Single-Source Precursors of Lead Titanate: Synthesis, Molecular Structure and Reactivity of $Pb_2Ti_2(\mu_4\text{-}O)(\mu_3\text{-}O\text{-}i\text{-}Pr)_2(\mu\text{-}O\text{-}i\text{-}Pr)_4(O\text{-}i\text{-}Pr)_4$

Stéphane Daniele, Renée Papiernik, and Liliane G. Hubert-Pfalzgraf*

Laboratoire de chimie moléculaire, URA-CNRS, Université de Nice-Sophia-Antipolis,
Parc Valrose, 06108 Nice Cédex 2, France

Susan Jagner* and Mikael Håkansson

Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Received June 24, 1994®

The reaction between $Ti(O\text{-}i\text{-}Pr)_4$ and $[Pb(O\text{-}i\text{-}Pr)_2]_\infty$ or $Pb_4O(O\text{-}i\text{-}Pr)_6$ offers the mixed-metal oxoalkoxide $Pb_2Ti_2(\mu_4\text{-}O)(\mu_3\text{-}O\text{-}i\text{-}Pr)_2(\mu\text{-}O\text{-}i\text{-}Pr)_4(O\text{-}i\text{-}Pr)_4$ (**1**) which has been characterized by crystallography at −120 °C. **1** belongs to the monoclinic space group $P2_1/n$ with $a = 10.286(14)$ Å, $b = 22.564(4)$ Å, $c = 18.709(5)$ Å, $\beta = 97.93(5)$, $V = 4301(6)$ Å^3, and $Z = 4$. Compound **1** represents the first example of a structurally characterized "single-source" precursor having a Pb:Ti stoichiometry appropriated for $PbTiO_3$. The 1:1 stoichiometry between the metals is retained by reaction between **1** and acetic acid or acetylacetone (1:2 molar ratio), $Pb_2Ti_2O(OAc)_2(O\text{-}i\text{-}Pr)_8$ (**2**) and $Pb_2Ti_2O(acac)_2(O\text{-}i\text{-}Pr)_8$ (**3**) being obtained respectively. All compounds have been isolated in high yields and were characterized by microanalysis, FT-IR and NMR (^1H, ^{13}C, and ^{207}Pb). Hydrolysis-condensation reactions of the various species giving lead titanate have been achieved.

Introduction

The lead titanate perovskite $PbTiO_3$ is an attractive ferroelectric material for applications in microelectronics (actuators, sensors, nonvolatile memories, ...).[1] Ceramic processing using chemical routes, in the vapor phase (MOCVD) or in solution (sol−gel process) are able to overcome some of the drawbacks of traditional high temperature routes, in particular poor control of the homogeneity and of the stoichiometry of the materials. The preparation of lead-containing mixed-metal oxides is especially difficult to control due to the volatility of PbO. Solution routes require soluble compounds and various precursors, based either on homometallic species or on heterometallic ("single-source") precursors have been used.[2,3] Typical experiments involve the use of hydrated lead acetate $Pb(OAc)_2{\cdot}3H_2O$ associated to titanium alkoxides, mostly isopropoxide, in various solvents, essentially 2-methoxyethanol[4,5] or diols.[6] The compositions of these solutions has generally been investigated by FT-IR and NMR spectroscopies and, less often, by mass spectroscopy. The presence of various Pb−Ti species has thus been postulated. $Pb_2Ti_4(\mu_4\text{-}O)(OAc)_2(\mu\text{-}OEt)_8(OEt)_6$ is the only structurally characterized lead−titanium species reported so far.[1,2,7] Attempts to control the stoichiometry between the metals by using functional carboxylates, either lead glycolate or lead dimethyl glycolate and $Ti(O\text{-}i\text{-}Pr)_4$[8] or $Ti(O\text{-}i\text{-}Pr)_2(acac)_2$[9] gave for instance a species believed to be $Pb(OOCCH_2O)_2Ti(acac)_2$, but the poor solubility precluded unequivocal characterization.

We report here the synthesis and the molecular structure of the first mixed-metal Pb−Ti species having a stoichiometry appropriate for its use as a "single-source" precursor for $PbTiO_3$. Controlled substitution of the alkoxide ligands of $Pb_2Ti_2O(O\text{-}i\text{-}Pr)_{10}$ by acetic acid and acetylacetone offered related Pb:Ti species with a 1:1 stoichiometry.

Experimental Section

All manipulations were routinely performed under nitrogen using Schlenk tubes and vacuum line techniques with solvents purified by standard methods. $[Pb(O\text{-}i\text{-}Pr)_2]_\infty$ and $Pb_4O(O\text{-}i\text{-}Pr)_6$ were obtained according to the literature.[10] $Ti(O\text{-}i\text{-}Pr)_4$ (Huls) was purified by distillation. Acetic acid and acetylacetone (Aldrich) were stored over molecular sieves. ^1H, ^{13}C, and ^{207}Pb NMR and IR spectra were run on Bruker AC-200 and IR-FTS 45 spectrometers respectively. ^{207}Pb NMR chemical shifts are given with respect to $Pb(NO_3)_2$ as an external reference and are positive to low field. IR spectra were obtained from Nujol mulls. Analytical data were obtained from the Centre de Microanalyses du CNRS.

Preparation of $Pb_2Ti_2O(O\text{-}i\text{-}Pr)_{10}$ (1). Method a. $Ti(O\text{-}i\text{-}Pr)_4$ (1 mL, 3.4 mmol) was added to a suspension of $[Pb(O\text{-}i\text{-}Pr)_2]_\infty$ (1 g, 3.08 mmol) in 40 mL of toluene and the mixture was refluxed for 16 h. After this mixture was cooled to room temperature, $[Pb(O\text{-}i\text{-}Pr)_2]_\infty$ (0.3g) was filtered off and the solvent removed in vacuo giving an oil. Addition of 2-propanol leads to colorless, crystals of **1** at 4 °C (0.9 g, yield : 55% /Pb).

Method b. $Ti(O\text{-}i\text{-}Pr)_4$ (0.5 mL, 1.67 mmol) was added to a solution of $Pb_4O(O\text{-}i\text{-}Pr)_6$ (0.5 g, 0.42 mmol) in 25 mL of toluene. The reaction mixture was stirred at room temperature over 20 h and the solvent removed. Crystallization in 2-propanol leads to **1** (0.6 g, 64% yield / Pb). Anal. Calcd for $C_{30}H_{70}O_{11}Pb_2Ti_2$: C, 32.25; H, 6.27; Pb, 37.12; Ti, 8.58. Found: C, 30.20; H , 5.90; Pb, 38.56; Ti, 8.70. IR (cm^{-1}): 1329 m; 1157 vs, 1128 vs ν(C−O); 1007 s, 966 vs, 851 m, 833 m,

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® Abstract published in *Advance ACS Abstracts,* January 1, 1995.

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667 w; 617 s, 597 s, 565 vs, 487 sh, 471 m, 420 w ν(M−OR). ^{1}H NMR (C_6D_6, 20 °C): 1.26 (d, J = 6 Hz, 54H, *Me*), 4.53(spt, J = 6 Hz, 4H, *CH*), 4.8 (m, 2H, *CH*); 5.1(br, 4H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): δ 26.4, 27.0, 27.6 (*Me*), 75.0, 76.1, 77.3 (*CH*). ^{207}Pb{^{1}H} NMR (toluene, 20 °C): 3870.

Preparation of $Pb_2Ti_2O(OAc)_2(O$-*i*-$Pr)_8$ (2). A solution of AcOH (49.3 mL, 0.90 mmol) in 5 mL of hexane was added to a solution of **1** (0.5 g, 0.45 mmol) in 20 mL of hexane. After 1 h at room temperature, the reaction medium was concentrated. A crop of colorless crystals of **2** was obtained at 4 °C in 95% yield (0.48 g). Anal. Calcd for $C_{28}H_{62}O_{13}Pb_2Ti_2$: C, 30.1; H, 5.55; Pb, 37.6; Ti, 8.69. Found: C, 28.63; H, 5.19; Pb, 36.29; Ti, 9.53. IR (cm^{-1}): 1576 s, 1553 s ν(COO)$_{as}$; 1442 s, 1409 s ν(COO)$_s$; 1330 s; 1163 vs, 1125 vs ν(C−O); 1011 vs, 968 vs, 847 s, 835 s, 747 m; 663 m, 644 m, 594 vs ν(M−OOC); 526 s, 493 s, 473 s, 436 s ν(M−O). ^{1}H NMR ($CDCl_3$, 20 °C): 1.24 (d, J = 6 Hz, 24H, *Me*), 1.95 (s, 3H, O*Ac*), 4.49 (spt, J = 6 Hz, 2H, *CH*), 5.05 (m, 2H, *CH*). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C) 25.35, 26.54 (*Me*), 76.42, 77.26 (*C*H), 179.05 (C=O). ^{207}Pb{^{1}H} NMR (toluene, 20 °C): 3016.

Preparation of $Pb_2Ti_2O(acac)_2(O$-*i*-$Pr)_8$ (3). A similar procedure applied to **1** (0.5 g, 0.45 mmol) in hexane (20 mL) and to acacH (93 mL, 0.90 mmol) in 5 mL of hexane offered yellowish crystals of **3** in 92% yield (0.5 g). Anal. Calcd for $C_{34}H_{70}O_{13}Pb_2Ti_2$: C, 34.11; H, 5.85; Pb, 34.64; Ti, 8.01. Found: C, 32.88; H, 5.57; Pb, 35.76; Ti, 8.23. IR (cm^{-1}): 1590 vs, 1522 vs ν(COO)$_{as}$; 1457 s, 1388 vs ν(COO)$_s$; 1328 m; 1163 vs, 1126 vs ν(C−O); 1012 vs, 977 vs, 928 w, 840 m, 818 w, 769 m; 658 m, 607 m, 582 vs, 508 s, 470 s, 407 s, 357 s ν(M−O). ^{1}H NMR ($CDCl_3$, 20 °C): 1.21 (d, J = 6 Hz, 48H, *Me*), 2.03, 1.92 (s, 12H, *Me*-acac), 4.04 (spt, J = 6 Hz, 4H, *CH*), 4.50 (spt, J = 6 Hz, 1H, *CH*), 4.78 (spt, J = 6 Hz, 3H, *CH*), 5.51 (s, 2H, *CH*-acac). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C): 25.14, 25.41, 26.56 (*Me*), 64.43 (*Me*-acac), 77.67, 78.69 (*CH*), 102.61 (*CH*-acac), 190.06 (C=O). ^{207}Pb{^{1}H} NMR (toluene, 20 °C): 3883.

All compounds are air-sensitive and soluble in common organic solvents including hexane; compound **1** dissolves slowly in the parent alcohol.

X-ray Structural Determination of 1. Colorless needles were obtained directly from the reaction medium (method a). A crystal with the approximate dimensions 0.20 × 0.10 × 0.10 mm was mounted in a glass capillary at −150 °C under a stream of argon[11] and transferred at the same temperature to a Rigaku AFC6R diffractometer, equipped with a rotating anode generator operated at 9 kW (50 kV, 180 mA). Diffracted intensities ($+h$, $+k$, $\pm l$) were measured at −120 °C, using graphite-monochromated Mo Kα radiation, for $3.5 < 2\theta < 50°$. The $\omega-2\theta$ scan mode was employed with an ω scan rate of 8 °min^{-1} and a scan width of $(1.26 + 0.30 \tan\theta)°$. Weak reflections ($I < 10\sigma(I)$) were rescanned three times and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time vs background counting time was 2:1. Of the 7772 independent reflections measured, 2889 had $I > 3\sigma(I)$ and were regarded as being observed. That the crystal was not subject to decay during measurement of intensities was checked by monitoring three reflections at regular intervals (after measurement of 150 reflections). Intensity data were corrected for Lorentz and polarization effects, but no correction was made for the effects of absorption, owing to inability to measure and index the faces of the extremely unstable crystal and to failure to obtain a more satifactory model from empirically corrected data (by means of azimuthal scans). Unit-cell parameters were obtained from diffractometer setting angles for 11 reflections in the range $14.5° < 2\theta < 18.7°$, They are given in Table 1 together with other basic crystallographic information.

Structure Determination and Refinement. The positions of the lead [Pb(1) and Pb(2)] and titanium atoms were obtained by direct methods (MITHRIL)[12] and those of the oxygen and carbon atoms from subsequent electron density calculations. Two peaks with coordination geometry consistent with lead but with considerably lower electron density were identified as partially occupied lead sites [Pb(3) and Pb(4)]. Initial refinement of the occupation factors for all four lead sites gave a total occupancy of 2.0, the individual occupancies indicating that Pb(3) was related to Pb(1) and Pb(4) to Pb(2). Therefore, in the final stages of refinement, the occupancies of Pb(1) and Pb(2) were refined and those of Pb(3) and Pb(4) reset, each pair thus being constrained to have occupancy 1.0. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms and with hydrogen atoms (apart from those associated with the carbons close to Pb(3) and Pb(4), *i.e.* C(12), C(25) and C(26) included as a fixed contribution in calculated positions (C−H = 1.0 Å, B = 1.2B_{eq} of the carrying carbon atom) gave a final R = 0.047, R_w = 0.050 for 426 parameters and 2889 reflections. The final occupancies for Pb(1) and Pb(2) were 0.821(2) and 0.883(2), respectively, and, in consequence, those of Pb(3) and Pb(4) 0.179 and 0.117, respectively. Since the positions of the ligand atoms are those corresponding to the aggregate with the orientation shown in Figure 1, some of the metal−ligand distances associated with Pb(3) and Pb(4) are obviously artifacts. It was considered neither feasible nor meaningful to attempt to resolve the positions of the ligand atoms into sites with major and minor occupation as for the lead atoms; that there is unresolved disorder associated with some of the carbon atoms is, however, indicated by large thermal parameters. Atomic scattering factors and anomalous dispersion correction factors were taken from ref 13, and the F_o values were weighted according to $w = [\sigma^2(F_o)]^{-1}$. A final difference map showed a maximum and minimum residual density of +0.79 and −1.40 e Å^{-3}, respectively. All calculations were carried out with the TEXSAN program system.[14]

Table 1. Crystallographic Data for $Pb_2Ti_2O(O$-*i*-$Pr)_{10}$

formula	$C_{30}H_{70}O_{11}Pb_2Ti_2$	V, Å^3	4301(6)
fw	1117.1	Z	4
cryst syst	monoclinic	T, °C	−120
space group	$P2_1/n$ (No. 14)	λ, Å	0.710 73
a, Å	10.286(14)	F(000)	2184
b, Å	22.564(4)	d_{calc}, g/cm^3	1.73
c, Å	18.709(5)	μ, cm^{-1}	82.7
α, deg	90	R^a	0.047
β, deg	97.93(5)	R_w	0.050
γ, deg	90		

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

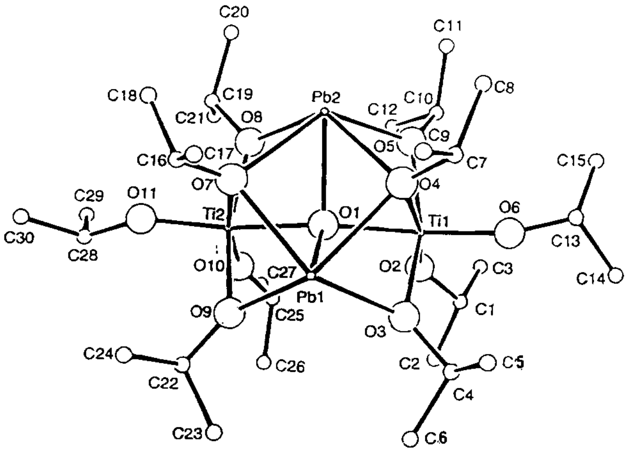

Figure 1. $Pb_2Ti_2(\mu_4$-O$)(\mu_3$-O-*i*-Pr$)_2(\mu$-O-*i*-Pr$)_4$(O-*i*-Pr$)_4$ molecule showing the crystallographic numbering. For clarity, the atoms have been drawn as spheres of arbitrary radius.

Results and Discussion

Lewis acid−base reactions between metal alkoxides are one of the most largely investigated route to mixed-metal oxide precursors.[2,7] Dissolution of polymeric alkoxides, mainly of d^n transition metals or of the p block in the presence of other

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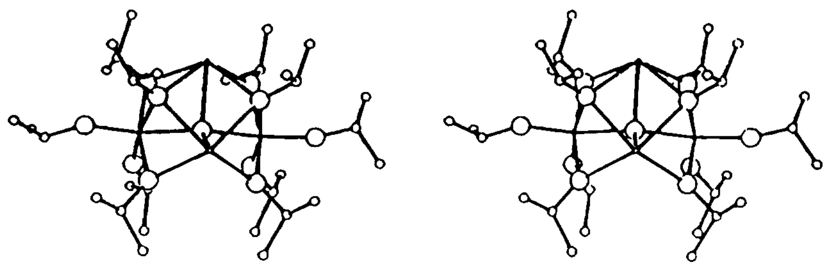
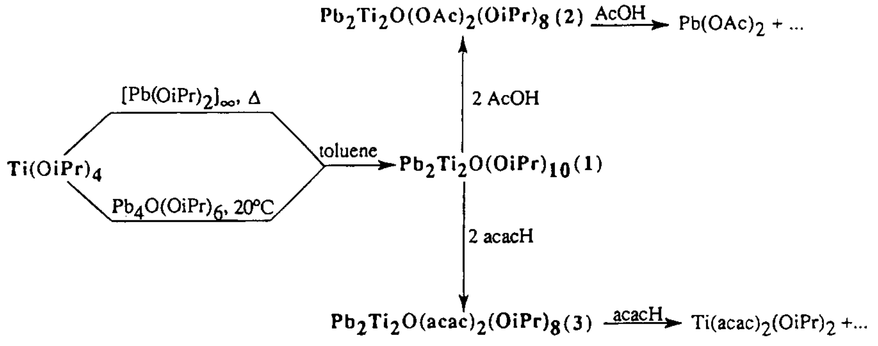


Figure 2. Stereoview of the $Pb_2Ti_2O(O\text{-}i\text{-}Pr)_{10}$ molecule.

Scheme 1. Synthetic Routes to the Various Pb:Ti Derivatives



metal alkoxides, has been emphasized. However, in many cases, such depolymerization reactions are inoperative in strictly anhydrous conditions, a soluble oxoalkoxide and not the initial insoluble alkoxide being the true reactive species.[2,15] Alternative ways to activate polymeric metal alkoxides have been considered.[16] In the case of lead, a variety of alkoxides and oxoalkoxides are known.[10,17] We have used these compounds as alternative sources of lead oxide for access to lead titanate or lead zirconate. Dissolution of $[Pb(O\text{-}i\text{-}Pr)_2]_\infty$ can be achieved in the presence of $Ti(O\text{-}i\text{-}Pr)_4$ on refluxing in toluene. A compound **1** whose analysis accounts for the presence of Ti and Pb in a 1:1 stoichiometry is isolated. The same compound results from the reaction at room temperature between $Ti(O\text{-}i\text{-}Pr)_4$ and a lead oxoalkoxide $Pb_4O(O\text{-}i\text{-}Pr)_6$, thus suggesting that compound **1** is actually a mixed-metal oxoalkoxide (Scheme 1). The same approach using $Ti(OEt)_4$ and $Pb_4O(OEt)_6$ or $[Zr(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)]_2$ and $[Pb(O\text{-}i\text{-}Pr)_2]_\infty$ did not give access to Pb:M species (M = Ti, Zr) of 1:1 stoichiometry.[18] Compound **1** was characterized by chemical analysis and spectroscopic data (IR, NMR: ^1H, ^{13}C, and ^{207}Pb) and its molecular structure established by single-crystal X-ray diffraction. Its reactivity toward acetic acid and acetylacetone has been investigated.

The molecule corresponds to a $Pb_2Ti_2(\mu_4\text{-}O)(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4(OR)_4$ aggregate depicted in Figure 1 and as stereoviews in Figure 2. Selected bond lengths and angles are collected in Table 2, and positional parameters and equivalent isotropic thermal parameters for the atoms comprising the core are given in Table 3. The metals are displayed around a μ_4-oxo ligand O(1) and form a quite regular tetrahedron (Pb···Ti values from 3.231(4) to 3.246(5) Å). The titanium centers diplay a distorted octahedral stereochemistry (angles from 72.4(5) to 170.1(6)°) while both lead atoms are 5-coordinate with a distorted tetragonal stereochemistry (angles from 62.0(4) to 130.1(4)°) and thus a stereochemically active lone pair. In addition to doubly bridging isopropoxide ligands connecting the lead and titanium atoms, two adjacent Pb_2Ti faces of the tetrahedron are capped by μ_3-OR ligands. The Ti−O bond distances range from 1.80(1) to 2.20(1) Å. The Pb−O bond distances are quite longer with values from 2.33(1) to 2.51(1) Å (Table 2) and are in agreement with values reported previously;[19] those associated with the disordered lead sites range from 2.56(1) to 2.69(1) Å for Pb(3)−O and from 2.44(1) to 2.73(1) Å for Pb(4)−O. The Ti−O−C angles associated with terminal OR groups are quite large (from 136(1) to 166(2)°) as usually observed for early transition metals. Although the tetrahedron is fairly regular, the coordination geometry of the μ_4-oxo ligand is severely distorted, approaching a seesaw arrangement [Ti(1)−O(1)−Ti(2) = 163.0(7)° whereas Pb(1)−O(1)−Pb(2) = 99.6(4)°], this perhaps representing the most salient structural feature. A somewhat similar situation in which a μ_4-oxo ligand is trapped on the surface of a metal cluster has been observed in $[Cu_{10}O_2(Mes)_6]$, the oxide ligand in this case exhibiting trigonal pyramidal coordination geometry.[20] Other unusual μ_4-oxo coordination geometries include a square-planar arrangement.[21] Concave distortions of the central tetrahedral μ_4-oxide leading to metal−oxide−metal angles of about 130−140°, i.e. considerably less than the value found here for Ti(1)−O(1)−Ti(2), have been observed in $PbZr_3O(\mu\text{-}OAc)_2(\mu\text{-}O\text{-}i\text{-}Pr)_5(O\text{-}i\text{-}Pr)_5$ or $Ce_4O(O\text{-}i\text{-}Pr)_{13}(i\text{-}PrOH)$[22] for instance.

The molecule crystallizes with a disordered structure, the positions of the partially occupied lead sites Pb(3) and Pb(4) with respect to the core being indicated in Figure 3. The disorder can be envisaged as arising from the presence of aggregates with orientations different from that depicted in

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Table 2. Selected bond lengths (Å) and Angles (deg) for $Pb_2Ti_2O(O\text{-}i\text{-}Pr)_{10}$

Ti(1)−O(1)	2.01(1)	Ti(2)−O(1)	2.03(1)
Ti(1)−O(2)	1.80(1)	Ti(2)−O(7)	2.17(1)
Ti(1)−O(3)	1.97(1)	Ti(2)−O(8)	1.98(1)
Ti(1)−O(4)	2.20(1)	Ti(2)−O(9)	2.00(1)
Ti(1)−O(5)	2.03(1)	Ti(2)−O(10)	1.83(1)
Ti(1)−O(6)	1.81(1)	Ti(2)−O(11)	1.81(1)
Pb(1)−O(1)	2.33(1)	Pb(2)−O(1)	2.36(1)
Pb(1)−O(3)	2.40(1)	Pb(2)−O(4)	2.44(1)
Pb(1)−O(4)	2.49(1)	Pb(2)−O(5)	2.36(1)
Pb(1)−O(7)	2.51(1)	Pb(2)−O(7)	2.43(1)
Pb(1)−O(9)	2.38(1)	Pb(2)−O(8)	2.41(1)
Pb(1)···Ti(1)	3.231(4)	Pb(2)···Ti(1)	3.243(4)
Pb(1)···Ti(2)	3.232(4)	Pb(2)···Ti(2)	3.246(5)
Pb(1)···Pb(2)	3.581(3)		
O(1)−Pb(1)−O(3)	67.0(4)	O(1)−Pb(2)−O(4)	62.5(4)
O(1)−Pb(1)−O(4)	62.2(4)	O(1)−Pb(2)−O(5)	67.9(4)
O(1)−Pb(1)−O(7)	62.0(4)	O(1)−Pb(2)−O(7)	62.7(4)
O(1)−Pb(1)−O(9)	68.0(4)	O(1)−Pb(2)−O(8)	66.8(4)
O(3)−Pb(1)−O(4)	70.3(4)	O(4)−Pb(2)−O(5)	70.7(5)
O(3)−Pb(1)−O(7)	128.8(4)	O(4)−Pb(2)−O(7)	86.0(4)
O(3)−Pb(1)−O(9)	94.2(4)	O(4)−Pb(2)−O(8)	129.3(4)
O(4)−Pb(1)−O(7)	83.3(4)	O(5)−Pb(2)−O(7)	130.5(4)
O(4)−Pb(1)−O(9)	130.1(4)	O(5)−Pb(2)−O(8)	92.2(4)
O(7)−Pb(1)−O(9)	70.2(4)	O(7)−Pb(2)−O(8)	69.4(4)
O(1)−Ti(1)−O(2)	97.7(54)	O(1)−Ti(2)−O(7)	72.8(5)
O(1)−Ti(1)−O(3)	82.0(5)	O(1)−Ti(2)−O(8)	81.7(5)
O(1)−Ti(1)−O(4)	72.4(5)	O(1)−Ti(2)−O(9)	81.6(5)
O(1)−Ti(1)−O(5)	81.6(5)	O(1)−Ti(2)−O(10)	97.3(6)
O(1)−Ti(1)−O(6)	165.6(6)	O(1)−Ti(2)−O(11)	163.7(6)
O(2)−Ti(1)−O(3)	92.9(6)	O(7)−Ti(2)−O(8)	83.2(5)
O(2)−Ti(1)−O(4)	170.1(6)	O(7)−Ti(2)−O(9)	84.9(5)
O(2)−Ti(1)−O(5)	96.0(6)	O(7)−Ti(2)−O(10)	170.1(6)
O(2)−Ti(1)−O(6)	96.5(6)	O(7)−Ti(2)−O(11)	90.9(6)
O(3)−Ti(1)−O(4)	84.7(5)	O(8)−Ti(2)−O(9)	161.7(6)
O(3)−Ti(1)−O(5)	161.4(5)	O(8)−Ti(2)−O(10)	96.4(6)
O(3)−Ti(1)−O(6)	94.7(6)	O(8)−Ti(2)−O(11)	96.1(6)
O(4)−Ti(1)−O(5)	82.0(5)	O(9)−Ti(2)−O(10)	93.1(6)
O(4)−Ti(1)−O(6)	93.4(6)	O(9)−Ti(2)−O(11)	97.9(6)
O(5)−Ti(1)−O(6)	99.0(6)	O(10)−Ti(2)−O(11)	99.0(6)
Pb(1)−O(1)−Ti(1)	96.0(5)	Pb(2)−O(1)−Ti(1)	95.4(5)
Pb(1)−O(1)−Ti(2)	95.5(5)	Pb(2)−O(1)−Ti(2)	95.0(5)
Pb(1)−O(1)−Pb(2)	99.6(4)	Ti(1)−O(1)−Ti(2)	163.0(7)
Pb(1)−O(3)−Ti(1)	94.9(5)	Pb(1)−O(9)−Ti(2)	94.7(5)
Pb(2)−O(8)−Ti(2)	94.9(5)	Pb(2)−O(5)−Ti(1)	95.0(5)
Pb(1)−O(4)−Ti(1)	86.9(4)	Pb(1)−O(7)−Pb(2)	92.9(4)
Pb(1)−O(4)−Pb(2)	93.4(4)	Pb(1)−O(7)−Ti(2)	87.1(4)
Pb(2)−O(4)−Ti(1)	88.6(4)	Pb(2)−O(7)−Ti(2)	89.6(4)
Ti(1)−O(6)−C(13)	166.1(16)		
Ti(1)−O(2)−C(1)	135.8(12)		
Ti(2)−O(11)−C(28)	149.9(15)		
Ti(2)−O(10)−C(25)	149.5(17)		

Figure 1 in a few unit cells. Since Pb(1) and Pb(3), and Pb(2) and Pb(4), are related pairwise, as described above, one possible orientation is seen from Figure 3 to be the mirror image over a plane through Ti(1), Ti(2), and Pb(2) and the other one over a plane through Ti(1), Ti(2), and Pb(1). An alternative, equivalent description of the disorder is that the orientations of the aggregates in a few unit cells are related to that in Figure 1 by a clockwise or an anticlockwise rotation of approximatively 90° about the Ti(1)−O(1)−Ti(2) axis.

Table 3. Positional Parameters and Equivalent Isotropic Thermal B_{eq} (Å^2) for the Atoms Comprising the core of $Pb_2Ti_2O(O\text{-}i\text{-}Pr)_{10}$

atom	*x*	*y*	*z*	*Beq*[b]
Pb(1)[a]	0.53981(9)	0.08439(4)	0.90306(5)	2.97(5)
Pb(2)[a]	0.74052(8)	0.14218(4)	0.77744(5)	2.90(4)
Pb(3)[a]	0.4373(5)	0.1704(2)	0.6571(2)	3.6(2)
Pb(4)[a]	0.2616(7)	0.1083(3)	0.7849(4)	4.2(4)
Ti(1)	0.5048(4)	0.0479(2)	0.7345(2)	3.3(2)
Ti(2)	0.4829(3)	0.2093(2)	0.8201(2)	3.2(2)
O(1)	0.517(1)	0.1254(5)	0.7879(6)	3.0(6)
O(2)	0.359(1)	0.0640(6)	0.6725(7)	4.1(7)
O(3)	0.409(1)	0.0245(6)	0.8144(7)	3.7(7)
O(4)	0.680(1)	0.0442(5)	0.8164(7)	3.5(6)
O(5)	0.631(1)	0.0897(6)	0.6775(7)	4.2(7)
O(6)	0.526(1)	−0.0271(5)	0.7042(7)	4.3(7)
O(7)	0.661(1)	0.1788(5)	0.8857(6)	3.2(6)
O(8)	0.605(1)	0.2285(6)	0.7503(7)	3.7(7)
O(9)	0.390(1)	0.1654(6)	0.8908(6)	3.6(7)
O(10)	0.331(1)	0.2221(6)	0.7582(7)	4.2(7)
O(11)	0.495(1)	0.2801(6)	0.8654(7)	4.4(8)

[a] Partially occupied atomic site: occupancies for Pb(1) and Pb(2) are 0.821(2) and 0.883(2), respectively, and for Pb(3) and Pb(4) are 0.179 and 0.117, respectively. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}\, a_i^* a_j^* a_i \cdot a_j$.

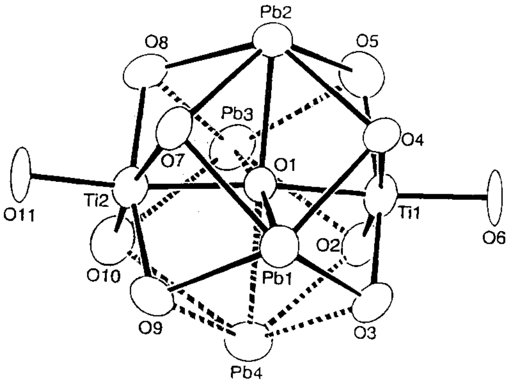

Figure 3. Core of the $Pb_2Ti_2O(O\text{-}i\text{-}Pr)_{10}$ molecule showing the positions of the partially occupied lead sites Pb(3) and Pb(4), with bonds as dotted lines. Thermal ellipsoids enclose 50% probability.

The structure of the mixed-metal oxoalkoxide **1** is retained in solution as shown by the presence, in the ^1H NMR spectra, of four types of methine groups in a 2:1:2 integration ratio. The molecule is fluxional on the ^1H NMR time scale due to a rapid exchange between the μ_3-OR and μ_2-OR groups although the process has not been extensively studied. Compound **1** is obtained in high and reproducible yield, thus excluding the generation of the oxo ligand by accidental hydrolysis. Its presence allows the transition metal to achieve its most common coordination number, namely 6. The mixed-metal oxoalkoxide **1** can be obtained either from the polymeric lead isopropoxide or from the tetranuclear oxoisopropoxide, the only difference being kinetic. The quite easy depolymerization of $[Pb(O\text{-}i\text{-}Pr)_2]_\infty$ by metal alkoxides is due to the facile formation of lead oxoalkoxides.[10] Attempts to build up mixed-metal species containing a chloride as a functional ligand by using $Ti(O\text{-}i\text{-}Pr)_3Cl$ as a starting material were prevented by the precipitation of $PbCl_2$.

The modification of **1** by acetic acid and acetylacetone, which are reactants commonly used in the sol−gel process[23] in order to control the hydrolysis rates and/or avoid precipitation, has been investigated. These reactions procceed smoothly to the formation of $Pb_2Ti_2O(OAc)_2(O\text{-}i\text{-}Pr)_8$ (**2**) or $Pb_2Ti_2O(acac)_2(O\text{-}i\text{-}Pr)_8$ (**3**), respectively, when small amounts (2 equiv) of reactant are used (Scheme 1). Larger amounts of acetic acid or acetylacetone lead to the precipitation of $Pb(OAc)_2$ or to the formation of $Ti(acac)_2(O\text{-}i\text{-}Pr)_2$ as a result of the segregation of the mixed-metal species **1**. Preliminary X-ray data of compound **2** indicate that the OAc ligands act as a bridging ligands (Figure 4).[2,23] By contrast, the acac ligands seem to behave as terminal-chelating ligands located on the titanium centers according to the IR ($\nu_{as}(CO) = 1590$; $\nu_s(CO) = 1521\ cm^{-1}$) and ^1H NMR data ($\delta(CH\text{−}acac) = 5.51$ ppm), which are close to those of

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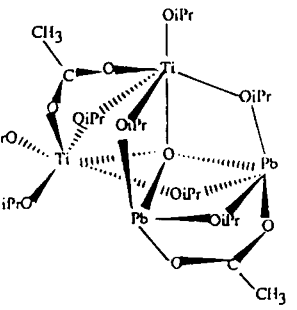
(23) Tohge, N.; Takahashi, S.; Minami, T. *J. Am. Ceram. Soc.* **1991**, *74*, 67.



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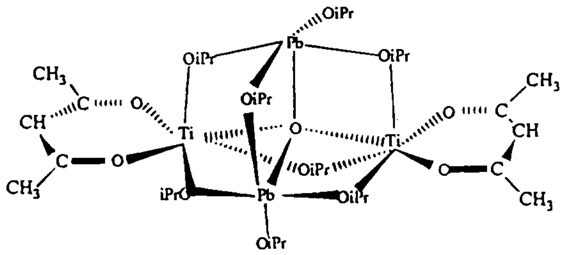

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Figure 4. Structures of compounds **2** and **3**.

Ti(O-*i*-Pr)$_2$(acac)$_2$ [ν(CO)$_{as}$ = 1609, 1587; ν(CO)$_s$ = 1527 cm^{-1}; δ(CH−acac) = 5.51 ppm]. Moreover the analogy in ^{207}Pb NMR chemical shifts between **1** (3870 ppm) and **3** (3883 ppm) suggests that the surrounding of the lead atoms is only slighly modified by the transformation of **1** into **3**. The overall spectroscopic data are in agreement with the structures depicted in Figure 4. Chemical modification reactions of mixed-metal alkoxides are generally difficult to control and involve an easy change of the stoichiometry between the metals, the main group element being often extruded as an insoluble derivative.[2] The structural similarity between compounds **1**, **2**, and **3** allows conservation of the Pb:Ti stoichiometry. This is no longer achieved when **2** is reacted with 1 equiv of acacH and precipitation of Pb(OAc)$_2$ is observed.

The Pb:Ti (1:1) stoichiometry of these compounds is attractive for their use as single-source precursors of PbTiO$_3$. Their hydrolysis−polycondensation reactions have been estimated. The amorphous powders have been characterized by FT-IR, thermogravimetric analysis (TGA), differential thermal analysis (DTA), and X-ray diffraction (XRD) at variable temperatures. The hydrolysis-polycondensation reactions of **1** in 2-propanol proceeds to the formation of the phases PbTiO$_3$ and the pyrochlore Pb$_2$Ti$_2$O$_6$ at 500 °C. In the case of **2** and **3**, differential hydrolysis is observed,[3,21] the residual acetate or acetylacetonate ligands being removed below 400 °C (as shown by TGA) and the pure perovskite phase PbTiO$_3$ is obtained directly at 550 and at 500 °C respectively.[18]

Conclusions

The synthesis of the mixed-metal species Pb$_2$Ti$_2$O(O-*i*-Pr)$_{10}$ (**1**) by reaction between Ti(O-*i*-Pr)$_4$ and [Pb(O-*i*-Pr)$_2$]$_\infty$ or Pb$_4$O(O-*i*-Pr)$_6$ has been achieved. **1** represents the first well-characterized mixed-metal species having a stoichiometry Pb: Ti = 1:1 attractive for its use as single-source precursor of PbTiO$_3$. Its reactivity toward acetic acid and acetylacetone offered two novel compounds Pb$_2$Ti$_2$OX$_2$(O-*i*-Pr)$_8$ (X = OAc (**2**), X = acac (**3**)) when 2 equiv of reactant are used. Larger amounts of reactant induced metal segregation of **1**.

Acknowledgment. We thank the GRECO 93 "Sol−gel inorganiques" and the Swedish Natural Science Research Council for financial support.

Supplementary Material Available: Fractional atomic coordinates (Table S1), anisotropic thermal parameters for non-hydrogen atoms (Table S2) and nonessential bond lengths and angles (Table S3) (5 pages). Ordering information is given on any current masthead page.

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