Inorganica Chimica Acta, *165* (1989) 1–2

Heavy Main Group Molecular Precursors of Oxides: Volatile and Soluble Lead(II) Alkoxides and Oxoalkoxides

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(Received February 20, 1989)

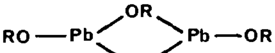
A variety of new materials of technological value – piezoelectric ceramics, opticoelectronic devices [1] and also superconductors [2] – consist of multicomponent oxides containing lead. Solid-state synthesis of these multicomponent materials is often particularly stringent, due to the volatility of the lead(II) oxide and/or the formation of highly stable perovskite intermediates [2, 3]. Synthesis of such materials by chemical routes (sol-gel technology or chemical vapor phase decomposition), using molecular precursors, might overcome some of these problems [4].

However, alkoxides, which are often the most suitable precursors of oxides, remain practically unknown for lead(II). Poorly characterized, insoluble polymeric alkoxides of formula $[Pb(OR)_2]_m$ have been reported to form through the disproportionation of alkyl derivatives (for R = Me) [5] or substitution reactions from $Pb(\eta^5\text{-}Cp)_2$ (for R = Me, ^tBu) or from PbX_2 [6] (X = I, NO_3 for R = Me). The formation of $Pb(OPr^i)_2$, starting from lead(II) acetate, has been claimed on the basis of its hydrolysis product, but it has not been isolated [7]. Monomeric $Pb(OAr)_2$ (Ar = 2,6-di-tert-butyl-4-methylphenyl) has been obtained by metathesis reaction of either $PbCl_2$ or $Pb[N(SiMe_3)_2]_2$ [8].

The discovery of a new family of superconductors based on lead(II), $Pb_2Sr_2ACu_3O_{8+\delta}$ (A is a lanthanide or a mixture of L + Sr or Ca) [2], prompts us to report the synthesis and characterization of soluble as well as volatile lead(II) oxide precursors $[Pb(OBu^t)_2]_2$ and $Pb_4O(OBu^t)_6$ [9].

Various routes to lead(II) alkoxides with classical alkoxo groups (R = Et, Pr^i, Bu^t) using $PbCl_2$, $Pb(\eta^5\text{-}Cp)_2$, $Pb(OAc)_2$ and $Pb[N(SiMe_3)_2]_2$ have been estimated. Butoxide derivatives obtained via the lead bistrimethylsilylamide or lead acetate routes appear to be the most interesting precursors.

The formation of homoleptic lead(II) alkoxides was limited to $[Pb(OBu^t)_2]_2$ (1), formed together with $Pb_4O(OBu^t)_6$ (2) by reaction between $Pb[N(SiMe_3)_2]_2$ and the alcohol in dilute pentane medium at low temperature (–70 °C). Purification of 1 was achieved by recrystallisation in hexane at –20 °C (~40%). The yield of $Pb_4O(OBu^t)_6$ was quantitative at high concentration and/or room temperature. This oxoalkoxide can also be obtained by metathesis between $Pb(OAc)_2$ and $NaOBu^t$ in refluxing toluene. The latter reaction proceeds in the same way with $NaOPr^i$, and no $Pb(OPr^i)_2$ was isolated [9].



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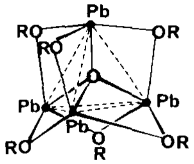

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The two products were characterized by elemental analysis, molecular weight data, IR and NMR spectroscopy. $[Pb(OBu^t)_2]_2$ and $Pb_4O(OBu^t)_6$ are white air-sensitive solids, both highly soluble in the usual solvents, including hexane. Compound 1 was found to be dimeric in benzene solution (M_{exp} 648 ± 65; calc. 353, Signer method [10]), as also found for the tin and germanium analogues [11]. They are also sublimable. However, sublimation of $[Pb(OBu^t)_2]_2$ results in its conversion into the more stable oxoalkoxide $Pb_4O(OBu^t)_6$. This conversion is partial at 110 °C (10^{-4} mmHg), but becomes quantitative under more drastic conditions (~200 °C at 10^{-2} mmHg). By contrast, $Pb_4O(OBu^t)_6$, slightly less volatile than 1 (sublimation 130 °C, 10^{-4} mmHg), can be sublimed without decomposition. Thermal gravimetry analysis confirms the conversion of 1 into 2, with the loss of dibutyl ether, according to eqn. (1)

$$2[Pb(OBu^t)_2]_2 \longrightarrow Pb_4O(OBu^t)_6 + Bu^t{}_2O \qquad (1)$$

The volatility of 2 also allows its isolation in an analytically pure form and in moderate yield (~40%) from reaction between $Pb(OAc)_2$ and $NaOBu^t$, although this reaction is non-selective and proceeds via acetatoalkoxides.

IR and ^1H NMR spectra offer less structural information, as they display mainly the pattern of the alkoxo group. For both compounds, all butoxo groups appear equivalent in the proton spectra and the exchange between the terminal and the bridging groups of 1 remains fast, even at low temperature (–60 °C). By contrast, ^{207}Pb NMR seems to be a convenient tool for lead(II) alkoxides. Despite attractive properties (I = 1/2 and adequate natural abundance ≃20%), lead NMR remains limited and mainly restricted to lead(IV) alkyl derivatives [12]. One single, sharp signal is observed for 1 and for 2. The high sensitivity of ^{207}Pb NMR to the stereochemistry around the metal is illustrated by the large variation

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0020-1693/89/$3.50

in the chemical shifts observed between $[Pb(OBu^t)_2]_2$ and $Pb_4O(OBu^t)_6$: 4152 and 5032 ppm, respectively (chemical shifts are given for C_6D_6 solution, relative to $Pb(NO_3)_2$ as an external reference).

The analytical and spectroscopic properties of $Pb_4O(OBu^t)_6$ are in agreement with an adamantane-like structure, as previously established for $Pb_4O(OSiPh_3)_6$ [13], in which the lead atoms have a distorted trigonal bipyramidal environment. Condensation to oxoalkoxides is favored for lead(II) alkoxides, especially for less bulky groups ($R = Pr^i$, Et), giving species such as $Pb_nO_{n-3}(OR)_6$ ($n = 4, 5, 6 \ldots$) [14].

The novel alkoxides $[Pb(OBu^t)_2]_2$ and $Pb_4O(OBu^t)_6$ have been used as precursors for the synthesis using sol-gel techniques of the pure perovskite phase of $PbMg_{1/3}Nb_{2/3}O_3$ (PNM), a ceramic with interesting dielectric and ferroelectric properties [15]. Further studies are in progress.

Acknowledgements

We are grateful to the CNRS GRECO 'Précurseurs Moléculaires de Matériaux Inorganiques' for financial support, and to Dr B. Septe for obtaining the lead NMR spectra.

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