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X-ray Structure and Raman Spectrum of [Ti$_4$(μ_3-O)$_2$(μ_2-O^{i}Pr)$_2$(O^{i}Pr)$_8$(acac)$_2$]: Presence of a Ti$_4$(μ_3-O)$_2$(μ_2-O^{i}Pr)$_2$ Ladder-like Core

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The study of organometallic and coordination compounds of titanium has been motivated by the applications that such compounds have found in several branches of chemistry. One such area is catalysis in organic chemistry.[1−3] Another is sol−gel chemistry, and the crystal structures of some titanium oxo−alkoxide complexes formed by the limited hydrolysis of alkoxides in the presence of or modified by acetic acid,[4−8] methacrylic acid,[9] and acetylacetone[10] have been determined in order to provide a better understanding of intermediates that may be involved in the formation of the oxide network from the reactive alkoxide. Transition-metal oxo−alkoxides are currently of mainstream interest in materials science, since their use as precursors minimizes the amount of carbon that must be eliminated during subsequent processing.[11] Better control of sol−gel processes requires an accurate characterization of intermediates formed during the change from the molecular precursor to the gel in such processes.[8] In most cases such intermediates are too unstable to allow their complete characterization. Here we describe the isolation of such a species, which is formed during the hydrolysis of titanium tetraisopropoxide (tetraisopropyltitanate, TPT) in the presence of acetylacetone.

Experimental Section

Colorless prisms of [Ti$_4$(μ_3-O)$_2$(μ_2-O^{i}Pr)$_2$(O^{i}Pr)$_8$(acac)$_2$] (**1**; Table 1) were initially obtained by the slow hydrolysis (by water vapor from the air) of a 2:1 mole ratio mixture of titanium tetraisopropoxide and acetylacetone (acac). The crystals grew on the inside of the glass container just below the interface of the solution with the air. On the basis of the composition determined from the X-ray structure of this compound, a bulk synthesis was devised as follows: A mixture of acetylacetone (0.5 g, 5 mmol) and water (0.09 g, 5 mmol) was added to titanium tetraisopropoxide (2.84 g, 10 mmol) in a container, which was then capped. The resulting yellow solution yielded the product as a colorless crystalline mass over a period of hours. The compound is stable in 2-propanol but readily hydrolyzes upon exposure to air. The Raman spectrum of the product of the bulk synthesis is identical to that of the crystals obtained by the first method described above. One of the latter crystals was removed under a dry nitrogen atmosphere, covered immediately with Paratone oil (Exxon) for protection against further hydrolysis, and transferred to a glass capillary for the X-ray measurements. These were carried out using a Nonius CAD-4 diffractometer [Mo Kα (monochromatic) $\omega/2\theta$ scan mode]. Of the 4696 reflections collected, 2996 with $I > 2\sigma(I)$ were used for the structure solution by direct methods (SHELXS-86). Empirical absorption corrections using ψ scans were applied, and refinement was carried out by full-matrix least-squares (SHELXL-93; 300 variable parameters). Non-hydrogen atoms were allowed to assume anisotropic thermal motion. It became apparent that the isopropyl groups were disordered. Where atom sites were resolved into two distinct peaks, half-weighted atoms were used to describe the disorder, and in other cases, the anisotropic thermal parameter was allowed to take up the disorder. Raman spectra were recorded at 4.5 cm^{-1} resolution using a Jobin-Yvon U1000 spectrometer equipped with a cooled photomultiplier (RCA C31034A) detector. The 514.5 nm exciting line from a Spectra-Physics model 2016 argon ion laser was used, and the samples were enclosed in glass capillaries.

Table 1. Crystallographic Data for [Ti$_4$(μ_3-O)$_2$(μ_2-O^{i}Pr)$_2$(O^{i}Pr)$_8$(acac)$_2$] (**1**)

empirical formula	$C_{40}H_{84}O_{16}Ti_4$
fw	1012.68
cryst size, mm	0.3 × 0.2 × 0.2
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	12.056(4)
b, Å	15.846(2)
c, Å	14.758(2)
β, deg	105.19(2)
V, Å^3	2720.9(10)
Z	2
d_{calc}, g cm^{-3}	1.236
T, °C	−80
λ, Å	0.710 69
2θ range, deg	2−50
μ, cm^{-1}	6.23
F(000)	2160
w$R(F^2)^a$	0.193
goodness-of-fit on F^2	1.062
$R(F)^b$ (obsd reflcns)	0.067

[a] $\mathrm{w}R(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$.

Results and Discussion

As illustrated in Figure 1, the complex **1** consists of a Ti$_4$(μ_3-O)$_2$(μ_2-O^{i}Pr)$_2$ core, producing a ladder-like arrangement. This is the second example of a new class of titanium oxo−alkoxide complexes, having an analogous structure to that of

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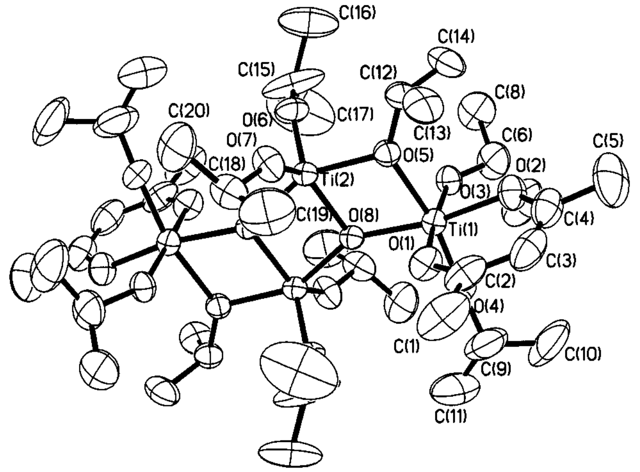

Figure 1. ORTEP representation of complex **1**. Selected bond lengths (Å) and bond angles: Ti(1)−O(1), 2.110(4); Ti(1)−O(3), 1.799(4); Ti(1)−O(5), 2.086(4); Ti(1)−O(8), 1.941(4); Ti(2)−O(6), 1.775(4); Ti(2)−O(8), 1.943(4); O(8)−Ti(1)−O(5), 72.8(2); O(8)#1−Ti(2)−O(5), 151.9; O(7)−Ti(2)−O(8), 130.1(2).

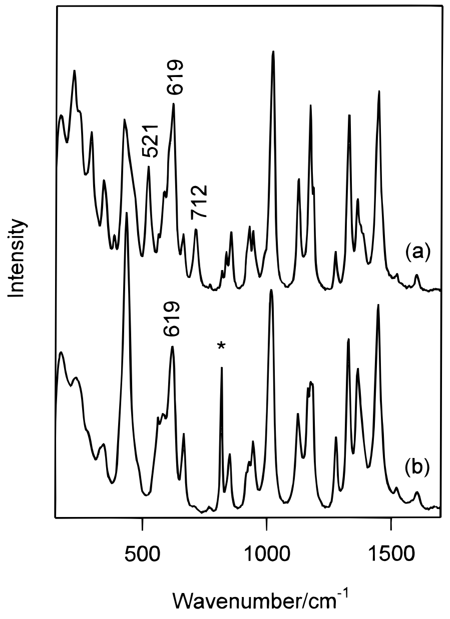

Figure 2. Raman spectra of titanium complexes: (a) **1**; (b) [Ti(O^{i}Pr)$_3$(acac)]. The band labeled with "*" in spectrum (b) is due to 2-propanol.

[Ti$_4$(HYDBINO)$_2$(O^{i}Pr)$_8$O$_2$].[12] The bulky HYDBINO (5,5′,6,6′,7,7′,8,8′-octahydrobinaphtho) ligands are bridging between adjacent titanium atoms on opposite sides of the tetranuclear core, preventing aggregation into a higher nuclearity cluster.

In the present complex, bidentate acac ligands and an isopropoxide ligand have taken the place of the HYDBINO ligand on each of the adjacent titanium atoms. The structure comprises [(acac)(O^{i}Pr)$_2$TiO(O^{i}Pr)Ti(O^{i}Pr)$_2$] units linked into dimers through the bridging oxide ion. The titanium atoms Ti(1) that bear the acetylacetone substituents are six-coordinate, with a distorted octahedral arrangement. The other titanium atoms Ti(2) are five-coordinate, with a distorted square-pyramidal arrangement. The oxide ion is three-coordinate and links the two units together through bonds to the five-coordinate titanium atom. The Ti−(μ_3-O)−Ti angles are approximately 75 and 152°, resulting in the ladder-like structure. The Ti−O bond lengths increase in the following order: terminal isopropoxide < oxo < bridging isopropoxide < acac.

It was noted by Eilerts et al.[12] that the ladder-like structure of [Ti$_4$(HYDBINO)$_2$(O^{i}Pr)$_8$O$_2$] was reminiscent of that observed in two tantalum complexes.[13,14] Structures similar to the ladder arrangement are also observed for Ti(OPh)$_2$Cl$_2$[15] and [LiTi(O^{i}Pr)$_5$]$_2$,[16] both involving five-coordinate titanium centers and both resembling a structure calculated for a (TiO$_2$)$_2$ cluster at the HF−SCF level with STO-4G basis sets by Hagfeldt *et al.*[17]

Notably, ladder-like structures were proposed for both [Ti$_3$(OEt)$_{12}$][18] and [Ti$_6$O$_4$(OEt)$_{16}$],[19] where all titanium atoms were six-coordinate. However, it was later discovered from EXAFS and XANES that [Ti$_3$(OEt)$_{12}$] is composed of a cyclic structure based on TiO$_5$ trigonal bipyramids linked through bridging alkoxide ligands,[20] and that the structure of [Ti$_6$O$_4$(OEt)$_{16}$] was in fact [Ti$_7$O$_4$(OEt)$_{20}$] (isostructural with [Mo$_7$O$_{24}$]$^{6-}$), with six-coordinate titanium centers.[21] Hence, it appears that the presence of five-coordinate titanium atoms is required for the formation of the ladder-like arrangement.

For the following structures, six-coordinate titanium atoms are observed where the distorted octahedra are connected through edge or corner sharing: [Ti$_4$(OMe)$_{16}$];[22] [Ti$_4$(OMe)$_4$(OEt)$_{12}$];[23] [Ti$_4$(OEt)$_{16}$];[24] [Ti$_6$(μ_3-O)$_2$(μ_2-O)$_2$(μ-OAc)$_4$(μ_2-OR)$_6$(OR)$_6$], where R = O^{i}Pr;[4,5] [Ti$_6$(μ_3-O)$_2$(μ_2-O)$_2$(μ-OAc)$_8$(μ_2-OR)$_2$(OR)$_6$], where R = OEt,[6,7] O^{i}Pr,[4] O^{n}Bu;[8] [Ti$_6$(μ_3-O)$_2$(μ_2-O)$_2$(μ-OMc)$_8$(μ_2-OEt)$_2$(OEt)$_6$] (Mc = OC−C(Me)═CH$_2$);[9] and [Ti$_{18}$(μ_5-O)$_2$(μ_4-O)$_2$(μ_3-O)$_{10}$(μ_2-O)$_8$(μ_2-O^{n}Bu)$_{14}$(O^{n}Bu)$_{12}$(acac)$_2$].[10] The octahedral coordination of titanium results either from bridging of alkoxide ligands of low steric hindrance or from relaxation of the steric hindrance through hydrolysis of the alkoxide ligands. Ti(OEt)$_4$ and Ti(O^{n}Bu)$_4$ are largely trimeric in the neat state, whereas Ti(O^{i}Pr)$_4$ is largely monomeric.[19] However, upon hydrolysis, the difference in the steric hindrance of ethoxy, isopropoxy, and *n*-butoxy ligands is reduced, allowing for the formation of [Ti$_6$(μ_3-O)$_2$(μ_2-O)$_2$(μ-OAc)$_8$(μ_2-OR)$_2$(OR)$_6$] from each of these alkoxides.

In the Raman spectrum of **1** (Figure 2a), the bands at 521 and 712 cm^{-1} are absent in the Raman spectrum of [Ti(O^{i}Pr)$_3$(acac)] (Figure 2b). These bands are assigned to ν(Ti−O) modes of bridging isopropoxide ligands and μ_3-oxo bonds, respectively, as these species are expected to be absent in Ti(O^{i}Pr)$_3$(acac). As expected, the wavenumber of the ν(Ti−O) band of the bridging isopropoxide ligands is significantly lower than those of the terminal ν(Ti−O) modes in Ti(O^{i}Pr)$_4$ (561 (A$_1$), 611 (T$_2$) cm^{-1}).[25] The wavenumber of the ν(Ti−O) band of the μ_3-oxo bonds is slightly higher than the highest

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wavenumber bands in the Raman spectra of the various polymorphs of TiO_2 (610−640 cm^{-1}).[26] A possible reason for this is that the titanium atoms in the TiO_2 polymorphs are all six-coordinate, whereas in **1** the oxo ligand is bonded to both five- and six-coordinate titanium. In the Raman spectrum of **1**, the ν_s(CCC) mode of bridging isopropoxide ligands[25] is observed as a shoulder at 833 cm^{-1}. The ν(C−O) and in-phase $\rho_r(CH_3)$ modes of terminal isopropoxide ligands appear as strong bands at 1018 and 1171 cm^{-1}, respectively, at similar wavenumbers to the same modes of $Ti(O^iPr)_4$.[25]

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Supporting Information Available: An X-ray crystallographic file in CIF for the structure of $[Ti_4(\mu_3\text{-}O)_2(\mu_2\text{-}O^iPr)_2(O^iPr)_8(acac)_2]$ is available on the Internet only. Access information is given on any current masthead page.

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