2240 *Inorg. Chem.* **1999,** *38,* 2240

An Improved Interpretation of a Lead Oxo Isopropoxide

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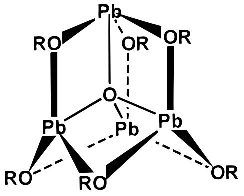
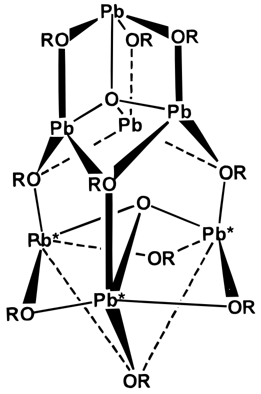
We reported recently[1] the ^{1}H, ^{13}C, ^{17}O and ^{207}Pb NMR characterization of a compound (**A**), believed to have the adamantane-like structure **I**,[2,3] whose C and H elemental analyses agreed "satisfactorily" with the formula $Pb_4O(O^iPr)_6$, but whose spectral features defied explanation with this formula. Subsequently, the ^{1}H, ^{13}C and ^{207}Pb NMR and crystal structure were reported for a molecule of formula $Pb_7(O)_2(OSiMe_3)_{10}$;[4] it has approximate C_{3v} symmetry (**II**). The ^{1}H NMR of our product **A** at −100 °C possesses equal intensity peaks (i.e., 3:3:3) consistent with C_{3v} symmetry. Also, there are three ^{207}Pb chemical shifts having an intensity ratio of 1:3:3 (1356, 996, 637 ppm, respectively) and satellites indicating Pb−Pb coupling between the 1356 and the 637 ppm signals. Further, the sharper of the *two* ^{17}O NMR signals for the μ-oxo groups shows *second-order* satellites from coupling to Pb. Considering these data, we now suggest that the elemental analysis mislead our assignment of the chemical formula and that what we characterized as **I** is in fact $Pb_7(O)_2(O^iPr)_{10}$, of structure **II**. The calculated and observed elemental analyses are shown below:



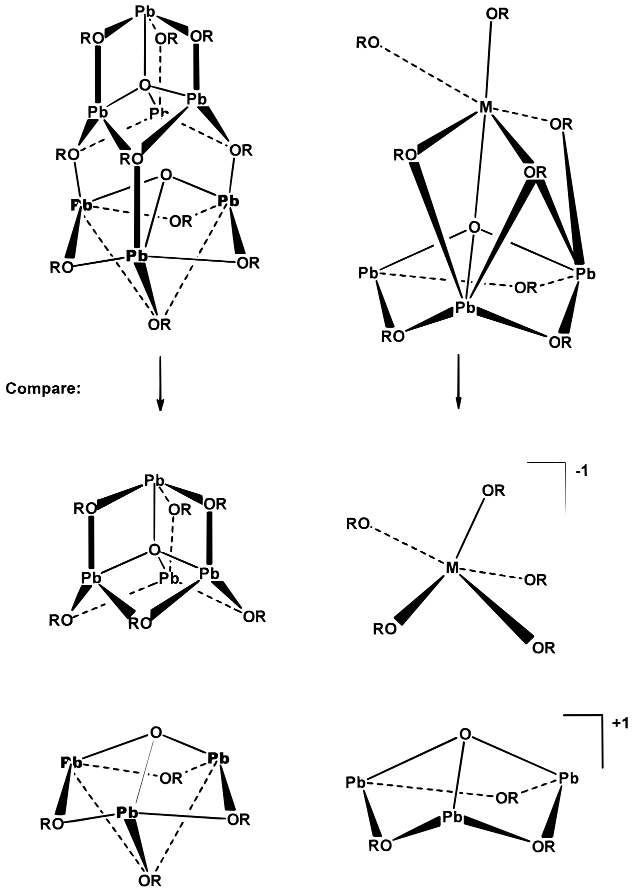
I



II

$Pb_4O(O^iPr)_6$ (**I**):	% C: 18.02,	% H: 3.53
$Pb_7(O)_2(O^iPr)_{10}$:	% C: 17.38,	% H: 3.40
Found:	% C: 18.02,	% H: 3.39

Scheme 1



Our isolated **A** is actually a product of slight (compare eqs 1 and 2) over-hydrolysis (by $^{1}/_{7}$ mol of H_2O per 4 Pb); in addition

$$4Pb(OR)_2 + H_2O \rightarrow Pb_4O(OR)_6 + 2ROH \tag{1}$$

$$7Pb(OR)_2 + 2H_2O \rightarrow Pb_7(O)_2(OR)_{10} + 4ROH \tag{2}$$

to this being simply a correction of our earlier report, this discovery proves the existence of molecular hydrolysis products with degrees of hydrolysis between 0.25 ($Pb_4O(OR)_6$) and 0.67 ($Pb_6O_4(OR)_4$): i.e., 0.286 for $Pb_7(O)_2(OR)_{10}$. Indeed, the structure of $Pb_7(O)_2(OR)_{10}$ is essentially an adduct of $Pb_4O(OR)_6$ and $Pb^*_3O(OR)_4$ (see the asterisks in **II**), the latter having a degree of hydrolysis of 0.33. We have already reported the synthesis of a fragment very similar to the latter structure in the compound $Pb_3ZrO(O^tBu)_8$ which is in fact $[Pb_3(\mu_3\text{-}O)(O^tBu)_3{}^+][Zr(O^tBu)_5{}^-]$, as shown in Scheme 1.[5] Such adduct formation raises the coordination number of Pb* in **II** from 4 to 5 and presumably provides the driving force for the aggregation.

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