Complexes of Early Transition Metal Alkoxides: Molecular Structure of $Ti(O\textit{i}Pr)_4[OPb_4(\textit{t}BuN)_3]$

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Received January 7, 1997

Keywords: Titanium / Lead / Alkoxides / Amides / Mixed-metal species

The reaction between $Ti(O\textit{i}Pr)_4$ and $[Pb(N\textit{t}Bu)_2SiMe_2]$ (1) in refluxing THF afforded the complex $Ti(O\textit{i}Pr)_4[OPb_4(N\textit{t}Bu)_3]$ (2) which has been characterized by X-ray diffraction studies and by ^1H- and ^{13}C-NMR spectroscopy. Titanium is five coordinate and it displays a trigonal bipyramidal stereochemistry with the $Pb_4(\textit{t}BuN)_3O$ cage ligand bonded to titanium through the oxygen atom and occupying an apical position. The origin of the cubane lead ligand is discussed.

Numerous electroceramics are based on multi-metallic oxides containing lead. Chemical routes involve reactions between metal alkoxides, alkoxides and carboxylates or alkoxides and β-diketonates, with the latter approach especially used for transformations occurring in the vapour phase[1]. Reactions between alkoxides and amides have been investigated for the formation of mixed-metal species using the enhanced acidity of coordinated alcohol molecules[2]. Mixed-metal aminoalkoxides are scarce[3], although such species could display volatility for MOCVD applications and/or induce different characteristics in the products resulting from hydrolyticpolycondensation processes due to the presence of the amine as a byproduct.

Lead amides in which the lead is unsaturated should be quite reactive[4]. $[Pb(N\textit{t}Bu)_2SiMe_2]$ was allowed to react with titanium isopropoxide and we report here the results of these investigations.

Results and Discussion

It was necessary for the reaction between $Ti(O\textit{i}Pr)_4$ and $[Pb(N\textit{t}Bu)_2SiMe_2]$ (1)[5] to be carried out in refluxing THF. After about 4 h a change in color from orange to yellow occurred, providing evidence of reaction, and the precipitation of lead indicated some degree of decomposition. Yellow crystals of compound **2**, containing lead and titanium, were isolated in low yield from hexane. The ^1H-NMR and FT-IR spectra of **2** indicate the absence of silicon moieties and thus the absence of **1**.

Single-crystal X-ray diffraction investigations proved difficult due to the instability of the crystals, but established that compound **2** is actually a complex of $Ti(O\textit{i}Pr)_4$ with the lead-containing cage ligand $Pb_4O(N\textit{t}Bu)_3$, the O-donor site ensuring coordination as depicted in Figure 1. Titanium is five-coordinate and has distorted trigonal bipyramidal stereochemistry, with the cage ligand in one of the apical positions. Titanium–oxygen bond lengths are in the range 1.76(5) to 2.09(3) Å and, as anticipated, the coordination bond Ti–O(1) is the longest. The other apical bond, Ti–O(5) is the shortest and this is probably the result of a *trans* effect. All lead atoms have a trigonal stereochemistry. The structural data are in agreement with the values reported in the literature[6,4].

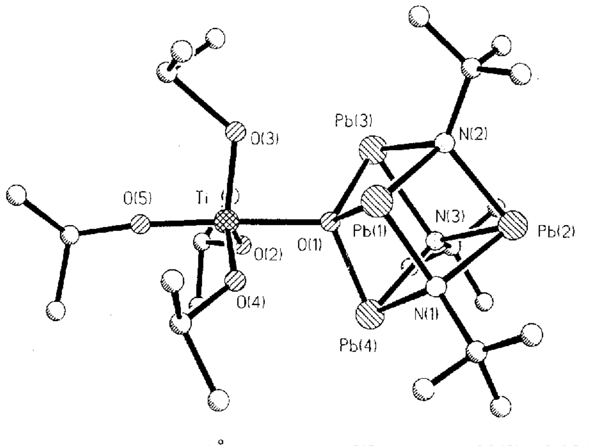

Figure 1. A graphical representation of compound $(\textit{i}PrO)_4Ti[OPb_4(N\textit{t}Bu)_3]$ (**2**)[a]

[a] Selected bond lengths [Å] and angles [°]: Pb–O 2.22(3)–2.23(3), Pb(1,2,4)–N 2.22(4)–2.35(4), Pb(2)–N 2.20(4)–2.35(4), Ti–O(1) 2.09(3), Ti–O(5) 1.76(5), Ti–O(2,3,4) 1.82(3)–1.84(3); Pb–O–Pb 104.1(13)–104.5(13), O(1)–Ti–O(5) 1.77(2), O(1)–Ti–O(2,3,4) 81(2)–84(2), N–Pb(2)–N 79.3(14)–83.0(14), O–Pb–N 76.2(12)–77.7(12), N–Pb(1,3,4)–N 77.7(14)–80.8(14).

The ^1H-NMR data of **2** in C_6D_6 solutions are consistent with the solid state structure. One type of signal is observed for the *t*Bu groups of the lead ligand. The isopropyl groups of the $Ti(O\textit{i}Pr)_4$ moiety appear magnetically equivalent (multiplet at $\delta = 4.99$) for the CH groups and at lower field than those of the uncomplexed alkoxide (multiplet at $\delta = 4.42$). These signals are independent of the dilution, thus

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excluding dissociation. A ^{207}Pb-NMR signal could not be observed for **2**. Similar difficulties in detecting Pb-NMR signals were encountered for other species in which lead is linked to nitrogen, such as $Pb[N(SiMe_3)_2]_2$.

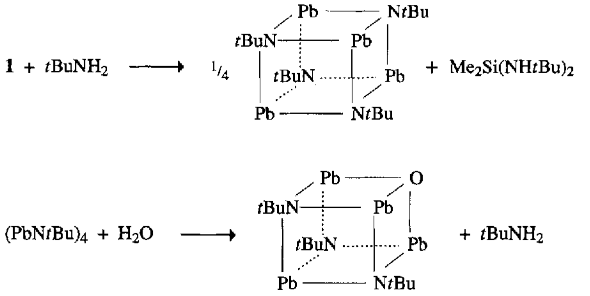
Examples of stable, isolable complexes of homoleptic early transition metal akoxides remain scarce, especially in the absence of fluorinated alkoxide[7] or aryloxide ligands[8]. Their stabilisation requires either hydrogen bonding[9] or hard O- or N-donors, essentially phosphorus or amine oxide derivatives[10]. The formation of complex **2**, and thus coordination via a trigonal oxo site of a Pb_3O moiety, is reminiscent of that in the complex $Pb_6(\mu_4\text{-}O)_4(\mu_3\text{-}OEt)_4[Nb(OEt)_5]_4$[11]. However, the formation of the hexanuclear lead species results from the self-assembly of $Pb_4O(OEt)_6$, and the Nb–Pb complex is thus isolated in a higher yield (46%) than for **2**. A quite similar metal complex of a cubane-like metal oxo amide $Sn_4(NtBu)_3O{-}AlCl_3$, has been described[12].

As shown in Figure 1, compound **2** cannot result from the direct reaction of **1** with $Ti(OiPr)_4$ but requires the formation of $Pb_4O(NtBu)_3$. Generation of this species, analogous to $Sn_4O(NtBu)_3$[12] obtained by a different procedure, is due to adventitious alcoholysis and hydrolysis. The following reactions have to be considered:

The formation of the tetrameric iminoplumbylene $(PbNtBu)_4$ according to eq. 2 has been established previously[5]. This reaction scheme is supported by the following observations: (i) no reaction was observed on using freshly distilled solvents and/or reactants [i.e. no 2-propanol coming from partial hydrolysis of $Ti(OiPr)_4$]; (ii) addition of $tBuNH_2$ and water to **1** before its reaction with $Ti(OtPr)_4$ increases the yield of **2** to 21% by the in situ formation of the $Pb_4O(NtBu)_3$ species, as indicated by FT-IR [the ν(Si–N) absorption bands at 930 and 660 cm^{-1} have disappeared after aminolysis, an additional band ν(Pb–O) is observed at 576 cm^{-1} after hydrolysis]; (iii) formation of $[Pb(OiPr)_2]$ as indicated in eq. 1 is confirmed by ^{207}Pb-NMR spectra of the reaction mixture. The only resonance detected (δ = 3865) corresponds to that of the mixed-metal isopropoxide $Pb_2Ti_2O(OiPr)_{10}$, **3**, obtained previously in our laboratory by reaction of $Ti(OiPr)_4$ with $[Pb(OiPr)_2]_\infty$ under reflux[13]. Compound **3** is thermodynamically more stable than **2**. Thus, whereas addition of 2-propanol favors the formation of **2**, the concomitant formation of $[Pb(OiPr)_2]$ (in significant amounts) precludes the isolation of **2**, since **3** is formed.

Controlled hydrolysis experiments with a hydrolysis ratio h = 100 (h = moles H_2O/moles PbTi precursor) have been performed on **1**, **2**, and on an equimolar mixture of **1** and $Ti(OiPr)_4$ in THF. TGA data of the resulting powders are featureless, showing weight losses of 9–13% below 300°C. Hydrolysis of **1** in THF at room temperature gave the crystalline oxohydroxide $Pb_6O_4(OH)_4$, which was converted into yellow lead oxide (massicot) at 700°C. The same oxide was obtained directly in its crystalline form when the hydrolysis was performed under reflux for 15 h. The hydrolysis behaviour of **1** is thus comparable to that of lead alkoxides for room temperature experiments, but, in contrast, gives pure and crystalline massicot under reflux; under similar conditions, the hydrolysis of $Pb(OCHMeCH_2NMe_2)_2$ afforded a mixture of red and yellow lead oxides (96:4%)[14]. Hydrolysis of **2** in refluxing THF gave an amorphous material together with crystalline yellow lead oxide. Subsequent thermal treatment led to the formation of quadratic $PbTiO_3$ at 550°C and finally to the $PbTiO_3$ perovskite at 650°C. Similar results, as shown by thermogravimetric analysis and powder X-ray diffraction, are obtained by cohydrolysis of **1** and $Ti(OiPr)_4$, but no crystalline material was observed for the initial powder. The perovskite is only stable at high temperature and is converted into quadratic $PbTiO_3$ by cooling to room temperature.

$$\mathbf{1} + 4\,HOiPr \longrightarrow [Pb(OiPr)_2]_\infty + Me_2Si(OiPr)_2 + 2\,tBuNH_2 \quad (1)$$



(2)

(3)

$$Pb_4O(NtBu)_3 + Ti(OiPr)_4 \longrightarrow [PbO(NtBu)_3][Ti(OiPr)_4] \quad (4)$$

Experimental Section

All manipulations were performed under dry nitrogen using Schlenk tubes and vacuum line techniques. The solvents were purified by standard methods. $Ti(OiPr)_4$ (Hüls) was purified by distillation and $Pb(NtBu)_2SiMe_2$ was prepared according to the literature[5]. – FT-IR spectra were obtained from Nujol mulls on a Bruker IR-FT 45 spectrometer. – ^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker AC200 spectrometer. ^{207}Pb-NMR chemical shifts are given with respect to $Pb(NO_3)_2$ in D_2O. – TGA data were obtained for the hydrolyzed products with a Setaram system operating with a heating rate of 5°C/min.

Preparation of $Ti(OiPr)_4[OPb_4(tBuN)_3$. – *Procedure a:* $Ti(OiPr)_4$ (1.16 g, 4.1 mmol) in 10 ml of THF was added to a solution of $Pb(NtBu)_2SiMe_2$ (1.67 g, 4.1 mmol) in 10 ml of THF. The reaction mixture was refluxed for 15 h and concentrated. The crude brown residue was dissolved in 10 ml of hexane and the black lead precipitate (80 mg) was removed by filtration. Crystallisation of the filtrate at –20°C gave yellow crystals of **2** (0.15 g; 8% yield/Pb), which is soluble in common organic solvents including hexane.

Procedure b: $tBuNH_2$ (2.0 g, 13.7 mmol) was added to a solution of **1** (1.30 g, 3.19 mmol) in 10 ml of toluene. After stirring for 1 h at room temperature, the orange solution turned to green, H_2O (0.014 g, 0.79 mmol) in 5 ml of $tBuNH_2$ was added to the reaction mixture. After 5 h, the reaction mixture was concentrated. The crude residue was dispersed in 10 ml of hexane and $Ti(OiPr)_4$ (0.224 g, 0.79 mmol) in 5 ml of hexane was added. After filtration and crystallisation at –20°C, yellow crystals of **2** were obtained (0.3 g, 21%). – IR (cm^{-1}): $\tilde{\nu}$ = 1390 (m), 1320 (m), 1200 (m), 1172 (vs), 1125 (s), 1020 (m), 983 (s), 934 (m), 841 (m); 609 (s), 569 (s), 503 (w) (ν Ti–OR), 487 (w), 431 (w), 397 (w), 357 (ν Pb–O, ν

Table 1. Crystal data, data collection and structure refinement for **1**

Empirical formula	$C_{24}H_{55}N_3O_5Pb_4Ti$
Formula weight	1342.37
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 10.24(2) Å, α = 80.4(2)° b = 10.26(2) Å, β = 85.2(2)° c = 21.62(5) Å, γ = 60.8(2)°
Volume	1957(8) Å^3
Z	2
Density (calculated)	2.278 Mg/m^3
Absorption coefficient	17.370 mm^{-1}
$F(000)$	1220
Crystal size	0.3 × 0.2 × 0.1 mm
Diffractometer used	Siemens Stoe AED 2
Temperature	293(2) K
Wavelength	0.71069 Å
Monochromator	graphite
Scan type	ω-θ scan
Standard reflections	3 measured every 90 min
θ range for data collection	1.91–22.49°
Index range	$-10 \leq h \leq 11$, $-10 \leq k \leq 11$, $0 \leq l \leq 23$
Reflections collected	5044
Independent reflections	5044 (R_{int} = 0.0000)
Observed reflection	3204 [$I > 2\sigma(I)$]
Absorption correction	Semi-empirical from ψ-scans
Max. and min. transmission	0.9990 and 0.2153
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5044/86/174
Goodness-of-fit on F^2	1.101
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0909, $wR2$ = 0.2686
R indices (all data)	$R1$ = 0.1502, $wR2$ = 0.2895
Hydrogen atoms	geometrical
Largest diff. peak and hole	2.269 and −4.155 eÅ^{-3}

Pb–N). – ^{1}H NMR (C_6D_6): δ = 1.22 (s, 27H, CH_3, *t*Bu), 1.39 (d, J = 5.7 Hz, 24H, CH_3, *i*Pr), 4.98 (m, 4H, CH). – $^{13}\{^1H\}$ NMR (C_6D_6): δ = 28 (CH_3, *i*Pr), 33.6 (CH_3, *t*Bu), 52.2 (C), 75.5 (CH).

Hydrolysis of **1** *and of* **2**. – *Compound* **1**: Water (6.3 g, 350 mmol) in 40 ml of THF was added to **1** (1.4 g, 3.5 mmol) in 50 ml of THF. After refluxing for 15 h, 0.77 g of yellow crystalline plates were obtained and identified as PbO massicot (yellow) by powder X-ray diffraction [XRD (JSPD file 381477)].

The same procedure at room temperature gave a white powder (0.8 g) which was identified as $Pb_6O_4(OH)_4$ by XRD (JSPD file 221134). It was converted into PbO at 300°C. Between 300 and 700°C, the product is a mixture of red PbO (litharge) (JSPD file 5-0561) and massicot, and complete conversion into yellow PbO is achieved at 700°C.

Compound 2: Water (0.27 g, 14.9 mmol) in 10 ml of THF was added to **2** (0.2 g, 0.15 mmol) in 10 ml of THF. After refluxing for 15 h the product was filtered off. 0.15 g of a light brown, amorphous solid was obtained. Crystallisation of $PbTiO_3$ (quadratic form, JSPD file 6-0452) starts at 550°C. It is converted into the cubic form (JSPD file 400099) at 750°C.

Crystallography of $Ti(OiPr)_4[OPb_4(tBuN)_3]$ (Table 1)[16]: Several crystals of **2**, which were not ideal (see standard deviations of the cell constants), have been used for an X-ray diffraction study on a four-circle diffractometer (Siemens/STOE AED 2) at ambient temperature.

The centrosymmetric space group $P\bar{1}$ was detected from inspection of the reflections and confirmed during refinement (Structure solution by Patterson methods)[15]. Severe decomposition of the crystals was noted by the standard reflections. Lowering of the temperature did not lead tobetter results. Empirical absorption corrections were performed from ψ-scans, but do not seem to be good enough, as the residual electron densities were found near the heavy atoms. Anisotropic temperature factors were used only for Pb and Ti atoms, all other atoms being refined with isotropic temperature factors.

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[1] L. G. Hubert-Pfalzgraf, *Polyhedron* **1994**, *13*, 1181; G. H. Haertling, *Electronic Ceramics* (Ed.: L. M. Levinson), M. Dekker, New York, **1988**.

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

[3] P. W. Wanandi, W. M. Davis, C. C. Cummins, *J. Am. Chem. Soc.* **1995**, *117*, 2110; F. T. Edelmann, A. Steiner, D. Stalke, J. W. Gilge, S. Jagner, M. Håkansson, *Polyhedron* **1994**, *13*, 539.

[4] M. Veith, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 3; *Angew. Chem.* **1987**, *99*, 1.

[5] M. Veith, M. Grosser, *Z. Naturforsch. B* **1982**, *37*, 1375.

[6] S. Daniele, L. G. Hubert-Pfalzgraf, J. C. Daran, R. Toscano, *Polyhedron* **1993**, *12*, 2091.

[7] C. Campbell, S. G. Bott, R. Larsen, W. G. Vandersluys, *Inorg. Chem.* **1994**, *33*, 1950.

[8] M. Barnhart, D. L. Clark, J. C. Gordon, J. C. Huffman, *Inorg. Chem.* **1994**, *33*, 3487.

[9] B. Vaartstra, J. C. Huffman, P. S. Gradeff, L. G. Hubert-Pfalzgraf, J. C. Daran, S. Parraud, K. Yunlu, K. G. Caulton, *Inorg. Chem.* **1990**, *29*, 3126.

[10] L. G. Hubert-Pfalzgraf, *Inorg. Chim. Acta* **1975**, *12*, 229.

[11] R. Papiernik, L. G. Hubert-Pfalzgraf, J. C. Daran, Y. Jeannin, *J. Chem. Soc., Chem. Commun.* **1990**, 695.

[12] M. Veith, H. Lange, *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 401; *Angew. Chem.* **1980**, *92*, 408.

[13] S. Daniele, R. Papiernik, L. G. Hubert-Pfalzgraf, M. Häkansson, S. Jagner, *Inorg. Chem.* **1994**, *34*, 628.

[14] S. C. Goel, M. Y. Chiang, W. E. Buhro, *Inorg. Chem.* **1990**, *29*, 4640.

[15] G. Sheldrick, *Program for Crystal Structure Determination*, Vers. SHELX-86 and SHELX-93, Göttingen, Germany.

[16] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-406431, the names of the authors, and the journal citation.

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