å) of Pb1; the latter thus becomes four-coordinate (Figure 2).

It is remarkable that $Zr/Pb/O^iPr$ compounds can exist in such different stoichiometries and, moreover, that an equimolar mixture of 2:4 and 4:2 compounds (i.e., the products of eq 1) does not comproportionate to a 1:1 compound (^1H NMR evidence). Indeed, the Pb_2Zr_4 species is formally derived from the Pb_4Zr_2 species by replacing both $Pb(2)(O^iPr)_2$ with $Zr(O^iPr)_4$ units. However, a mixture of the Pb_2Zr_4 and Pb_4Zr_2 compounds shows no coalescence (25 °C, 300 MHz) in the ^1H NMR which would be caused by their facile interconversion, in spite of the simple equations for such interconversion (eq 2).

$$Pb_4Zr_2(O^iPr)_{16} \underset{?}{\overset{\mp Pb_2(O^iPr)_4 \pm Zr_2(O^iPr)_8}{\rightleftharpoons}} Pb_2Zr_4(O^iPr)_{20} \quad (2)$$

The stoichiometries of the serpentine compounds suggest another approach to their possible interconversion. Reaction according to eq 3 in C_6D_6 (0.5 mL) occurs upon placing the inhomogeneous mixture in an 80 °C bath for 5 min.[16] Likewise, conversion to the zirconium-rich species (eq 4)[17] occurs upon heating the reagents briefly in the mole ratio shown.

$$Pb_2Zr_4(O^iPr)_{20} + 6Pb(O^iPr)_2 \rightarrow 2Pb_4Zr_2(O^iPr)_{16} \quad (3)$$

$$Pb_4Zr_2(O^iPr)_{16} + 6Zr(O^iPr)_4 \rightarrow 2Pb_2Zr_4(O^iPr)_{20} \quad (4)$$

The syntheses of these products also extend to direct reaction of the two alkoxide species in correct stoichiometric proportions with gentle warming in benzene (eqs 5 and 6).

$$4Pb(O^iPr)_2 + 2Zr(O^iPr)_4 \rightarrow Pb_4Zr_2(O^iPr)_{16} \quad (5)$$

$$2Pb(O^iPr)_2 + 4Zr(O^iPr)_4 \rightarrow Pb_2Zr_4(O^iPr)_{20} \quad (6)$$

The overall picture which emerges from this work and the varied synthetic procedures employed is that these molecules are made up of the neutral substructural units ("building blocks") $Zr_2(O^iPr)_8$, $PbZr(O^iPr)_6$ and $Pb_2(O^iPr)_4$. It is interesting that each of the first two units in effect "solubilizes" $Pb(O^iPr)_2$ and causes Pb in that polymer to decrease its coordination number by 1, in order to donate its alkoxide bridge to Zr or to another Pb.

The alternative octahedral (*closo*) form for these six-metal species is not adopted because it would lead to higher metal coordination numbers for Pb, which is less compatible with a stereochemically-active lone pair. It is also clear that O^iPr and O^tBu (*cf.* $PbZr(O^tBu)_6$) yield vastly different Pb/Zr heterometallic aggregates. This we attribute to the bulkier O^tBu group disfavoring the higher Pb(II) coordination numbers present in the Pb_4Zr_2 and Pb_2Zr_4 species reported here. While M_2M' closed triangles are not adopted (*cf.* $[BaZr_2(O^iPr)_{10}]_2$), it is clear from Figures 1 and 2 that this is due to the lone pair on Pb1 and its inhibition to forming the additional $\mu\text{-}O^iPr$ linkages necessary for a closed triangle.

Acknowledgment. This work was supported by the Department of Energy. We thank Professor L. G. Hubert-Pfalzgraf for useful exchange of information on the $Zr/Pb(II)/O^iPr$ system and the reviewers for useful comments.

Supplementary Material Available: Listings of crystallographic data and refinement details and positional and thermal parameters for $Pb_4Zr_2(O^iPr)_{16}$ and $Pb_2Zr_4(O^iPr)_{20}$ (5 pages). Ordering information is given on any current masthead page.

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(14) Crystallographic data (−174 °C): $a = 16.996(6)$ Å, $b = 10.014(3)$ Å, $c = 24.924(9)$ Å, $\beta = 105.86(1)°$ with $Z = 2$ in space group $P2_1/c$. $R(F) = 0.0913$ for 3079 reflections with $F > 2.33\sigma(F)$.

(15) $[Pb_2Zr_4(O^iPr)_{20}]$: ^1H NMR (toluene-d_8, 25 °C, 300 MHz) δ 4.67 (br septet, 20H, $^3J_{H-H} = 6$ Hz), 1.44 (d, 120H, $^3J_{H-H} = 6$ Hz); ^1H NMR (−60 °C) δ 6.21 (br, 2H), 4.94 (br, 4H), 4.73 (br septet, 2H, $^3J_{H-H} = 6$ Hz), 4.58 (br septet, 12 H, $^3J_{H-H} = 6$ Hz), 1.74−1.47 (br, 120H). Satisfactory C and H analyses were obtained.

(16) Note that thermal decomposition of lead alkoxides to oxo species has been observed when these are heated for extended periods of time. See: (a) Gaffney, C.; Harrison, P. G.; King, T. J. *J. Chem. Soc., Chem. Commun.* **1980**, 1251. (b) Papiernik, R.; Hubert-Pfalzgraf, L. G.; Chaput, F. *J. Non-Cryst. Solids* **1992**, *147*, 36.

(17) A 79% yield of $Pb_2Zr_4(O^iPr)_{20}$ is isolated by adding $Pb[N(SiMe_3)_2]_2$ (2 mmol) to $Zr_2(O^iPr)_8(^iPrOH)_2$ (2 mmol) in pentane.