

## Lead(II) Oxoalkoxides as Complex Ligands: Synthesis and Molecular Structure of the First Heterometallic Oxoalkoxide, $\text{Pb}_6\text{Nb}_4(\mu_4\text{-O})_4(\mu_3\text{-OEt})_4(\mu_2\text{-OEt})_{12}(\text{OEt})_8$

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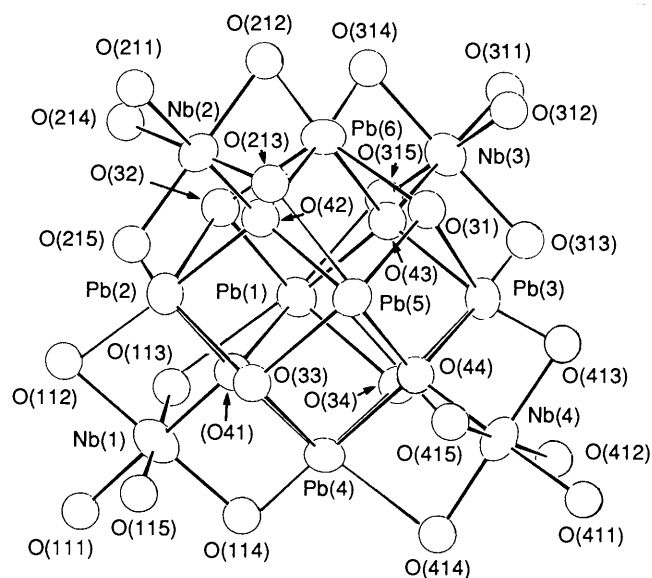
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The compound  $\text{Pb}_6\text{Nb}_4(\mu_4\text{-O})_4(\mu_3\text{-OEt})_4(\mu_2\text{-OEt})_{12}(\text{OEt})_8$  has been obtained in 46% yield by reaction between  $\text{Pb}_4\text{O}(\text{OEt})_6$  and  $\text{Nb}_2(\text{OEt})_{10}$  in ethanol at room temperature; its X-ray structure analysis shows an octahedral  $\text{Pb}_6$  framework, four of the faces of this octahedron being capped by a  $\mu_4$ -oxo ligand connected to a  $\text{Nb}(\text{OEt})_5$  moiety, and the overall structure can be viewed as a complex of the tetradentate ligand  $\text{Pb}_6(\mu_3\text{-O})_4(\mu_3\text{-OEt})_4$ .

Multicomponent oxides display a large range of properties, and are thus of high interest for advanced materials such as superconductors, ferroelectrics, *etc.*<sup>1</sup> Chemical routes using molecular precursors, such as the sol-gel process or vapour phase decomposition techniques, appear to be promising alternatives to the traditional solid-state synthesis for a better control of the properties required.<sup>2</sup> Alkoxides are often considered as the most suitable precursors of oxides, especially for the hydrolysis-polycondensation process. This interest arises mainly from the lability of their co-ordination sphere, which allows the design of precursors for tailored applications, as well as from the ability to form heterometallic (double) alkoxides by simple mixing of the monometallic derivatives, and thus leads to a homogeneity of multicomponent systems at a molecular level. However, structural data of heterometallic alkoxides remain scarce,<sup>3</sup> especially for bimetallic alkoxides in which no alkaline or alkaline rare-earth metal is involved. There are even fewer structural data for heterometallic oxoalkoxides, which may result from direct reaction between monometallic derivatives or by hydrolysis of a heterometallic alkoxide.

We now report the synthesis and structural characterization of  $\text{Pb}_6\text{Nb}_4(\mu_4\text{-O})_4(\mu_3\text{-OEt})_4(\mu_2\text{-OEt})_{12}(\text{OEt})_8$ , the first example, to our knowledge, of a heterometallic oxoalkoxide involving a heavy main group element and a transition metal



**Figure 1.** ORTEP view of  $\text{Pb}_6\text{Nb}_4\text{O}_4(\text{OEt})_{24}$  showing the  $\text{Pb}_4\text{Nb}_4\text{O}_{28}$  core and the atom numbering scheme. Selected bond lengths (Å):  $\text{Pb}-\mu_4\text{-O}$  2.38(8)(av.),  $\text{Pb}-\mu_3\text{-O}$ (av.) 2.47(8),  $\text{Pb}-\mu_2\text{-O}$ (av.) 3.0(1),  $\text{Nb}-\text{O}$ (av.) 2.0(1).

characterized by X-ray diffraction. Furthermore, its composition is in agreement with the stoichiometry required by the synthesis of  $\text{PbNb}_{2/3}\text{Mg}_{1/3}\text{O}_3$ , a piezoelectric ceramic.<sup>4</sup>

Reaction between a suspension of the lead(II) oxoalkoxide  $\text{Pb}_4\text{O}(\text{OEt})_6$  and  $\text{Nb}_2(\text{OEt})_{10}$  in ethanol at 30 °C led to the almost immediate dissolution of the lead derivative and to the isolation, after concentration and cooling, of a crystalline product isolated in 46% yield. Its high solubility, even in pentane, and analytical as well as spectroscopic data (IR, <sup>1</sup>H and <sup>207</sup>Pb NMR) indicated the formation of a heterometallic species.† <sup>207</sup>Pb NMR data were especially useful. Formation of the same heterometallic Nb–Pb species, either from  $[\text{Pb}(\text{OEt})_2]_2$  or from  $\text{Pb}_4\text{O}(\text{OEt})_6$ , is shown in the <sup>207</sup>Pb{<sup>1</sup>H} spectra by a notable shift to higher frequencies (around 2800 ppm) with respect to that of the homometallic derivatives (4181 and 4977 ppm respectively),<sup>5</sup> and suggests an increase in the co-ordination number<sup>6</sup> of the lead atoms [relative to  $\text{Pb}(\text{NO}_3)_2$  used as an external reference].

The heterometallic nature of (1) was confirmed by an X-ray structure determination.‡ The molecular structure of the decanuclear species  $\text{Pb}_6\text{Nb}_4\text{O}_4(\text{OEt})_{24}$  (Figure 1) includes an octahedral  $\text{Pb}_6$  framework. Four of the faces of this octahedron are capped by a  $\mu_4$ -oxo ligand connected to a  $\text{Nb}(\text{OEt})_5$  moiety and to three lead atoms. The remaining faces of the lead octahedron are capped by  $\mu_3$ -ethoxo groups. The structure of the  $\text{Pb}_6$  octahedron bears some resemblance to that of the lead(II) oxoalkoxide  $\text{Pb}_6(\mu_3\text{-O})_4(\mu_3\text{-OPr})_4$ <sup>7</sup> or the hydroxide  $\text{Pb}_6\text{O}_4(\text{OH})_4$ .<sup>8</sup> However, the presence of the  $\text{Nb}(\text{OEt})_5$  moiety allows the lead to attain hexa-co-ordination, and the heterometallic oxoalkoxide can be viewed as the

$\text{Pb}_6\text{O}_4(\text{OR})_4$  unit acting as a tetradentate oxo ligand towards the Lewis acid  $\text{Nb}(\text{OEt})_5$ , and thus formulated as  $\text{Pb}_6\text{O}_4(\text{OEt})_4[\text{Nb}(\text{OEt})_5]_4$ . In addition to the co-ordination by the oxo functionality, each niobium atom is linked to three lead atoms by a doubly bridging ethoxo group, while two additional terminal alkoxo groups allow the metal to reach its most common co-ordination number of six. All lead atoms are hexa-co-ordinated by oxygen atoms: two  $\mu_4$ -oxo ligands, two triply bridging, and two doubly bridging alkoxo groups. The Pb–O distances follow the pattern  $\text{Pb}-\mu_4\text{-O} < \text{Pb}-\mu_3\text{-OR} < \text{Pb}-\mu_2\text{-OR}$  with values ranging from 2.28(8) to 3.1(1) Å ( $\Sigma r_{\text{cov}} = 2.20$  Å). The Nb–O distances are shorter [ $\text{Nb}-\text{O}_{\text{av}} 2.0(1)$  Å,  $\Sigma r_{\text{cov}} = 2.07$  Å], but their poor values do not allow comparison between the oxo ligands and/or the structurally different alkoxo ones. The oxygen environment of the various metallic atoms: octahedron for the niobium, trigonal prismatic for lead, is only slightly distorted. The  $\text{Pb}_6$  octahedral core is quite regular (Pb–Pb distances ranging from 3.88 to 3.93 Å); no metal–metal bonding is involved (sum of the covalent radii 2.94 Å).

$\text{Pb}_6\text{Nb}_4(\mu_4\text{-O})_4(\mu_3\text{-OEt})_4(\mu_2\text{-OEt})_{12}(\text{OEt})_8$  displays a complex behaviour in solution: different molecular species in dynamic equilibrium were obtained upon its redissolution even in a non-polar medium such as toluene (singlets at 2896, 2855, and 2826 ppm in the <sup>207</sup>Pb{<sup>1</sup>H} spectra). The variation in the relative areas of these singlets (all vary independently and thus belong to different molecular species) as a function of the molar ratio (1):  $[\text{Nb}(\text{OEt})_5]_2$  suggests that disproportionation reactions occur in solution, as sometimes observed for heterometallic alkoxides. Further evidence for dissociation reactions comes from the detection of uncomplexed  $[\text{Nb}(\text{OEt})_5]_2$  (IR; <sup>1</sup>H and <sup>13</sup>C NMR) in solution. <sup>1</sup>H and <sup>13</sup>C NMR spectra provide information mainly about the different structural OEt types, independently of the various Nb/Pb molecular species present in solution. The <sup>13</sup>C{<sup>1</sup>H} spectra show four types of methyl as well as methine groups at room temperature, tentatively attributed to the triply bridging, doubly bridging, and terminal ethoxo groups of the various heterometallic species and to those of the homometallic  $[\text{Nb}(\text{OEt})_5]_2$  alkoxide. <sup>1</sup>H NMR spectra are coalesced at room temperature, but at –60 °C four types of CH<sub>2</sub> groups are observed, in agreement with the <sup>13</sup>C{<sup>1</sup>H} spectra.

Dissociation reactions are favoured by dilution and are supported by the fact that the Lewis acid  $\text{Nb}(\text{OEt})_5$  displays a limited co-ordination chemistry.<sup>9</sup> Its dimerisation is the favoured thermodynamic process; the formation of complexes is restricted to hard N donors, alcohols, and ligands having oxo functionalities such as phosphoryl derivatives or amine N-oxides. Displacement of the  $\text{Nb}(\text{OEt})_5$  moiety could be achieved by using an excess of pyridine, leaving the poorly soluble homometallic  $\text{Pb}_6\text{O}_4(\text{OEt})_4$  alkoxide.

Low-valent main-group alkoxides or oxoalkoxides appear to be complex ligands; the lone pair of the metal might act as a Lewis base towards transition metal carbonyl derivatives,<sup>10</sup> while the electronic density available on alkoxo groups or external oxo ligands can be used to build up heterometallic alkoxides.  $\text{Pb}_6\text{O}_4(\text{OEt})_4[\text{Nb}(\text{OEt})_5]_4$  represents the first example of an alkoxide adduct of a *closo*-oxoalkoxide. Stabilisation of lead(II) derivatives with anionic oxygen donor ligands as hexanuclear clusters seems strongly favoured,<sup>11</sup> and the addition of  $[\text{Nb}(\text{OEt})_5]_2$  to  $\text{Pb}_4\text{O}(\text{OEt})_6$  promotes its evolution to a hexanuclear cluster, even under mild conditions.

Further studies to gain insight into the reactivity of (1) in solution and its behaviour towards hydrolysis are in progress.

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†  $\text{Pb}_4\text{O}(\text{OEt})_6$  (0.53 g) and  $\text{Nb}_2(\text{OEt})_{10}$  (0.604 g) yielded crystalline  $\text{Nb}_4\text{Pb}_6\text{O}_4(\text{OEt})_{24}$ . Satisfactory microanalysis (C, H, Nb, Pb). *Selected spectroscopic data*: IR ( $\text{cm}^{-1}$ ; Nujol): 584, 524s, 472m, and 416m ( $\nu \text{M}-\text{OR}$ ); <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 0.003 M, –60 °C):  $\delta$  1.24 (t, J 7 Hz), 3.82 (m), 4.26 (q), 4.38 (q, J, 7 Hz), and 4.50 (m); <sup>207</sup>Pb NMR [ $\text{C}_7\text{D}_8$ ; ppm relative to  $\text{Pb}(\text{NO}_3)_2$ ] 2828, 2854, and 2898; <sup>13</sup>C{<sup>1</sup>H} NMR 19.8, 20.5, 20.7, 21.1 ( $\text{CH}_3$ ), 60.0, 66.7, 67, 67.2 ( $\text{CH}_2$ ).

‡ *Crystal data*:  $\text{C}_{48}\text{H}_{120}\text{O}_{28}\text{Nb}_4\text{Pb}_6$ ,  $M = 2760.3$ , monoclinic, space group  $P2_1/n$ ,  $a = 15.444(5)$ ,  $b = 23.403(5)$ ,  $c = 23.572(8)$  Å,  $\beta = 92.630(3)^\circ$ ,  $U = 8511(11)$  Å<sup>3</sup>,  $D_c = 2.15$  g cm<sup>–3</sup> for  $Z = 4$ ,  $\mu(\text{Mo}-K_\alpha) = 17.51$  cm<sup>–1</sup>. The crystals were very unstable, and required handling *in vacuo*. After many unsuccessful attempts, a crystal of poor quality was sealed in a Lindemann capillary *in vacuo* and set up on a CAD-4 diffractometer. 8814 Reflexions ( $3^\circ < 2\theta < 40^\circ$ ) were collected at room temperature. The intensities of two standard reflections monitored every hour decayed uniformly to final values about 40% less than the initial ones; the data were scaled accordingly. 2647 Data [ $I > \sigma(I)$ ] were used to solve the structure. Niobium and lead atoms were found using SHELXS.<sup>12</sup> Oxygen atoms were located on successive difference electron density maps. Carbon atoms of the ethyl groups could not be unambiguously located, and they have not been included in subsequent refinements. The structure was refined by least-squares techniques with approximation (in three blocks) to the normal matrix using CRYSTALS.<sup>13</sup> Only 1660 reflexions with  $I > 3\sigma(I)$  were used to refine the structure:  $R = 0.0740$ ,  $R_w = 0.0889$ , 178 variables. In view of the poor quality and the small amount of data available, only Nb and Pb atoms were refined anisotropically. Oxygen atoms were given refinable overall isotropic thermal parameters. Anomalous dispersion terms were applied. Empirical absorption corrections (Psi scan),<sup>14</sup> DIFABS<sup>15</sup> were used. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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