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Dodecatitanates: A New Family of Stable Polyoxotitanates

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Fundamental studies of metal alkoxide hydrolysis/condensation, the chemical basis of sol–gel polymerization,[2] are complicated by two factors: the extreme moisture sensitivity of most metal alkoxide precursors and the tendency of alkoxides to form mixtures of structurally complex species upon hydrolysis.[3] In the research reported here, we demonstrate that both of these complications can be circumvented in titanium alkoxide chemistry by using isopropyl titanate precursors. Two titanium alkoxides, α_1- and α_2-$[Ti_{12}O_{16}](OPr^i)_{16}$, are reported that display very low moisture sensitivity in alcohol solution. A third alkoxide, $[Ti_{11}O_{13}](OPr^i)_{18}$, is identified as the sole (>95%) reaction product of $Ti(OPr^i)_4$ hydrolysis by *ca.* $^1/_2$ equiv of water in *i*-PrOH solution. All these new complexes are members of a new structural family of remarkably stable polyoxotitanate derivatives that display unusual regioselective alkoxide exchange with alcohols.

Reaction of $Ti(OPr^i)_4$ with 1 equiv of water in *i*-PrOH solution at 100 °C for 3 days yields as the sole products a 1:1 mixture of two isomeric complexes, α_1-$[Ti_{12}O_{16}](OPr^i)_{16}$, **1**, and α_2-$[Ti_{12}O_{16}](OPr^i)_{16}$, **2**. These materials can be isolated in pure form and characterized using elemental analysis, ^{17}O and $^{13}C\{^1H\}$ NMR spectroscopy, and in the case of **1** only, single-crystal X-ray diffraction.[4] Pure samples of **1** or **2** are isomerized to a 1:1 equilibrium mixture of **1** and **2** by heating to 90 °C in toluene for 3 h.

In the solid state, α_1-$[Ti_{12}O_{16}](OPr^i)_{16}$ (**1**) has the C_{2h} structure shown in Figure 1a. Its α-$Ti_{12}O_{32}^{16-}$ titanate framework,[5] shown in Figure 2a, is identical to the organostannate framework previously observed for $[(RSn)_{12}O_{14}(OH)_6]^{2+}$ complexes, R = Pr^i [8] and Bu^n,[9] and the fluorovanadate framework observed for $[V_{12}O_{24}F_2(OH)_6]^{6-}$.[10] This D_{3d} framework comprises a cage of 18 bridging oxygen atoms occupying the vertices of an elongated triangular gyrobicupola, a distorted icosahedron of 12 TiO groups capping the square faces of this cage, plus two oxygen atoms that are encapsulated by the cage. Compound **1** retains its structure in hydrocarbon solution according to NMR spectroscopic measurements:[4] five methylene ^{13}C resonances, one μ_2-oxide ^{17}O resonance,[11] and four μ_3-oxide ^{17}O resonances[11] are observed (see Figure 2a). The isomeric α_2-$[Ti_{12}O_{16}](OPr^i)_{16}$ molecule is assigned the C_2 structure shown in Figure 2b using solution NMR

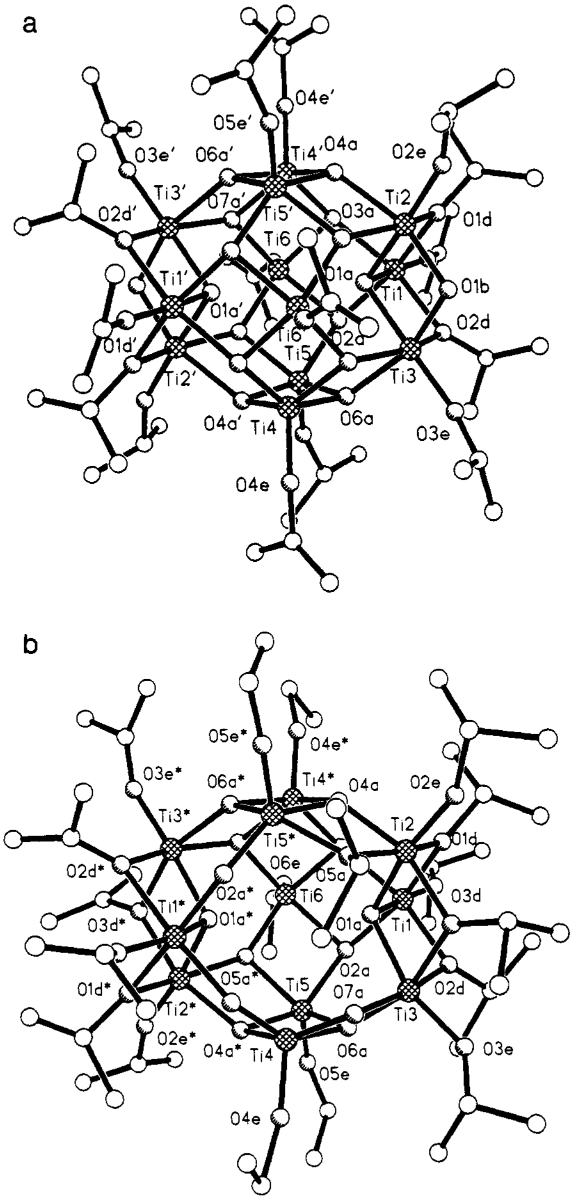

Figure 1. (a) The X-ray crystallographically-determined pseudo-C_{2h} structure for α_1-$[Ti_{12}O_{16}](OPr^i)_{16}$ (**1**) with Ti, O, and C atoms represented by cross-hatched, shaded, and open spheres, respectively. The molecule possesses rigorous crystallographic *Ci*-1 symmetry: atoms labeled with a prime (′) are related to those labeled without by this inversion center. Half of the Ti atoms in **1** are 6-coordinate, and the other half are 5-coordinate. Each molecule of **1** contains two μ_3-O^{2-} ligands that bridge three 6-coordinate Ti atoms, 12 μ_3-O^{2-} ligands that bridge one 6-coordinate and two 5-coordinate Ti atoms, and two μ_2-O^{2-} ligands that bridge two 6-coordinate Ti atoms. Each molecule of **1** also contains four μ_2-$(OPr^i)^-$ ligands that bridge two 6-coordinate Ti atoms and 12 terminally-bonded (OPr^i) ligands. (b) The X-ray crystallographically-determined structure of $[Ti_{11}O_{13}](OPr^i)_{13}(OEt)_5$ (**3a**) with all atoms represented as in Figure 1a. The structure of **3a** can be derived from **1** by removing one of the 5-coordinate Ti atoms of **1** and its terminally bonded $(OPr^i)^-$ ligand, replacing one of its basal O^{2-} ligands with an $(OPr^i)^-$ ligand, replacing the two μ_2-O^{2-} ligands in **1** by μ_2-$(OPr^i)^-$ ligands, and finally replacing the terminally-bonded $(OPr^i)^-$ ligands on each of the five remaining 5-coordinate "girdle" Ti atoms by terminally-bonded $(OEt)^-$ ligands. Atoms of **3a** are labeled similarly to those of **1**: atoms labeled with an asterisk (*) are related to those labeled without by a *pseudo* inversion center which is rigorously present in **1** but which *cannot* be present in **3a**.

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(4) For preparative, analytical spectroscopic, and X-ray crystallographic details, see the paragraph at the end of this paper regarding supplementary material.

(5) Just as the T_d α-$SiW_{12}O_{40}^{4-}$ Keggin structure can be converted to its C_{3v} β isomer by rotation of a W_3O_{13} group by 60°,[6] so can the D_{3d} α-$Ti_{12}O_{32}^{16-}$ framework be converted to a D_{3h} β isomer by rotating a Ti_3O_{13} group by 60°. Although the β-$Ti_{12}O_{32}^{16-}$ framework has not been observed yet in polytitanate chemistry, a derivative is known in polyvanadate chemistry, namely, the $V_{15}O_{36}Cl^{6-}$ ion.[7]

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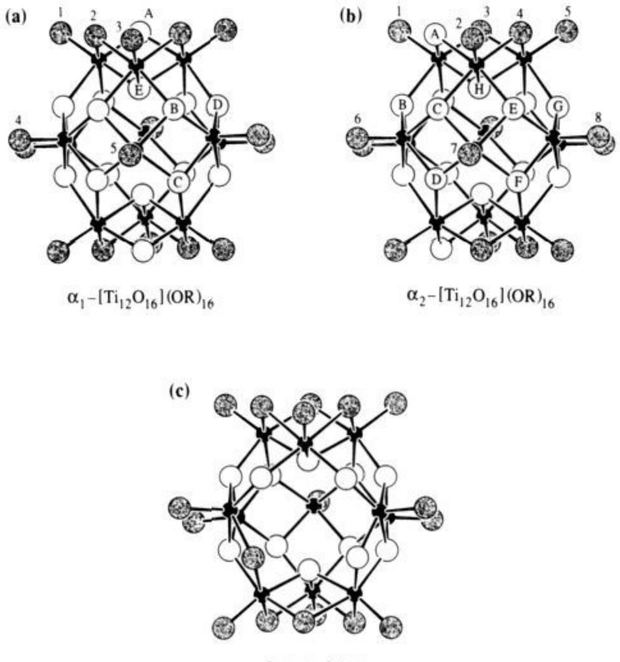

α_1-[Ti$_{12}$O$_{16}$](OR)$_{16}$ α_2-[Ti$_{12}$O$_{16}$](OR)$_{16}$

α-[Ti$_{11}$O$_{13}$](OR)$_{18}$

Figure 2. (a) α-$Ti_{12}O_{32}^{16-}$ core of the C_{2h} α_1-[$Ti_{12}O_{16}$](OR)$_{16}$ structure, (b) α-$Ti_{12}O_{32}^{16-}$ core of the proposed C_2 α_2-[$Ti_{12}O_{16}$](OR)$_{16}$ structure, and (c) α-$Ti_{11}O_{31}^{18-}$ core of the C_1 α-[$Ti_{11}O_{13}$](OR)$_{18}$ structure. Titanium atoms are represented by small filled spheres, oxide oxygens by large open spheres, and alkoxide oxygens by large shaded spheres. In parts a and b one member from each set of symmetry-equivalent oxygen atoms is labeled, using numerals for alkoxide oxygens and letters for oxide oxygens.

spectroscopy: the expected eight methine ^{13}C resonances and single μ_2-oxide ^{17}O resonance[11] are observed; five of the expected seven μ_3-oxide ^{17}O resonances[11] are resolved.

When compounds **1** and **2** are treated repeatedly with ethanol, two new compounds are obtained, α_1-[$Ti_{12}O_{16}$](OPr^i)$_{10}$(OEt)$_6$ (**1a**) and α_2-[$Ti_{12}O_{16}$](OPr^i)$_{10}$(OEt)$_6$ (**2a**).[4] In both cases, alkoxide exchange is effected with retention of the titanium oxide core structure, since the ^{17}O NMR spectra of oxide oxygens in **1** and **1a** (and **2** and **2a**) are virtually indistinguishable. A single-crystal X-ray diffraction study and a $^{13}C\{^1H\}$ solution NMR spectroscopic study define a structure for **1a** derived from the structure of **1** by replacing with ethoxide groups those six isopropoxide groups that are terminally bonded to five-coordinate titanium centers. $^{13}C\{^1H\}$ NMR spectroscopy supports an analogous structure for **2a** derived from the structure of **2**, α_2-[$Ti_{12}O_{16}$](OPr^i)$_{16}$ (see Figure 2b): five isopropoxide methine carbon resonances and three ethoxide methylene carbon resonances are observed.[4]

Both α_1- and α_2-[$Ti_{12}O_{16}$](OPr^i)$_{16}$ fail to react measurably with water after 12 h under conditions typically associated with sol–gel polymerization, namely, addition of 4 equiv of water to a 0.03 M 2-propanol solution. Sol–gel polymerization proceeds readily, however, if alcohol solvent is avoided. Addition of 6 equiv of water to a 0.05 M solution of α_1-[$Ti_{12}O_{16}$](OPr^i)$_{16}$ in 5/1 v/v toluene/acetonitrile, for example, yields a cloudy gel within 2 h at ambient temperature.

Hydrolysis of Ti(OPr^i)$_4$ with 0.3–0.8 equiv of water at ambient temperature in 2-propanol solution yields a solution whose ^{17}O NMR spectrum shows three μ_2-oxide resonances plus an unresolved set of overlapping μ_3-oxide resonances.[12] These resonances arise from a single complex, α-[$Ti_{11}O_{13}$](OPr^i)$_{18}$, **3**, that has been isolated and converted into the mixed alkoxide α-[$Ti_{11}O_{13}$](OPr^i)$_{13}$(OEt)$_5$, **3a**, by reaction with ethanol. Both complexes have been formulated and characterized using elemental analysis, $^{13}C\{^1H\}$ and ^{17}O NMR spectroscopy, and in the case of **3a** only, single-crystal X-ray diffraction.[4] The α-[$Ti_{11}O_{13}$](OPr^i)$_{13}$(OEt)$_5$ molecule, **3a**, has the solid-state structure shown in Figure 1b containing the titanium–oxygen framework of Figure 2c. Comparison of Figure 1b with Figure 1a (or Figure 2c with Figure 2a,b) reveals that the α-$Ti_{11}O_{31}^{18-}$ structural framework of compound **3a** is derived from the α-$Ti_{12}O_{32}^{16-}$ framework of compounds **1** and **1a** by removal of a single titanium atom and its terminal oxygen ligand. Compound **3** is proposed to have the same C_1 α-[$Ti_{11}O_{13}$](OR)$_{18}$ structure since its ^{17}O NMR spectrum is virtually identical to the ^{17}O NMR spectrum of **3a** and its $^{13}C\{^1H\}$ NMR spectrum displays 18 fully resolved methine carbon resonances.

The results reported here strongly suggest, but by no means demonstrate, that Ti(OPr^i)$_4$ titania sol–gel polymerization follows fundamentally different molecular growth pathways than analogous silica sol–gel polymerization. In Si(OCH$_3$)$_4$ silica sol–gel polymerization, for example, individual monosilicate units serve as monomer units.[13] In the Ti(OPr^i)$_4$ case, however, our results show that α-[$Ti_{11}O_{13}$](OPr^i)$_{18}$ molecules are formed initially, and these may serve as molecular building blocks for further polymerization reactions, a possibility now under investigation.

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Supplementary Material Available: Details of all sample preparations and characterization and crystal structure reports, listings of positional and thermal parameters, listings of bond lengths and angles, and persepective structural drawings for **1**, **1a**, and **3a**·C_2H_5OH (66 pages); structure factor tables for **1**, **1a**, and **3a**·C_2H_5OH (33 pages). Ordering information is given on any current masthead page.

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