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Low-nuclearity titanium oxoalkoxides: the trititanates $[Ti_3O](OPr^i)_{10}$ and $[Ti_3O](OPr^i)_9(OMe)$ ☆

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Abstract

The trititanate $[Ti_3O](OPr^i)_9(OMe)$ was isolated from the reaction of $Ti(OPr^i)_4$ with water and methanol in isopropanol solution and characterized by elemental analysis, multinuclear NMR spectroscopy, and single-crystal X-ray diffraction ($a=23.295(5)$, $b=19.560(4)$, $c=18.661(4)$ Å, $\beta=108.39(3)°$; $Z=8$; space group $P2_1/c-C_{2h}^5$). The $[Ti_3O](OPr^i)_9(OMe)$ molecule has a $Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OMe)(\mu_2\text{-}OPr^i)_3(OPr^i)_6$ structure in the solid state and in solution, but is unstable in solution at ambient temperature even in hydrocarbon solvents where it is in quasi-equilibrium with $Ti(OPr^i)_{4-x}(OMe)_x$, $[Ti_3O](OPr^i)_{10}$, and more highly condensed polytitanates. The isostructural trititanate $[Ti_3O](OPr^i)_{10}$ could not be isolated from isopropanol solutions of hydrolyzed $Ti(OPr^i)_4$, but was identified as the sole hydrolysis product at low degrees of hydrolysis using ^{17}O, $^{13}C\{^1H\}$ and ^1H NMR spectroscopy.

Keywords: Crystal structures; Titanium complexes; Oxoalkoxide complexes

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1. Introduction

At present, six structurally-characterized titanium(IV) polyoxoalkoxides are known: $[Ti_7O_4](OEt)_{20}$ [1–3], $[Ti_8O_6](OBz)_{20}$ [3], $[Ti_{10}O_8](OEt)_{24}$ [3], $[Ti_{16}O_{16}](OEt)_{32}$ [2,4], $[Ti_{11}O_{13}](OPr^i)_{18}$ [5] and $\alpha_1\text{-}[Ti_{12}O_{16}](OPr^i)_{16}$ [5]. As a first step toward establishing structure–reactivity correlations in this class of compounds, the relative stabilities of these complexes have been studied in hydrocarbon solvents [6,7]. One outcome of these studies was a correlation between the degree of condensation, defined as y/x for $[Ti_xO_y](OR)_{4x-2y}$, and the kinetic stability of the $[Ti_xO_y]$ titanium oxide core. Highly condensed species such as $\alpha_1\text{-}[Ti_{12}O_{16}](OPr^i)_{16}$, $[Ti_{11}O_{13}](OPr^i)_{18}$ and $[Ti_{16}O_{16}](OEt)_{32}$, with $y/x=1.33$, 1.18 and 1.00, respectively, showed no detectable metal oxide core degradation after 24 h at ambient temperature in methylcyclohexane or in 1/3 (vol./vol.) parent alcohol/toluene solutions [6,7]. The less highly condensed species $[Ti_{10}O_8](OEt)_{24}$, $[Ti_8O_6](OBz)_{20}$ and $[Ti_7O_4](OEt)_{20}$, with $y/x=0.80$, 0.75 and 0.57, respectively, showed less than 10% metal oxide core degradation after 1 h at ambient temperature in methylcyclohexane solution, but showed extensive degradation in the presence of their parent alcohols [6,7]. Since the degrees of condensation for these species lie in the relatively narrow range of 0.57 to 1.33 (see Fig. 1), the isolation of more or less highly condensed species

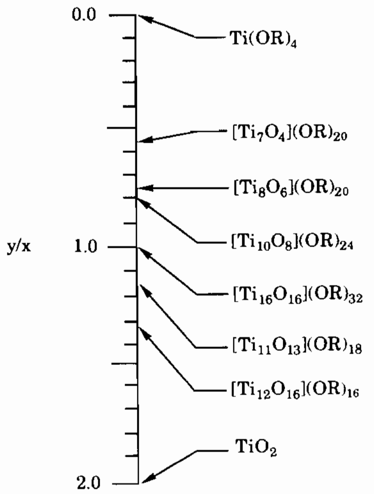

Fig. 1. Formulas of structurally-characterized titanium(IV) polyoxoalkoxides $[Ti_xO_y](OR)_{4x-2y}$ arranged in order of their degrees of condensation relative to $Ti(OR)_4$ and TiO_2.

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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is of interest if the scope of the relation is to be established. Reported here are: (i) the synthesis and characterization of the titanium(IV) oxoalkoxide $[Ti_3O](OPr^i)_9(OMe)$ having a metal oxide core whose relative instability is in accord with its low degree of condensation (0.33); (ii) ^{17}O, ^{1}H and $^{13}C\{^{1}H\}$ NMR evidence for the formation of the isostructural complex $[Ti_3O](OPr^i)_{10}$ as the predominant species formed during the very early stages of $Ti(OPr^i)_4$ hydrolysis in isopropanol solution; (iii) a conformational analysis of $[Ti_3O](OPr^i)_9(OMe)$ and the isostructural $[Mo_3O](OPr^i)_{10}$ [8] molecule that identifies steric crowding as a source of instability in the trititanates.

2. Results

2.1. $[Ti_3O](OPr^i)_9(OMe)$ (1)

The hydrolysis/methanolysis of $Ti(OPr^i)_4$ in isopropanol was studied through a series of titrations performed by introducing 0.05, 0.2, 0.5 and 0.8 equiv. of ^{17}O enriched water into a 0.20 M solution of $Ti(OPr^i)_4$ in isopropanol containing 0.6 equiv. of methanol. ^{17}O NMR spectra were measured for each sample 15 min, 6 h and 24 h after sample preparation. At a water to titanium mole ratio $r = 0.05$, two sharp singlets at δ 558 and 553 with relative intensities of about 3:1 were observed in the δ 450–650 OTi_3 oxygen chemical shift region [3] 15 min after the sample was prepared (see Fig. 2(a)). When the ratio r was 0.2, the δ 558 and 553 resonances were more intense, and a broad OTi_3 resonance appeared at about δ 515 (see Fig. 2(b)). As the water to titanium isopropoxide ratio was further increased to 0.5, another broad absorption band appeared in the δ 650–850 OTi_2 region [3] at about 725 ppm, the broad δ 515 band increased in intensity, and the sharp δ 558 and 554 resonances suffered a slight reduction in intensity (Fig. 2(c)). At $r = 0.8$, the two sharp resonances at δ 558 and 553 had lost still more intensity at the expense of the broad absorption bands in the OTi_2 and OTi_3 regions. Spectra of the $r = 0.05$ sample measured after 6 and 24 h at ambient temperature were almost indistinguishable from the spectrum measured after 15 min. Corresponding spectra of the remaining samples having $r = 0.2$, 0.5 and 0.8 showed increased intensity of the broad bands at ~515 and 725 ppm and decreased intensity of the 558 and 553 ppm resonances as the samples aged.

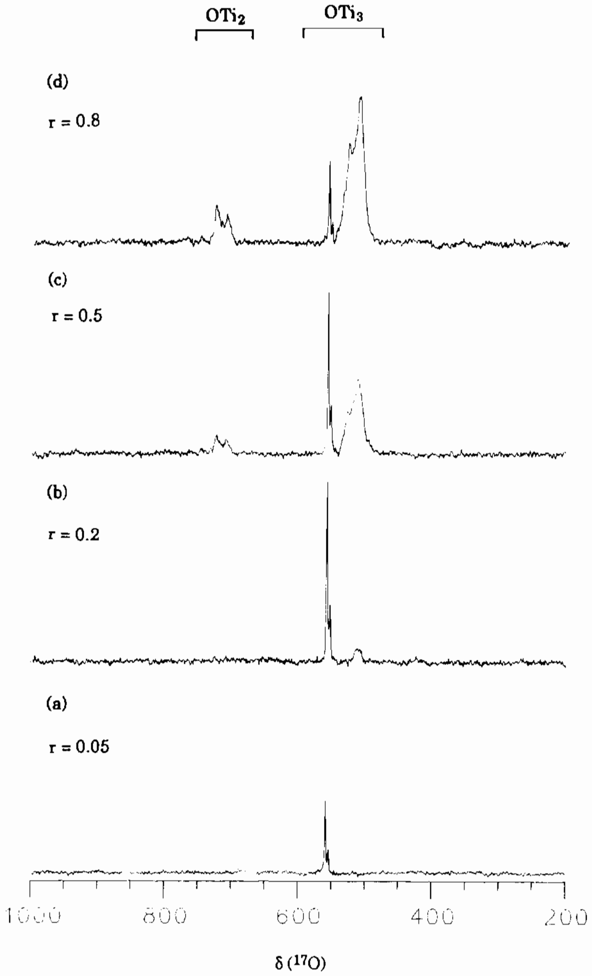

Fig. 2. 40.7 MHz ^{17}O FTNMR spectra of isopropanol solutions of $Ti(OPr^i)_4$ (0.20 M) and MeOH (0.12 M), recorded at ambient temperature 15 min after addition of (a) 0.05, (b) 0.2, (c) 0.5, and (d) 0.8 equiv. of 10 at.% ^{17}O-enriched water per mole $Ti(OPr^i)_4$. In each spectrum, the vertical intensity scale was normalized to the same intensity as the isopropanol oxygen resonance.

The species responsible for the δ 558 ^{17}O NMR absorption (see below) was isolated in crystalline form by reacting $Ti(OPr^i)_4$ with 0.6 equiv. of methanol and 0.078 equiv. of ^{17}O-enriched water in isopropanol solution, concentrating the solution under vacuum, and cooling the solution to −15 °C. Following recrystallization from isopropanol solution, the product was identified as $[Ti_3O](OPr^i)_9(OMe)$ using X-ray crystallographic and NMR spectroscopic results presented below. The overall yield was 81% based on water, but only 19% based on titanium.

A solid state structure determination using X-ray diffraction techniques revealed that single crystals of $[Ti_3O](OPr^i)_9(OMe)$ (1) are composed of discrete trinuclear molecules having the $[M_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6]$ structure previously observed for $[Mo_3O](OR)_{10}$, R = isopropyl and neopentyl [8]. Fractional atomic coordinates for all non-hydrogen atoms of **1** are given with e.s.d.s in Table 1. Selected bond lengths and angles involving non-hydrogen atoms of **1** are given in Table 2. The asymmetric unit of crystalline **1** contains the two crystallographically-independent molecules shown in Fig. 3(a) and (b) and Fig. 4(a) and (b).

The Ti_3O_{11} core observed for crystalline $[Ti_3O](OPr^i)_9(OMe)$ is comprised of three TiO_6 octahedra, each of which shares two of its adjacent

Table 1
Atomic coordinates for non-hydrogen atoms in crystalline $[Ti_3(\mu_3\text{-}O)](\mu_3\text{-}OCH_3)(\mu_2\text{-}O\text{-}i\text{-}C_3H_7)_3(O\text{-}i\text{-}C_3H_7)_6$ (1) [a]

Atom type [b]	Fractional coordinates			Equivalent isotropic thermal parameter B [c] (Å^2 × 10)
	10^4x	10^4y	10^4z	
Molecule a				
Ti1	4593(1)	2042(1)	−1652(1)	27(1)
Ti2	3261(1)	2064(1)	−2178(1)	28(1)
Ti3	3945(1)	3359(1)	−1938(1)	28(1)
O1	3938(2)	2475(3)	−2454(3)	26(2)
O1b	3928(2)	2509(3)	−1195(2)	23(2)
O1c	3912(2)	1350(3)	−1884(3)	29(2)
O2c	3064(2)	3067(3)	−2277(3)	33(2)
O3c	4814(2)	3044(3)	−1588(3)	29(2)
O1d	5057(2)	1753(3)	−738(3)	38(2)
O2d	5032(2)	1747(3)	−2215(3)	38(2)
O3d	2795(2)	1793(3)	−1621(3)	40(2)
O4d	2835(2)	1733(3)	−3073(3)	42(2)
O5d	3951(3)	3972(3)	−1220(3)	38(2)
O6d	3921(3)	3920(3)	−2690(3)	41(2)
C1	3928(4)	2524(5)	−433(4)	35(3)
C1a	3876(4)	647(4)	−1681(5)	39(3)
C1b	3910(5)	593(5)	−852(5)	53(4)
C1c	4348(5)	246(5)	−1864(7)	61(4)
C2a	2551(4)	3493(5)	−2319(5)	47(3)
C2b	2444(4)	3510(6)	−1562(6)	62(4)
C2c	2030(5)	3223(7)	−2938(6)	80(5)
C3a	5390(3)	3338(5)	−1171(5)	41(3)
C3b	5417(4)	3471(5)	−362(5)	52(4)
C3c	5482(4)	3980(5)	−1569(6)	58(4)
C4a	5554(5)	1441(8)	−227(6)	94(6)
C4b	5619(5)	1512(7)	528(6)	90(5)
C4c	6040(4)	1285(7)	−512(6)	89(5)
C5a	5059(5)	1811(7)	−2967(7)	74(5)
C5b	5620(7)	2176(8)	−2905(8)	136(9)
C5c	4991(10)	1216(10)	−3336(9)	197(13)
C6a	2262(5)	1484(7)	−1559(7)	92(6)
C6b	2220(5)	1529(8)	−818(6)	89(6)
C6c	2047(5)	936(6)	−2041(7)	76(5)
C7a	2860(8)	1560(8)	−3799(7)	99(6)
C7b	2859(8)	854(8)	−3904(8)	137(9)
C7c	2538(11)	1958(10)	−4346(8)	213(14)
C8a	3987(5)	4625(5)	−927(5)	51(4)
C8b	3896(7)	4636(6)	−173(6)	89(6)
C8c	3592(6)	5108(5)	−1455(7)	93(6)
C9a	3810(7)	3928(10)	−3479(8)	119(8)
C9b	3313(9)	4333(10)	−3845(8)	187(11)
C9c	4270(7)	3984(12)	−3684(8)	190(12)
Molecule b				
Ti1	−377(1)	2887(1)	−642(1)	27(1)
Ti2	−1701(1)	3039(1)	−1201(1)	30(1)
Ti3	−1157(1)	1666(1)	−982(1)	28(1)
O1	−1080(2)	2528(3)	−407(2)	25(2)
O1b	−1063(2)	2535(2)	−1666(3)	25(2)
O1c	−978(2)	3666(3)	−909(3)	31(2)
O2c	−2001(2)	2069(3)	−1349(3)	31(2)
O3c	−258(2)	1863(3)	−597(3)	29(2)
O1d	124(2)	3143(3)	−1154(3)	34(2)
O2d	53(2)	3146(3)	282(3)	34(2)
O3d	−2126(2)	3390(3)	−2110(3)	40(2)
O4d	−2138(2)	3354(3)	−647(3)	38(2)
O5d	−1168(3)	1079(3)	−1731(3)	40(2)
O6d	−1218(2)	1084(3)	−283(3)	38(2)
C1	−1050(4)	2532(4)	−2422(4)	36(3)
C1a	−872(4)	4367(5)	−1050(5)	43(3)
C1b	−900(5)	4455(5)	−1869(5)	56(4)
C1c	−1307(5)	4810(5)	−844(6)	74(5)
C2a	−2579(4)	1817(5)	−1800(5)	46(3)
C2b	−2609(5)	1754(6)	−2627(5)	62(4)
C2c	−2718(4)	1152(5)	−1493(6)	62(4)
C3a	239(4)	1416(4)	−578(5)	39(3)
C3b	359(4)	1421(5)	−1324(5)	53(4)
C3c	775(4)	1621(5)	75(5)	51(4)
C4a	656(5)	3398(7)	−1252(6)	68(4)
C4b	616(5)	3448(7)	−2045(6)	83(5)
C4c	952(6)	3905(8)	−748(7)	131(8)
C5a	17(5)	3175(6)	1036(5)	59(4)
C5b	627(6)	3150(8)	1564(6)	121(6)
C5c	−306(6)	3801(8)	1125(7)	114(7)
C6a	−2587(5)	3809(8)	−2551(7)	94(6)
C6b	−2592(5)	3873(7)	−3304(6)	87(5)
C6c	−3131(4)	3799(6)	−2363(6)	81(5)
C7a	−2218(5)	3352(6)	67(6)	65(4)
C7b	−2511(7)	3981(7)	194(8)	115(7)
C7c	−2498(9)	2743(7)	189(9)	169(12)
C8a	−1155(8)	404(6)	−2011(8)	108(7)
C8b	−1373(6)	336(6)	−2788(7)	99(6)
C8c	−953(7)	−104(6)	−1485(8)	114(7)
C9a	−1231(7)	993(7)	462(7)	85(6)
C9b	−1545(7)	355(7)	509(7)	125(8)
C9c	−668(7)	1084(10)	1017(7)	166(10)

[a] The numbers in parentheses are the e.s.d.s in the last significant digit.

[b] Atoms are labeled in agreement with Figs. 3, 4 and 5.

[c] This is one-third of the trace of the orthogonalized B_{ij} tensor.

octahedral faces with the two neighboring octahedra. It thus contains as subunits confacial octahedra Ti_2O_9 of the type observed in titanate lattice compounds such as hexagonal $BaTiO_3$ [9] and in titanium alkoxides such as $Ba[Ti_2(OR)_9]$, R = Et [10] and Pr^n [11]. Within the Ti_3O_{11} core, each d^0 Ti^{IV} center is octahedrally coordinated by one μ_3-oxo, one μ_3-methoxy, two *trans* μ_2-isopropoxy, and two *cis* terminal isopropoxy ligands.

The hydrocarbon moieties surrounding the Ti_3O_{11} cores of the $[Ti_3O](OPr^i)_9(OMe)$ molecules in crystalline **1** all adopt well-defined conformations such that the molecules have virtual C_3 symmetry. In the μ_3-methoxy methyl groups, which were refined as rigid rotors, the methyl hydrogens are rotated away from the adjacent terminal isopropoxy oxygen centers O1d, O3d and O5d, presumably as a result of the close, 3.21(1,2,4,6) [1] Å

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[1] The first number in parentheses following an average value of a bond length or angle is the root-mean-square e.s.d. of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

Table 2
Selected bond lengths (Å) and angles (°) involving non-hydrogen atoms in crystalline $[Ti_3(\mu_3\text{-}O)](\mu_3\text{-}OCH_3)(\mu_2\text{-}O\text{-}i\text{-}C_3H_7)_3(O\text{-}i\text{-}C_3H_7)_6$ (**1**)[a]

Molecule a		Molecule b	
Bond lengths (Å)			
Ti1...Ti2	2.944(2)	Ti1...Ti2	2.943(2)
Ti1...Ti3	2.947(2)	Ti1...Ti3	2.945(2)
Ti2...Ti3	2.950(2)	Ti2...Ti3	2.943(2)
Ti1–O1	1.961(4)	Ti1–O1	1.954(5)
Ti2–O1	1.977(6)	Ti2–O1	1.984(4)
Ti3–O1	1.976(5)	Ti3–O1	1.976(5)
Ti1–O1b	2.187(5)	Ti1–O1b	2.180(4)
Ti2–O1b	2.177(4)	Ti2–O1b	2.181(6)
Ti3–O1b	2.173(5)	Ti3–O1b	2.176(5)
Ti1–O1c	2.026(5)	Ti1–O1c	2.022(5)
Ti2–O1c	2.007(5)	Ti2–O1c	2.014(5)
Ti2–O2c	2.010(5)	Ti2–O2c	2.011(5)
Ti3–O2c	2.030(5)	Ti3–O2c	2.026(5)
Ti3–O3c	2.017(5)	Ti3–O3c	2.024(5)
Ti1–O3c	2.021(5)	Ti1–O3c	2.022(5)
Ti1–O1d	1.799(5)	Ti1–O1d	1.797(6)
Ti1–O2d	1.778(6)	Ti1–O2d	1.774(5)
Ti2–O3d	1.804(6)	Ti2–O3d	1.807(5)
Ti2–O4d	1.776(5)	Ti2–O4d	1.774(6)
Ti3–O5d	1.795(6)	Ti3–O5d	1.803(6)
Ti3–O6d	1.769(6)	Ti3–O6d	1.773(6)
Bond angles (°)			
O1–Ti1–O1b	69.0(2)	O1–Ti1–O1b	69.5(2)
O1–Ti2–O1b	69.0(2)	O1–Ti2–O1b	68.9(2)
O1–Ti3–O1b	69.1(2)	O1–Ti3–O1b	69.2(2)
O1–Ti1–O1c	75.9(2)	O1–Ti1–O1c	76.2(2)
O1–Ti1–O3c	75.5(2)	O1–Ti1–O3c	75.4(2)
O1–Ti2–O1c	76.0(2)	O1–Ti2–O1c	75.8(2)
O1–Ti2–O2c	75.9(2)	O1–Ti2–O2c	76.5(2)
O1–Ti3–O2c	75.5(2)	O1–Ti3–O2c	76.3(2)
O1–Ti3–O3c	75.2(2)	O1–Ti3–O3c	74.9(2)
O1b–Ti1–O1c	76.1(2)	O1b–Ti1–O1c	76.3(2)
O1b–Ti1–O3c	76.8(2)	O1b–Ti1–O3c	77.1(2)
O1b–Ti2–O1c	76.8(2)	O1b–Ti2–O1c	76.4(2)
O1b–Ti2–O2c	76.7(2)	O1b–Ti2–O2c	76.6(2)
O1b–Ti3–O2c	76.4(2)	O1b–Ti3–O2c	76.4(2)
O1b–Ti3–O3c	77.2(2)	O1b–Ti3–O3c	77.1(2)
O1–Ti1–O2d	98.2(2)	O1–Ti1–O2d	98.1(2)
O1–Ti2–O4d	99.1(2)	O1–Ti2–O4d	99.1(2)
O1–Ti3–O6d	99.4(2)	O1–Ti3–O6d	99.4(2)
O1b–Ti1–O1d	92.9(2)	O1b–Ti1–O1d	92.4(2)
O1b–Ti2–O3d	91.8(2)	O1b–Ti2–O3d	92.2(2)
O1c–Ti1–O1d	100.9(2)	O1c–Ti1–O1d	100.1(2)
O3c–Ti1–O1d	100.6(2)	O3c–Ti1–O1d	101.2(2)
O1c–Ti1–O2d	102.3(2)	O1c–Ti1–O2d	99.2(2)
O3c–Ti1–O2d	99.5(3)	O3c–Ti1–O2d	102.4(2)
O1d–Ti1–O2d	99.9(3)	O1d–Ti1–O2d	100.0(2)
O1c–Ti2–O3d	100.3(2)	O1c–Ti2–O3d	100.7(2)
O2c–Ti2–O3d	100.3(3)	O2c–Ti2–O3d	99.6(2)
O1c–Ti2–O4d	98.8(2)	O1c–Ti2–O4d	102.5(2)
O2c–Ti2–O4d	103.0(2)	O2c–Ti2–O4d	99.8(3)
O3d–Ti2–O4d	100.1(3)	O3d–Ti2–O4d	99.8(3)
O1b–Ti3–O5d	91.8(2)	O1b–Ti3–O5d	91.3(2)
O2c–Ti3–O5d	100.9(3)	O2c–Ti3–O5d	102.2(2)
O3c–Ti3–O5d	101.1(2)	O3c–Ti3–O5d	99.0(3)
O2c–Ti3–O6d	98.6(2)	O2c–Ti3–O6d	101.7(3)
O3c–Ti3–O6d	102.9(3)	O3c–Ti3–O6d	100.0(2)
O5d–Ti3–O6d	99.7(3)	O5d–Ti3–O6d	100.1(3)
O1c–Ti1–O3c	146.0(2)	O1c–Ti1–O3c	146.4(2)
O1c–Ti2–O2c	146.7(2)	O1c–Ti2–O2c	146.7(2)
O2c–Ti3–O3c	145.9(2)	O2c–Ti3–O3c	146.2(2)
O1–Ti1–O1d	161.9(3)	O1–Ti1–O1d	161.9(2)
O1–Ti2–O3d	160.8(2)	O1–Ti2–O3d	161.1(3)
O1–Ti3–O5d	160.9(2)	O1–Ti3–O5d	160.3(3)
O1b–Ti1–O2d	167.2(2)	O1b–Ti1–O2d	167.4(3)
O1b–Ti2–O4d	167.9(3)	O1b–Ti2–O4d	167.9(2)
O1b–Ti3–O6d	168.2(2)	O1b–Ti3–O6d	168.6(2)
Ti1–O1–Ti2	96.8(2)	Ti1–O1–Ti2	96.7(2)
Ti1–O1–Ti3	96.9(2)	Ti1–O1–Ti3	97.1(2)
Ti2–O1–Ti3	96.5(2)	Ti2–O1–Ti3	96.0(2)
Ti1–O1b–Ti2	84.9(2)	Ti1–O1b–Ti2	84.9(2)
Ti1–O1b–Ti3	85.0(2)	Ti1–O1b–Ti3	85.1(2)
Ti2–O1b–Ti3	85.4(2)	Ti2–O1b–Ti3	85.0(2)
Ti1–O1c–Ti2	93.8(2)	Ti1–O1c–Ti2	93.6(2)
Ti2–O2c–Ti3	93.8(2)	Ti2–O2c–Ti3	93.6(2)
Ti1–O3c–Ti3	93.7(2)	Ti1–O3c–Ti3	93.4(2)
Ti1–O1b–C1	128.5(4)	Ti1–O1b–C1	129.3(5)
Ti2–O1b–C1	128.7(5)	Ti2–O1b–C1	128.9(4)
Ti3–O1b–C1	128.9(5)	Ti3–O1b–C1	128.1(4)
Ti1–O1c–C1a	133.6(4)	Ti1–O1c–C1a	128.3(5)
Ti2–O1c–C1a	129.6(5)	Ti2–O1c–C1a	135.4(4)
Ti2–O2c–C2a	137.0(5)	Ti2–O2c–C2a	128.8(5)
Ti3–O2c–C2a	126.6(5)	Ti3–O2c–C2a	134.2(5)
Ti1–O3c–C3a	126.6(5)	Ti1–O3c–C3a	134.5(5)
Ti3–O3c–C3a	136.1(5)	Ti3–O3c–C3a	128.8(4)
Ti1–O1d–C4a	155.8(7)	Ti1–O1d–C4a	156.8(5)
Ti1–O2d–C5a	139.8(6)	Ti1–O2d–C5a	140.7(6)
Ti2–O3d–C6a	150.9(6)	Ti2–O3d–C6a	150.3(7)
Ti2–O4d–C7a	144.0(8)	Ti2–O4d–C7a	145.6(6)
Ti3–O5d–C8a	153.9(6)	Ti3–O5d–C8a	151.5(7)
Ti3–O6d–C9a	141.6(9)	Ti3–O6d–C9a	146.9(6)

[a] The numbers in parentheses are the e.s.d.s in the last significant digit. Atoms are labeled in agreement with Figs. 3, 4 and 5.

contact [2] between the methyl carbon and these adjacent oxygens. The space-filling models shown in Fig. 5 illustrate how each methoxy methyl group is surrounded by six isopropyl methyl groups, three from bridging isopropoxy groups (C1b, C2b and C3b with d(C1...Cb) = 3.89(2,3,5,6) Å) and three from terminal isopropoxy groups (C4b, C6b and C8b with d(C1...Cb) = 4.26(2,7,13,6) Å). Viewed from the perspective employed in Fig. 3(a) and (b), the methoxy C–O vector and the surrounding isopropyl methyl-to-methine C–C vectors are seen to be approximately parallel, with the result that the top surfaces of the two independent molecules can be viewed as approx-

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[2] van der Waals contacts are defined here using Pauling's van der Waals radii for H (1.2 Å), O (1.4 Å) and CH_3 (2.0 Å) [12].

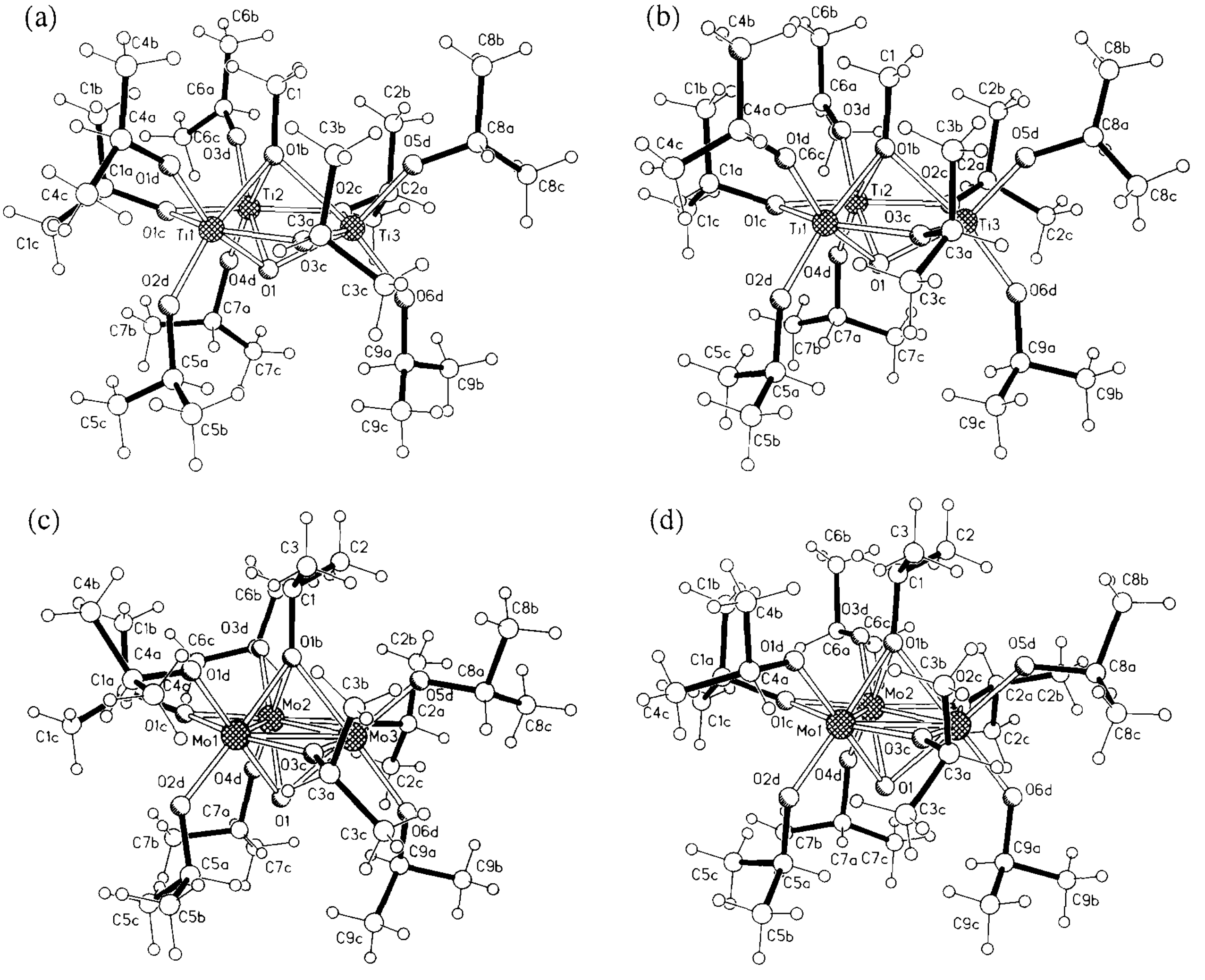

Fig. 3. Perspective drawings of the two crystallographically-independent molecules present in both $[Ti_3O](OPr^i)_9(OMe)$ (**1**) and $[Mo_3O](OPr^i)_{10}$ (**3**): (a) **1**, molecule a; (b) **1**, molecule b; (c) **3**, molecule a; (d) **3**, molecule b. For purposes of comparing molecules **1** and **3**, the numbering system employed in Ref. [8] was changed and hydrogen atoms were placed at idealized sp^3-hybridized positions on the carbon atoms with a C–H bond length of 0.96 Å. For purposes of clarity, metal atoms are represented by large-sized cross-hatched spheres, oxygen atoms are represented by medium-sized shaded spheres, and carbon and hydrogen atoms are represented by medium-sized and small open spheres, respectively. These views are nearly perpendicular to the pseudo-C_3 axis of the molecule which passes through the oxygen atoms of the two μ_3-bonded ligands in each molecule.

imately close-packed C–C and C–O rods or columns. The remaining six methyl groups in the puckered ring of isopropyl groups under discussion are disposed in a fashion that avoids overlap of these methyl groups, and the result is a herringbone-like cyclic arrangement of six isopropyl groups. As shown in Fig. 3(a) and (b), the C–O bonds to the remaining three isopropyl groups at the 'bottom' of each $[Ti_3O](OPr^i)_9(OMe)$ molecule are approximately parallel to the molecular pseudo-C_3 axis, and are able to avoid close contacts with the μ_2-isopropoxy groups 'above' them as well as the μ_3-oxo group. Note that the isopropoxy groups are rotated about their C–O bonds such that their methine hydrogens avoid contact with the μ_3-oxo ligand lying on the pseudo-C_3 axis (d(C...O) = 3.40(1,6,8,6) for C5a, C7a, C9a and O1) (see Fig. 4(a) and (b)). Moreover, this off-axis rotation occurs in the same sense at each C–O bond such that overlap of the isopropyl methyl groups is avoided. The result is a configuration where the isopropyl C–H vectors are approximately parallel to the Ti...Ti edges of the metal triangle, with each vector pointing in the same sense about the virtual C_3 molecular symmetry axis in each molecule. Since the herringbone configuration of six isopropyl groups can point in one of two possible directions about the pseudo-C_3 axis at the top of each molecule and the array of three isopropyl groups at the bottom of each molecule can similarly point in one of two different directions about the same axis, four isomeric molecular configurations are possible: Dd, Dl, Ld and Ll, where upper and lower case letters represent the chirality of the upper and lower parts of the molecule. All four isomers are observed in

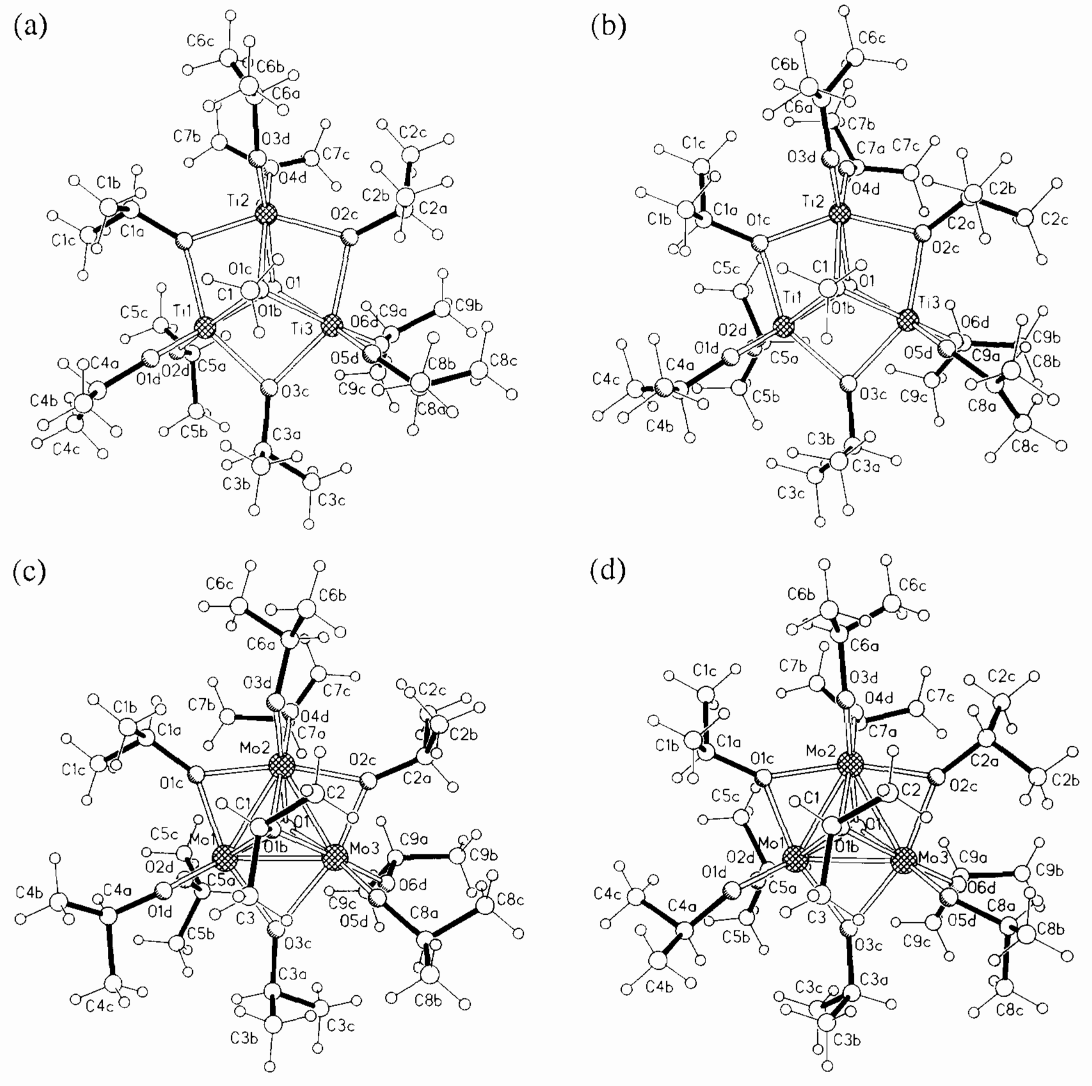

Fig. 4. Perspective drawings of the same molecules shown in Fig. 3, but viewed nearly along the pseudo-C_3 axis.

crystalline compound **1**, but only two diastereomers are shown in Figs. 3 and 4: the Ld isomer in Figs. 3(a) and 4(a) (molecule a) and the Dd isomer in Figs. 3(b) and 4(b) (molecule b).

Solution ^{17}O, ^{13}C{^{1}H} and ^{1}H NMR spectra of $[Ti_3O](OPr^i)_9(OMe)$ measured in methylcyclohexane solution were consistent with the $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OMe)(\mu_2\text{-}OPr^i)_3(OPr^i)_6]$ structure observed in the solid state (see Fig. 6), but these spectra had to be measured at −70 °C in order to avoid sample decomposition and ligand site exchange processes that were rapid on the NMR time scale at ambient temperature (see below). A single ^{17}O NMR absorption was observed at δ 554 in the 450–650 ppm region associated with OTi_3 triply-bridging oxygens in titanium oxoalkoxides [3]. This chemical shift value was observed to be temperature-dependent, shifting to 558 ppm at ambient temperature. As shown in Fig. 6(b), three isopropoxy methine carbon resonances, one methoxy carbon resonance and three isopropoxy methyl carbon resonances were observed at δ 70–80, 57 and 20–30, respectively. Corresponding ^{1}H NMR resonances were also observed (see Fig. 6(c)): three isopropoxy methine proton septets (δ 4–6), a methoxy methyl singlet (δ 3.6) and three isopropoxy methyl doublets (δ 1–2).

2.2. $[Ti_3O](OPr^i)_{10}$ (2)

Hydrolysis of $Ti(OPr^i)_4$ in isopropanol at ambient temperature was studied by adding 0.05 and 0.2 equiv. of ^{17}O-enriched water and observing the ^{17}O NMR spectra of the resulting solutions after 15 min, 6 h and 24 h. The spectrum measured 15 min after adding 0.2 equiv. of water displayed seven strong NMR resonances (see Fig. 7(b)). Six of these, labeled with crosses in Fig. 7(b), were assigned to $[Ti_{11}O_{13}](OPr^i)_{18}$. This species is known to form under very similar conditions and displays six resolved ^{17}O resonances at δ 770, 728, 711, 537, 530, 515 [5], chemical shift values in good agreement with those observed here (see Fig. 7 caption). The

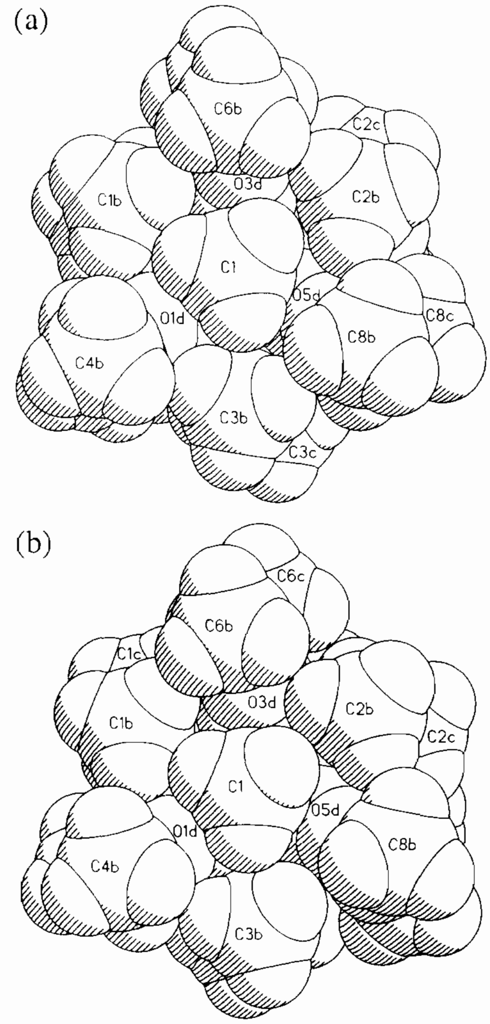

Fig. 5. Space-filling drawings of the two crystallographically-independent molecules of 1 present in the crystal: (a) molecule a; (b) molecule b. These views are down the pseudo-C_3 axis of the molecule which passes through the non-hydrogen atoms of the two μ_3-bonded ligands. These drawings were made using a C–H bond distance of 1.09 Å and van der Waals radii of 1.2, 1.4 and 1.7 Å for H, O and C atoms, respectively.

remaining strong resonance, labeled with a triangle in Fig. 7(b), had a chemical shift value of 553 ppm, the same value observed for the less intense of the two narrow resonances observed upon hydrolysis/methanolysis of Ti(OPr^i)$_4$ in isopropanol (see Fig. 2). In the spectrum measured 15 min after addition of 0.05 equiv. of water (Fig. 7(a)), the [Ti$_{11}$O$_{13}$](OPr^i)$_{18}$ resonances were far less intense relative to the δ 553 resonance. The intensity of the δ 553 resonance diminished with time, however, relative to the [Ti$_{11}$O$_{13}$](OPr^i)$_{18}$ resonances. 24 h after addition of 0.05 equiv. of water, the relative intensities of the δ 553 resonance and the [Ti$_{11}$O$_{18}$](OPr^i)$_{18}$ resonances were the same as the relative intensities measured 15 min after addition of 0.2 equiv. of water. The same effect was noted 24 h after addition of 0.2 equiv. of water, but it was far less dramatic. Measured relative to the intensity of the

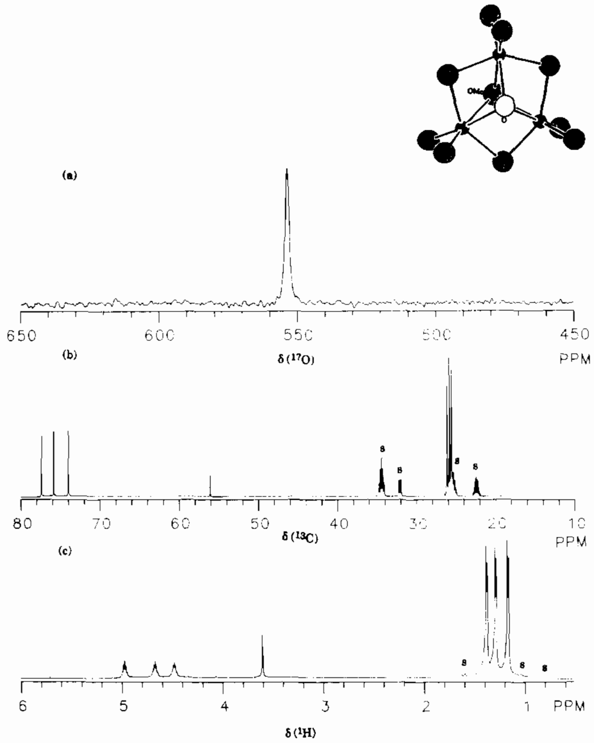

Fig. 6. (a) 40.7 MHz ^{17}O FTNMR, (b) 125.7 MHz ^{13}C FTNMR, and (c) 500 MHz ^{1}H FTNMR spectra of 0.4 M [Ti$_3$O](OPr^i)$_9$(OMe), enriched in ^{17}O at the oxide oxygen site, in methylcyclohexane-d$_{14}$ at −70 °C. See Section 4 for chemical shift data. Solvent resonances are labeled with the letter 's'. The Ti$_3$O$_{11}$ metal oxygen core structure of [Ti$_3$O](OPr^i)$_9$(OMe) is shown at the top of the Figure with titanium atoms represented by small filled circles, alkoxide oxygen atoms by large shaded circles, and the unique oxygen atom by a large open circle.

[Ti$_{11}$O$_{13}$](OPr^i)$_{18}$ resonance, the δ 553 resonance was reduced, after 24 h, to about 1/4 the intensity measured after 15 min.

Although the species responsible for the δ 553 ^{17}O NMR resonance in hydrolyzed Ti(OPr^i)$_4$ solutions could not be isolated in pure form, addition of extremely small amounts of water to Ti(OPr^i)$_4$ was observed to generate mixtures of this species and Ti(OPr^i)$_4$ containing no other titanium oxoalkoxides at concentrations detectable by ^{17}O NMR spectroscopy. Such mixtures could then be isolated and characterized using ^{13}C{^{1}H} and ^{1}H NMR spectroscopy. Specifically, addition of 0.02 equiv. of ^{17}O-enriched water to Ti(OPr^i)$_4$ in isopropanol followed by concentration of the solution, addition of toluene and cooling to −15 °C yielded a solid precipitate that could be isolated by filtration and warmed to ambient temperature to yield an oil. The ^{17}O NMR spectrum of this oil dissolved in isopropanol at ambient temperature contained only a solvent resonance, a Ti(OPr^i)$_4$ resonance at δ 290, plus a δ 554 resonance. Its ^{13}C{^{1}H} NMR spectrum in toluene at −70 °C displayed broad, intense Ti(OPr^i)$_4$ resonances at δ 77.1 and 26.4 plus narrow, weak resonances for four additional types of isopropoxide groups. Three

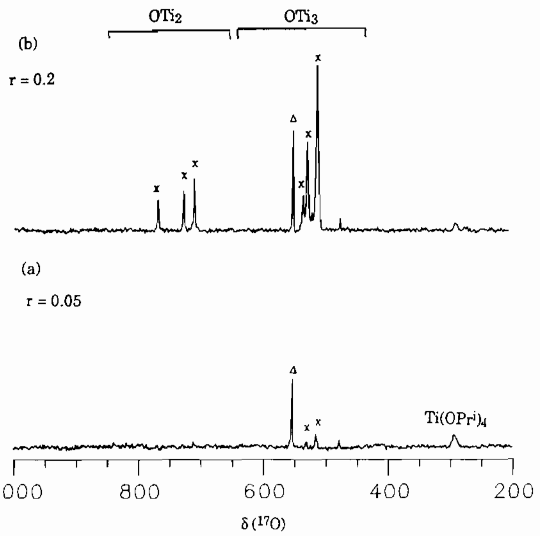

Fig. 7. 40.7 MHz ^{17}O FTNMR spectra of isopropanol solutions of $Ti(OPr^i)_4$ (0.20 M) 15 min after addition of (a) 0.05 and (b) 0.2 equiv. of 10 at.% ^{17}O-enriched water. In both spectra the vertical intensity scale was normalized to the same intensity as the isopropanol oxygen resonance. The resonances assigned to $[Ti_{11}O_{13}](OPr^i)_{18}$ are labeled with crosses and have chemical shift values of δ 769, 728, 711, 537, 530 and 515. The resonance assigned to $[Ti_3O](OPr^i)_{10}$, labeled with a triangle, appears at δ 553.

methine carbon resonances having equal intensity were observed in the δ 74–78 region together with a less intense resonance at δ 70.7. The relative intensities of the four methyl carbon resonances observed in the δ 25–27 region could not be estimated since the resonances all overlapped with the broad, δ 26.4 $Ti(OPr^i)_4$ resonance. ^1H NMR spectra of the oil in methylcyclohexane were fully resolved only in the methine proton region at −70 °C: a very intense, broad δ 4.76 $Ti(OPr^i)_4$ resonance was observed in addition to four much less intense septets, three in the δ 4.5–5.1 region having approximately equal intensity plus one at δ 4.19 with lower intensity.

Multinuclear NMR spectra of the species responsible for the δ 553–554 ^{17}O NMR absorption in hydrolyzed $Ti(OPr^i)_4$ solutions therefore resembled spectra of $[Ti_3O](OPr^i)_9(OMe)$ in several respects. Both displayed a single μ_3-O oxide resonance, and both displayed four types of alkoxide resonances, three with equal intensity and a fourth having lower intensity. Since both species were formed under very similar hydrolysis conditions, they were likely to have similar stoichiometries, i.e. similar degrees of condensation. The δ 553 ^{17}O NMR resonance was therefore assigned to the trititanate $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OPr^i)(\mu_2\text{-}OPr^i)_3(OPr^i)_6]$, a structural analogue of the $[Ti_3O](OPr^i)_9(OMe)$ molecule shown in Figs. 3 and 4. As would be expected for a simple derivative, $[Ti_3O](OPr^i)_9(OMe)$ could be generated from $[Ti_3O](OPr^i)_{10}$ by simple methanolysis. Addition of small amounts of methanol at ambient temperature to an isopropanol solution of hydrolyzed $Ti(OPr^i)_4$ containing the δ 554 ^{17}O NMR absorption led to the appearance of the δ 558 resonance assigned above to $[Ti_3O](OPr^i)_9(OMe)$.

2.3. Solution stability of $[Ti_3O](OPr^i)_9(OMe)$

The reactivity of $[Ti_3O](OPr^i)_9(OMe)$ toward isopropanol and methanol at ambient temperature was investigated using ^{17}O-enriched material dissolved in 1/3 (vol./vol.) alcohol/toluene solutions. ^{17}O NMR spectra of 0.05 M solutions measured 15 min after sample preparation are shown in Fig. 8. In isopropanol/toluene solution (see Fig. 8(a)), small resonances were observed for $[Ti_3O](OPr^i)_9(OMe)$ at δ 558 and $[Ti_3O](OPr^i)_{10}$ at δ 554, but most of the ^{17}O NMR absorption intensity was concentrated in two bands centered at about 720 and 520 ppm arising from decomposition products. The δ 558 and 554 resonances became weaker with time, and could no longer be observed after 24 h. In methanol/toluene solution, the δ 558 $[Ti_3O](OPr^i)_9(OMe)$ resonance was not observed 15 min after sample preparation (see Fig. 8(b)). Instead, two narrow resonances appeared at δ 528 and 357. These resonances were assigned to $[Ti_7O_4](OMe)_{20}$ for two reasons. First, the OTi_2 and OTi_3 oxide oxygen resonances for $[Ti_7O_4](OEt)_{20}$ were known to have similar ^{17}O NMR chemical shift values, namely, δ 537 and 365, respectively [3]. Second, hydrolysis of $Ti(OMe)_4$ in 1/3 vol./vol. methanol/toluene with 0.2 equiv. of ^{17}O-enriched water yielded a solution whose ^{17}O NMR spectrum contained only a solvent resonance and two additional resonances at 528 and 357 ppm.

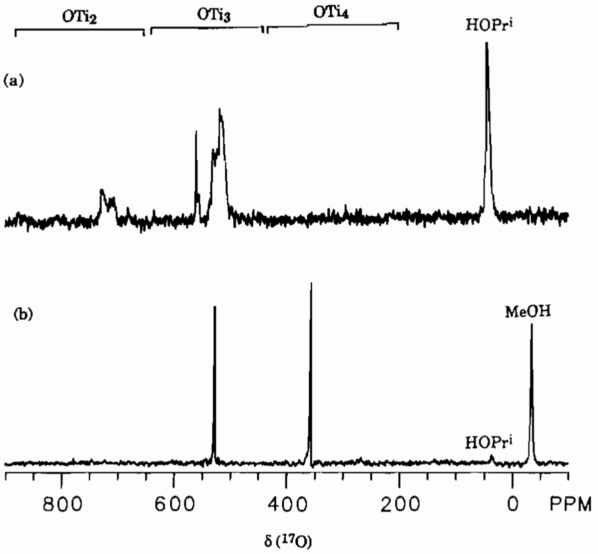

Fig. 8. 40.7 MHz ^{17}O FTNMR spectra of 0.05 M $[Ti_3O](OPr^i)_9(OMe)$ in (a) 1/3 (vol./vol.) isopropanol/toluene and (b) 1/3 (vol./vol.) methanol/toluene measured at 20 °C 15 min after the solutions were prepared. The $[Ti_3O](OPr^i)_9(OMe)$ employed was enriched to 10 at.% ^{17}O at the oxide oxygen site.

The stability of $[Ti_3O](OPr^i)_9(OMe)$ in methylcyclohexane was first probed by ^{17}O NMR spectroscopy. A 0.05 M solution of $[Ti_3O](OPr^i)_9(OMe)$ enriched in ^{17}O at its oxide oxygen site was examined at ambient temperature 1 h after sample preparation. The spectrum displayed a sharp δ 558 $[Ti_3O](OPr^i)_9(OMe)$ resonance, a much less intense δ 554 $[Ti_3O](OPr^i)_{10}$ resonance, and a series of broad, overlapping resonances in the 500–550 and 700–750 ppm regions, indicating extensive (>50%) $[Ti_3O]$ core degradation.

A more detailed variable temperature ^1H NMR spectroscopic study of $[Ti_3O](OPr^i)_9(OMe)$ was also performed in methylcyclohexane solution. A series of spectra was recorded at 20, −10, −30, −50 and −70 °C from a 0.28 M solution that had been stored at ambient temperature for 3 h. These spectra contained useful information in the δ 3.5–5.5 methoxy methyl and isopropoxy methine region (see Fig. 9), and provided evidence for two types of dynamic behavior: irreversible decomposition of $[Ti_3O](OPr^i)_9(OMe)$, evident in the −70 °C spectrum, and reversible alkoxide ligand site exchange, evident from the reversible temperature dependence of the NMR lineshapes. The more intense resonances in the −70 °C spectrum of Fig. 9 were assigned as follows. First, the three septets at δ 4.97, 4.67 and 4.48 and the singlet at δ 3.60 were assigned to $[Ti_3O](OPr^i)_9(OMe)$ by comparison of their chemical shift values with those observed for pure material in methylcyclohexane at −70 °C (see Fig. 6(c) and Section 4). These resonances are labeled with the letter 'a' in Fig. 9. Second, the three resonances or groups of resonances at δ 4.85, 4.75 and 4.06 labeled with the letter 'b' were assigned to the mixture of compounds $Ti(OPr^i)_{4-x}(OMe)_x$, since the same pattern of resonances was observed in the ^1H NMR spectrum of $Ti(OPr^i)_4$ plus MeOH in methylcyclohexane at −70 °C (see Section 4). Four of the remaining resonances or partially obscured resonances, those labeled with the letter 'c', were assigned to $[Ti_3O](OPr^i)_{10}$: the δ 5.10 septet, the much less intense septet at δ 4.19, and the multiplets at 4.64 and 4.52 that are partially obscured by $[Ti_3O](OPr^i)_9(OMe)$ multiplets at δ 4.67 and 4.48. These chemical shifts are in reasonable agreement with those observed for $[Ti_3O](OPr^i)_{10}$ when measured from a mixture of $[Ti_3O](OPr^i)_{10}$ plus $Ti(OPr^i)_4$ in methylcyclohexane at −70 °C (see above): three septets of equal intensity at δ 5.09, 4.64 and 4.51, plus a weaker septet at δ 4.19.

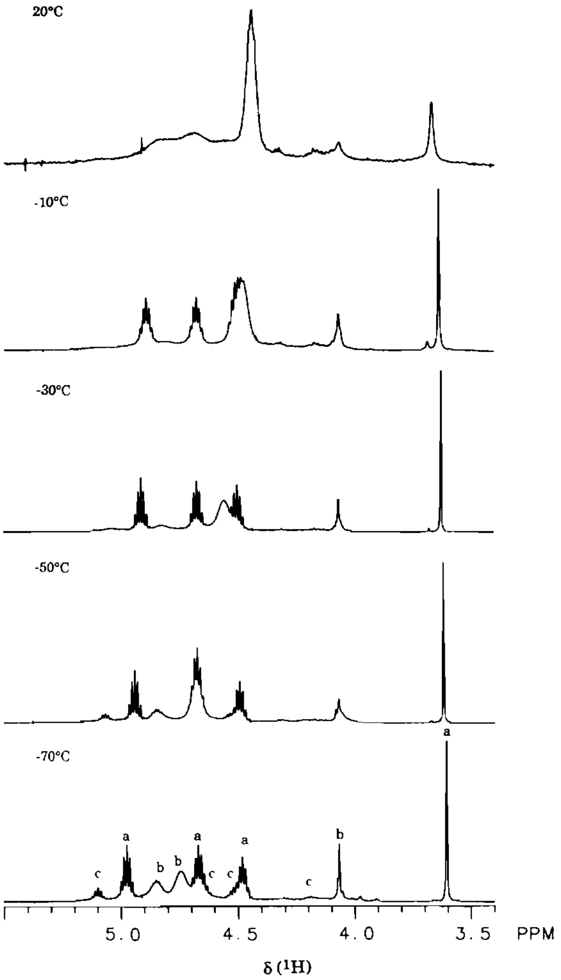

Fig. 9. 500 MHz ^1H NMR spectra in the δ 3.5–5.5 region of a 0.28 M methylcyclohexane solution of $[Ti_3O](OPr^i)_9(OMe)$ measured after the solution was stored for 3 h at ambient temperature. In the spectrum measured at −70 °C, $[Ti_3O](OPr^i)_9(OMe)$ resonances are labeled with the letter 'a', $Ti(OPr^i)_{4-x}(OMe)_x$ resonances are labeled with the letter 'b', and $[Ti_3O](OPr^i)_{10}$ resonances are labeled with the letter 'c'.

The progress of $[Ti_3O](OPr^i)_9(OMe)$ decomposition at ambient temperature to $Ti(OPr^i)_{4-x}(OMe)_x$, $[Ti_3O](OPr^i)_{10}$, and more highly condensed titanium oxoalkoxides was monitored by comparing the intensities of the δ 3.58 $[Ti_3O](OPr^i)_9(OMe)$ methyl ^1H resonance and the overlapping $Ti(OPr^i)_{4-x}(OMe)_x$ methyl ^1H resonances at δ 4.06 with the intensity of the methyl ^1H resonance of an internal standard, toluene (see Section 4). This comparison showed that the $[Ti_3O](OPr^i)_9(OMe)$ concentration dropped to one-half of its original value during the first 3 h of decomposition, remained constant within experimental error during the next 9 h, but dropped to one-third of its original value during the following week. Given that the $[Ti_3O]$ titanium oxide core was present in both $[Ti_3O](OPr^i)_{10}$ and $[Ti_3O](OPr^i)_9(OMe)$ and that $[Ti_3O](OPr^i)_9(OMe)$ was always accompanied by significant amounts of $[Ti_3O](OPr^i)_{10}$ throughout the stability study, $[Ti_3O]$ core degradation was significantly less than 50% after 3–12 h at ambient temperature. Note that this was less degradation than was observed after 1 h in the ^{17}O NMR stability study in methylcyclohexane solution just described. This apparent inconsistency was resolved by noting that the ^{17}O NMR study employed a lower $[Ti_3O](OPr^i)_9(OMe)$ initial concentration than the ^1H NMR study, namely, 0.05 versus 0.2 M. This concentration dependence, coupled with the rate observations just cited, suggested a quasi-equilibrium between the oxoalkoxides $[Ti_3O](OR)_{10}$ and the alkoxides $Ti(OR)_4$ plus the more highly condensed alkoxides $[Ti_xO_y](OR)_{4x-2y}$, $y/x > 1/3$, observed by ^{17}O NMR.

Reversible lineshape changes observed in the variable temperature ^1H NMR spectra shown in Fig. 9 were not analyzed quantitatively, but qualitative information could nonetheless be obtained in conjunction with ^{17}O NMR data just presented. First, the fact that all resonances were exchange-broadened at ambient temperature implied that all alkoxide ligands were involved in some type of chemical site exchange process. The fact that distinct ^{17}O resonances were observed for $[Ti_3O](OPr^i)_{10}$ and $[Ti_3O](OPr^i)_9(OMe)$ under these same conditions implied, however, that the $[Ti_3O]$ cores of these species nonetheless retained their non-equivalence. Second, the spectra measured at −50 and −30 °C showed significant exchange-broadening of the δ 5.11 $[Ti_3O](OPr^i)_{10}$ isopropoxy methine resonance but no broadening of the three $[Ti_3O](OPr^i)_9(OMe)$ isopropoxy methine resonances. This observation implied (i) that the site exchange process responsible for isopropoxy exchange in $[Ti_3O](OPr^i)_{10}$ did not involve $[Ti_3O](OPr^i)_9(OMe)$ isopropoxy groups, and (ii) site exchange of $[Ti_3O](OPr^i)_{10}$ isopropoxy groups was more rapid than the site exchange involving $[Ti_3O](OPr^i)_9(OMe)$ isopropoxy groups, i.e. isopropoxy groups in $[Ti_3O](OPr^i)_{10}$ were more labile than those in $[Ti_3O](OPr^i)_9(OMe)$. Note, however, that the experiment failed to rule out either an intramolecular or an intermolecular mechanism for alkoxide site exchange: either or both were consistent with the experimental results.

3. Discussion

3.1. Synthesis

The chemistry of $[Ti_3O](OPr^i)_{10}$ and $[Ti_3O](OPr^i)_9(OMe)$ illustrates the general difficulty of identifying and isolating kinetically labile, thermodynamically unstable oxoalkoxides having low degrees of condensation. The synthesis of $[Ti_3O](OPr^i)_{10}$ should in theory proceed optimally by addition of 0.33 equiv. of water to $Ti(OPr^i)_4$:

$$3Ti(OPr^i)_4 + H_2O = [Ti_3O](OPr^i)_{10} + 2i\text{-}PrOH \qquad (1)$$

In practice, however, the far greater stability of $[Ti_{11}O_{13}](OPr^i)_{18}$ and the lability of the trititanate favor the formation of the undecatitanate under these conditions, as do entropic considerations:

$$13[Ti_3O](OPr^i)_{10} = [Ti_{11}O_{13}](OPr^i)_{18} + 28Ti(OPr^i)_4 \qquad (2)$$

Thus, as shown above in Fig. 7(b), the trititanate and undecatitanate concentrations are comparable only when 0.2 equiv. of water per $Ti(OPr^i)_4$ have been added, even though the degree of condensation of $[Ti_{11}O_{13}](OPr^i)_{18}$ is 1.18:

$$11Ti(OPr^i)_4 + 13H_2O = [Ti_{11}O_{13}](OPr^i)_{18} + 26i\text{-}PrOH \qquad (3)$$

As a result, $[Ti_3O](OPr^i)_{10}$ could be obtained relatively free from contamination by other polyoxoalkoxides only when very small amounts of water were added to $Ti(OPr^i)_4$. Addition of 0.02 equiv. of water was found to be appropriate, but yielded a formidable product separation problem, since each mole of trititanate formed was accompanied by 47 equiv. of $Ti(OPr^i)_4$, assuming a 100% reaction yield based on water. This dilemma could fortunately be circumvented since the replacement of isopropoxide in the $[Ti_3O](OPr^i)_{10}$ structure with methoxide was found to significantly stabilize the $[Ti_3O](OR)_{10}$ framework. Addition of 0.2 equiv. of water to an isopropanol solution of $Ti(OPr^i)_4$ in the presence of 0.6 equiv. of methanol suppressed almost completely the formation of higher titanates (compare Figs. 2(b) and 7(b)), and allowed the more stable methoxy derivative $[Ti_3O](OPr^i)_9(OMe)$ to be isolated. Even these conditions had to be carefully controlled, however, because excess methanol caused conversion of this methoxy derivative to the pure methoxide $[Ti_7O_4](OMe)_{20}$ (see Fig. 8(a))!

3.2. Structure and stability

It is clear that the choice of alkyl group plays a key role in determining which titanium oxoalkoxides are formed upon hydrolysis of simple alkoxides. For example, the present study plus earlier studies reported in Ref. [5] show that the two oxoalkoxides $[Ti_3O](OPr^i)_{10}$ and $[Ti_{11}O_{13}](OPr^i)_{18}$ are the principal species formed in solution upon hydrolysis of $Ti(OPr^i)_4$ with up to 1/2 equiv. of water at ambient temperature. On the other hand, the oxoalkoxides $[Ti_7O_4](OEt)_{20}$ and $[Ti_8O_6](OEt)_{20}$ are among the species formed in solution upon hydrolysis of $Ti(OEt)_4$ at ambient temperature [3]; neither $[Ti_7O_4](OPr^i)_{20}$ nor $[Ti_8O_6](OPr^i)_{20}$ is produced in measurable amounts upon hydrolysis of $Ti(OPr^i)_4$ under the same conditions. A reasonable explanation for this effect is the steric bulk of the isopropoxy group which destabilizes the $[Ti_7O_4](OR)_{20}$ and $[Ti_8O_6](OR)_{20}$ configurations. Such general explanations have credibility, however, only if specific statements can be made concerning the energetic consequences of increasing steric bulk at a specific alkoxide site within a specific oxoalkoxide molecule. The $[Ti_3O](OPr^i)_9(OMe)$ molecule provides a good system for understanding steric effects from this point of view: replacement of its methoxy group with a bulkier isopropoxy group clearly destablizes the molecule, and the conformational analysis presented below clearly identifies this destabilization as at least in part a steric effect.

We begin with the $[Ti_3O](OPr^i)_9(OMe)$ molecules in crystalline **1**, and consider the consequences of replacing the μ_3-methoxy group with a μ_3-isopropoxy group simply by replacing two methoxy methyl hydrogens with two methyl groups. Assuming a true C–H bond distance of 1.09 Å, the shortest H...C distances between the methoxy methyl hydrogen atoms and the closest isopropyl methyl carbon atoms C1b, C2b and C3b (see Fig. 5) range from 2.97 to 3.15 Å. Increasing the methoxy C–H distance to 1.54 Å, a C–C single bond distance, reduces the corresponding interatomic separations to 2.63–2.93 Å. These separations represent the distances between μ_3-isopropoxy methyl carbons and the adjacent μ_2-isopropoxy methyl carbons, assuming no structural relaxation, and are significantly less than the van der Waals contact distance, 4.0 Å [12]. Clearly, the true structure of $[Ti_3O](OPr^i)_{10}$ will have to relax in order to relieve this steric crowding. The precise nature of this structural relaxation is unknown, since the detailed geometry of the $[Ti_3O](OPr^i)_{10}$ molecule is unknown, but the known $[Mo_3O](OPr^i)_{10}$ structure [8] can be used as a qualitative model for this relaxation, since it has a very similar M_3O_{11} core structure (see Fig. 3(c) and (d) and Fig. 4(c) and (d)). As was the case for crystals of **1**, crystals of $[Mo_3O](OPr^i)_{10}$ contain two crystallographically-independent, diastereomeric molecules, and one of them, molecule b shown in Figs. 3(d) and 4(d), has a distorted Dd conformation (see above) and therefore can be directly compared with molecule b observed in crystals of $[Ti_3O](OPr^i)_9(OMe)$, which also has a Dd conformation. As expected, the major consequence of replacing the μ_3-OMe group with a μ_3-OPr^i group is a bending of the 'top' terminal isopropoxy groups and the μ_2-isopropoxy groups away from the μ_3-isopropoxy group toward the 'bottom' of the molecule, and the resulting change in Ti–O–C angles at the terminally-bonded groups is evident from comparison of Fig. 3(b) and (d): in Fig. 3(d), the O–C bonds for these six groups appear perpendicular to the molecular axis; in Fig. 3(b), they are definitely bent upwards. The conformational change is more subtle than a simple bending motion, and also involves rotation about C–O bonds to relieve steric crowding. This rotation can be discerned by comparison of the 'top' views given in Fig. 4(b) and (d), and is particularly pronounced for the isopropyl group bonded to O2c. The net effect of the isopropoxy bending and rotation motions just described is an exertion of steric pressure on the three isopropoxy groups at the bottom of the molecule, and a consequence is short contacts between the isopropyl methine groups and the μ_3-O ligand (d(C...O) = 2.97(2,2,3,3) Å for C5a, C7a, C9a and O1). Since there is little space to allow bending of these isopropoxy groups away from the μ_2-isopropoxy groups as a means of relieving this pressure, more space is created by rotation about isopropoxy C–O bonds at the 'bottom' of the molecule (see Fig. 4(b) and (d)). This gearing effect between the μ_2-isopropoxy groups and the 'bottom' terminal isopropoxy groups is seen most graphically for the C7b–C7a–C7c isopropyl group bonded to O4d: rotation of the μ_2-isopropoxy group bonded to O2c brings the C2c methyl group in close proximity to the C7c methyl group (3.47(3) Å), which has responded by reducing its off-axis rotation, thus generating a close C7b...C5c methyl–methyl contact (3.83(3) Å) between two of the isopropoxy groups at the bottom of the molecule. Conformational analysis of molecule a in crystalline $[Mo_3O](OPr^i)_{10}$ (Figs. 3(c) and 4(c)) is seen to proceed in a similar fashion by comparison with the Ld conformation of molecule a in crystalline **1** (see above) shown in Figs. 4(a) and 5(a). Here, the perturbation of the μ_3-isopropoxy methyl groups also propagates to the bottom of the molecule, but the consequences are even more pronounced: the isopropyl groups at the 'bottom' of the molecule are no longer rotated off-axis in the same sense (see above), leading to severe crowding, i.e. a C5c...C7b methyl group to methyl group contact of 3.70(3) Å.

The preceding analysis qualitatively demonstrates how sterically crowded and hence sterically destabilized the $[Mo_3O](OPr^i)_{10}$ molecule, and presumably the $[Ti_3O](OPr^i)_{10}$ molecule, is relative to $[Ti_3O](OPr^i)_9$-(OMe): introduction of the μ_3-OPr^i group in place of the μ_3-OMe group introduces steric repulsion even at remote sites of the molecule. While only qualitative in character and failing to separate intra- from intermolecular interactions in the crystal structure, it raises the interesting possibility that the relative stabilities of titanium polyoxoalkoxides derived from the same parent alkoxide might in general be strongly influenced by steric repulsion. Specifically, the greater stability observed for larger, more highly condensed titanium polyoxoalkoxides might arise not from a greater oxide content but from a lower alkoxide content that implies less steric repulsion between organic groups. Steric repulsion of this type is known to influence the stability of simple alkoxides [13], phosphine complexes [14], metal cluster complexes [15], and even ambiphile assemblies [16] in precisely the same fashion.

3.3. Relevance to sol–gel processing

A key result of the present study is the observed instability of the $[Ti_3O](OPr^i)_9(OMe)$ metal oxide core structure in hydrocarbon solutions at ambient temperature, which establishes it as the least stable of the known titanium(IV) polyoxoalkoxides. The correlation between stability and degree of condensation referred to in Section 1 is thus extended to a compound having a lower degree of condensation than those previously available. The question of stability in solution as a function of degree of condensation relates directly to the question of structure evolution during sol–gel polymerization of titanium alkoxides and oxoalkoxides [17]. Clearly, the structure of unstable, early intermediates having low degrees of condensation is irrelevant to the structure, on a molecular level, of colloids and gels formed as the polymerization proceeds. Conversely, if more highly condensed species have greater stability, the structures of more highly condensed molecular intermediates formed as sol–gel polymerization proceeds might serve as molecular building-blocks for the colloids and gels ultimately produced [6].

4. Experimental

4.1. General procedures

Unless otherwise noted, all solvents were reagent grade and were dried before use. Toluene (Fisher) and isopropyl alcohol (Baxter) were refluxed and distilled from sodium under nitrogen. Methyl alcohol (Baxter) was refluxed over $Mg(OCH_3)_2$ under nitrogen and distilled before use. Methylcyclohexane (Fisher) was distilled from sodium and stored over Na/K alloy. Methylcyclohexane-d_{14} (Cambridge Isotope Laboratories) was dried over and distilled from sodium/potassium alloy. Toluene-d_8 (Cambridge Isotope Laboratories) was dried over 3 Å molecular sieves (Linde). The molecular sieves were activated by heating at 350 °C for 24 h and cooling under vacuum. Water enriched in ^{17}O to 10 at.% (Aldrich) was used as received, without further purification. Tetraisopropylorthotitanate (Aldrich) was vacuum distilled at 80 °C (0.02 mm Hg).

All manipulations of the titanium oxoalkoxides were carried out under a nitrogen or argon atmosphere using standard Schlenk and dry box techniques. NMR sample tubes that were capped with rubber septa were also tightly sealed with Parafilm™ laboratory film (American National Can) and stored under nitrogen in Schlenk tubes.

Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois. ^{17}O NMR spectra were measured at 40.7 MHz in 10 or 5 mm o.d. vertical sample tubes without sample spinning on an unlocked General Electric GN-300NB or GN-300WB spectrometer. The chemical shifts were externally referenced to fresh tap water ($\delta = 0.0$) by the sample replacement method. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 500 and 125.8 MHz, respectively, on a General Electric GN-500 spectrometer with chemical shifts internally referenced either to tetramethylsilane ($\delta = 0.00$) or in the case of toluene-d_8 solutions, to the toluene-d_8 resonances: δ 2.09 (^1H), 137.5 ($^{13}C\{^1H\}$). The coupling constant $^3J(^1H-^1H)$ observed for all isopropoxy methine proton septets and methyl doublets is not reported below; its value is 6 Hz in each case.

4.2. Hydrolysis of $Ti(OPr^i)_4$ in MeOH/i-PrOH

A 0.27 M $Ti(OPr^i)_4$ stock solution containing MeOH was prepared by adding 100 μl (2.46 mmol) of MeOH and 13.7 ml of i-PrOH to 1.14 g of $Ti(OPr^i)_4$ (4.01 mmol). A water stock solution was prepared by adding 23.0 μl (1.28 mmol) of 10 at.% ^{17}O-enriched water to 2 ml of i-PrOH. A 1.5 ml aliquot of the $Ti(OPr^i)_4$/MeOH stock solution was then added to each of four 10 mm o.d. NMR sample tubes and the tubes were capped with rubber septa. A 30 μl aliquot of the water stock solution was added to 470 μl of i-PrOH, and the resulting solution was added to one of the NMR sample tubes, with vigorous shaking, using a syringe. The sample was then stored at ambient temperature, and ^{17}O NMR spectra were recorded at ambient temperature 15 min (see Fig. 2), 6 h and 24 h after the sample preparation was completed. Precisely the same procedure was followed for three further samples, except for the amounts of water stock solution and isopropanol added: for the second sample, a 125 μl aliquot of the water stock solution plus 375 μl isopropanol were added; for the third sample, a 310 μl aliquot of the water stock solution plus 190 μl of isopropanol were added; and for the fourth sample, 500 μl of the water stock solution only were added. The initial concentrations of $Ti(OPr^i)_4$ and MeOH in each of the samples were 0.20 and 0.12 M, respectively. The equivalents of water added per mole $Ti(OPr^i)_4$ in the four samples were (1) 0.05, (2) 0.2, (3) 0.5 and (4) 0.8.

4.3. Preparation of $[Ti_3O](OPr^i)_9(OMe)$

A solution of 0.24 ml (5.9 mmol) of methanol in 6 ml of isopropanol was added to a solution of $Ti(OPr^i)_4$ (2.85 g, 10.0 mmol) in 20 ml of isopropanol with stirring. A solution of 14 μl (0.78 mmol) of 10 at.% ^{17}O-enriched water in 15 ml of isopropanol was then added dropwise to this solution with vigorous stirring over a 30 min time period using a syringe. 30 min after addition of the water solution was completed, the solution was concentrated to about 10 ml under vacuum and cooled to −15 °C for 12 h. The crystalline solid that had formed was collected by filtration and washed with 2×3 ml of isopropanol. This crude reaction product was dissolved in 8 ml of isopropanol and cooled to −15 °C for 12 h. The crystalline solid obtained was isolated by filtration and dried in vacuo, yielding 0.462 g (0.633 mmol) product, 19% based on Ti, 81% based on water. *Anal.* Calc. for $C_{28}H_{66}O_{11}Ti_3$: C, 46.55; H, 9.21; Ti, 19.88. Found: C, 46.21; H, 9.45; Ti, 19.68%.

NMR spectra were measured from 0.4 M methylcyclohexane-d_{14} solutions prepared at low temperature as follows. A 0.6 ml sample of C_7D_{14}, which had been dried over Na/K and degassed using three freeze–pump–thaw cycles, was vacuum distilled into a cold ($T = 77$ K) 5 mm o.d. NMR sample tube containing solid $[Ti_3O](OPr^i)_9(OMe)$ (0.18 g, 0.25 mmol). This tube was then flame sealed under vacuum, keeping the sample at 77 K. The solid was dissolved by shaking the sealed NMR sample tube in a −90 °C cold bath immediately before insertion into the spectrometer probe, which had been precooled to −90 °C. An initial $^{13}C\{^1H\}$ NMR spectrum was measured at −90 °C to establish sample purity, but all further measurements were made at −70 °C where viscosity line broadening was avoided but slow sample decomposition was observed. 40.7 MHz ^{17}O NMR (see Fig. 6(a)): δ 554 (s). 125.7 MHz $^{13}C\{^1H\}$ NMR (see Fig. 6(b)): δ 77.4 (s), 75.8 (s), 74.0 (s) $[O\mathit{C}H(CH_3)_2]$; 56.0 (s, $O\mathit{C}H_3$); 26.1 (s), 25.8 (s), 25.5 (s) $[OCH(\mathit{C}H_3)_2]$. 500 MHz ^1H NMR (see Fig. 6(c)): δ 4.97 (sept, 3H), 4.67 (sept, 3H), 4.48 (sept, 3H) $[OC\mathit{H}(CH_3)_2]$; 3.60 (s, 3H, $OC\mathit{H}_3$); 1.38 (d), 1.29 (d), 1.16 (d) $[OCH(C\mathit{H}_3)_2]$.

4.4. Hydrolysis of $Ti(OPr^i)_4$ in i-PrOH

A 0.27 M $Ti(OPr^i)_4$ stock solution was prepared by adding 4.6 ml of i-PrOH to 0.380 g of $Ti(OPr^i)_4$ (1.35 mmol). A water stock solution was prepared by adding 23.0 μl (1.28 mmol) of 10 at.% ^{17}O-enriched water to 2 ml of i-PrOH. These solutions were used to prepare two NMR samples having 0.20 M initial $Ti(OPr^i)_4$ concentrations plus 0.05 and 0.2 equiv. of water by following precisely the same procedure described above for hydrolysis of $Ti(OPr^i)_4$ in MeOH/i-PrOH. ^{17}O NMR spectra were recorded at ambient temperature after storing the samples for 15 min (see Fig. 7), 6 h and 24 h at ambient temperature.

4.5. Generation of $[Ti_3O](OPr^i)_{10}$

A solution of 13.5 μl (0.75 mmol) of 10 at.% ^{17}O-enriched water in 15 ml isopropanol was added to a solution of $Ti(OPr^i)_4$ (12.35 g, 43.7 mmol) in 30.5 ml of isopropanol with vigorous stirring over a 30 min time period at ambient temperature. About 30 min after the addition was completed, the resulting solution was concentrated to one-half of its volume under vacuum, and 5 ml of toluene were added. The solution was then stored at −15 °C for 24 h, and the solid that precipitated from solution was separated by cannula filtration at 0 °C. When warmed to ambient temperature, the solid melted to afford a colorless oil. Samples for NMR spectroscopic studies were prepared by dissolving the oil in solvents at ambient temperature, transferring the solutions to NMR sample tubes, and flame sealing the tubes. ^{17}O NMR (40.7 MHz, i-PrOH, 20 °C): δ 554 (s, $\mathit{O}Ti_3$), 292 (br, $Ti(\mathit{O}Pr^i)_4$), 41 (br, i-PrOH). $^{13}C\{^1H\}$ NMR (75.6 MHz, toluene-d_8, −70 °C): δ 78.0 (s), 77.1 (s, br), 76.5 (s), 74.7 (s), 70.7 (s) $[O\mathit{C}H(CH_3)_2]$; 26.7 (s), 26.4 (s, br), 26.0 (s), 25.9 (s), 25.7 (s) $[OCH(\mathit{C}H_3)_2]$. ^1H NMR (500 MHz, methylcyclohexane-d_{14}, −70 °C): δ 5.09 (sept), 4.76 (s, br), 4.64 (sept), 4.51 (sept), 4.19 (sept) $[OC\mathit{H}(CH_3)_2]$; 1.25 (s, br) $[OCH(C\mathit{H}_3)_2]$.

4.6. $[Ti_3O](OPr^i)_9(OMe)$ stability studies

Stability in isopropanol/toluene was studied using a 0.05 M solution of $[Ti_3O](OPr^i)_9(OMe)$ that was 10 at.% enriched in ^{17}O at its oxide oxygen site. A solution of 72 mg of $[Ti_3O](OPr^i)_9(OMe)$ (0.1 mmol) in 0.5 ml of isopropanol and 1.5 ml of toluene was prepared in a 10 mm o.d. NMR sample tube. The NMR sample tube was then capped with a rubber septum, and 40.7 MHz ^{17}O NMR spectra were recorded at ambient temperature after storing the sample at ambient temperature for 15 min (see Fig. 8(a)), 6 h and 24 h after sample preparation.

Stability in methanol/toluene was studied using precisely the same procedure just described for stability studies in isopropanol/toluene, except that samples were prepared using 0.5 ml of methanol instead of 0.5 ml of isopropanol (see Fig. 8(b)).

Stability studies in methylcyclohexane solution were performed using both ^{17}O NMR and ^1H NMR spectroscopy. For the ^{17}O NMR study, a 0.05 M solution of $[Ti_3O](OPr^i)_9(OMe)$ was prepared from 72 mg (0.1 mmol) of material enriched to 10 at.% at its oxide oxygen site and 2 ml methylcyclohexane in a 10 mm o.d. NMR sample tube which was subsequently flame-sealed under vacuum. The ^{17}O NMR spectrum was measured 1 h after sample preparation. For the ^1H NMR study, a 0.28 M methylcyclohexane solution was prepared as follows. A solution of 8 μl of tetramethylsilane (NMR chemical shift reference) and 1.2 μl of toluene (NMR integration standard) in 0.5 ml of methylcyclohexane-d_8 was dried over Na/K, degassed using three freeze–pump–thaw cycles, and vacuum distilled into a 5 mm o.d. NMR sample tube containing 0.10 g (0.14 mmol) of $[Ti_3O](OPr^i)_9(OMe)$ at 77 K. The NMR sample tube was then flame-sealed, the $[Ti_3O](OPr^i)_9(OMe)$ was brought into solution by shaking the sample tube in a −90 °C cold bath, and the sample tube was inserted into the NMR spectrometer probe, which had been precooled to −90 °C. An ^1H NMR spectrum was then measured at −70 °C, and the sample was warmed to ambient temperature and stored at ambient temperature for 3 h. 500 MHz ^1H NMR spectra were then recorded at 20, −10, −30, −50, −70 and −90 °C (see Fig. 9). The sample was then warmed to ambient temperature and the same sequence of spectra was measured twice more, after being stored at ambient temperature for a total of 12 h and 1 week. The course of decomposition was monitored by measuring, at −70 °C, the integrated intensities of the methyl proton resonances for $Ti(OPr^i)_x(OMe)_{4-x}$ at δ 4.06 and the methyl proton resonance for $[Ti_3O](OPr^i)_9(OMe)$ at δ 3.60 relative to the methyl proton resonance for the integration standard, toluene. By arbitrarily assigning the reference integral a value of 110, the integrated intensity of the δ 4.06 resonances was 53, 55 and 64 relative to the toluene methyl resonance after 3 h, 12 h and 1 week at ambient temperature, respectively. The corresponding integrated intensity for the δ 3.60 resonance was 47, 44 and 33.

4.7. Reaction of $Ti(OPr^i)_4$ with MeOH

A solution of methanol (0.24 ml, 5.97 mmol) in 5 ml of toluene was added to a solution of $Ti(OPr^i)_4$ (3.8 g, 13.2 mmol) in 10 ml of toluene with vigorous stirring. After 15 min, the solvent was removed to afford a colorless oil. ^1H NMR (500 MHz, methylcyclohexane-d_{14}, −70 °C): δ 4.85 (br, $CH(CH_3)_2$), 4.75 (br, $CH(CH_3)_2$), 4.06 (s, OCH_3), 1.25 (br, $OCH(CH_3)_2$).

4.8. X-ray crystallographic study of $[Ti_3O](OPr^i)_9(OMe)$

Crystals suitable for X-ray crystallographic study were grown by cooling a solution of 0.100 g of $[Ti_3O](OPr^i)_9(OMe)$ in 1 ml of isopropanol to −15 °C for 2 days. Single crystals of $[Ti_3(\mu_3\text{-}O)](\mu_3\text{-}OCH_3)(\mu_2\text{-}O\text{-}i\text{-}C_3H_7)_3(O\text{-}i\text{-}C_3H_7)_6$ (**1**) are, at 20 ± 1 °C, monoclinic, space group $P2_1/c\text{-}C_{2h}^5$ (No. 14) with $a = 23.295(5)$, $b = 19.560(4)$, $c = 18.661(4)$ Å, $\beta = 108.39(3)°$, $V = 8069(4)$ Å^3, $Z = 8$ formula units ($D_{calc} = 1.190$ g cm^{-3}; μ(Mo Kα) = 0.62 mm^{-1}). The computer programs and procedures used for data collection, data reduction, structure solution and refinement of **1** have been reported elsewhere [18]; a summary of the crystallographic data for the present study is given in Table 3. A total of 11 273 independent reflections having 2θ(Mo Kα) < 45.8° (the equivalent of 0.6 limiting Cu Kα spheres) was collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromated Mo Kα radiation. The structure was solved using 'direct methods' techniques with the Siemens SHELXTL-PC software package. The resulting structural parameters have been refined to convergence (R_1 (unweighted, based on F) = 0.046 for 4551

Table 3
Summary of crystallographic data for $[Ti_3(\mu_3\text{-}O)](\mu_3\text{-}OCH_3)(\mu_2\text{-}O\text{-}i\text{-}C_3H_7)_3(O\text{-}i\text{-}C_3H_7)_6$ (**1**)

Empirical formula	$[Ti_3(\mu_3\text{-}O)](\mu_3\text{-}OCH_3)(\mu_2\text{-}O\text{-}i\text{-}C_3H_7)_3(O\text{-}i\text{-}C_3H_7)_6$
Color of crystal	colorless
Crystal dimensions (mm)	0.40 × 0.70 × 0.85
Crystal system	monoclinic
Space group	$P2_1/c\text{-}C_{2h}^5$ (No. 14)
Cell dimensions	
a (Å)	23.295(5)
b (Å)	19.560(4)
c (Å)	18.661(4)
β (°)	108.39(3)
Z (formula units)	8
Volume (Å^3)	8069(4)
Calculated density (g cm^{-3})	1.190
Wavelength (Å)	0.71073
Molecular weight	722.51
Linear absorption coefficient (mm^{-1})	0.62
Scan type	ω
Average ω scan width at half height (°)	0.38
Scan speed (° min^{-1})	6.0–1.0
Scan width (°)	0.90
2θ Range (°)	3.0–45.8
Total no. reflections collected	11591
No. unique reflections	11273
No. with $I > 3\sigma(I)$	4551
R (unweighted, based on F)	0.046
R_w (weighted, based on F)	0.057
Data to parameter ratio	5.7:1
Goodness of fit for the last cycle	1.303
Largest and mean shift/error	0.290, 0.008
Largest difference peak (e Å^{-3})	0.30

independent reflections having $2\theta(\text{Mo K}\alpha) < 45.8°$ and $I > 3\sigma(I)$) using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic thermal parameters for all hydrogen atoms. Fifteen of the thirty-eight methyl groups (carbon atoms C1, C1b, C1c, C2b, C2c, C3b, C3c, C6b and C8b of molecule a and C1, C1b, C2b, C2c, C3b and C3c of molecule b with their hydrogens) refined satisfactorily as rigid rotors with sp^3-hybridized geometry and a C–H bond length of 0.96 Å. The initial orientation of each refined methyl group was determined from difference Fourier positions for the hydrogen atoms. The final orientation of each refined methyl group was determined by three rotational parameters. The refined positions for these rigid-rotor methyl groups gave C–C–H angles which ranged from 100 to 123°. Since all attempts to refine the remaining methyl groups as rigid rotors resulted in unacceptably small C–C–H angles, they were included in the structure factor calculations as fixed atoms at idealized (staggered) tetrahedral positions. Methine hydrogen atoms were also included in the structural model at fixed idealized tetrahedral positions with a C–H bond length of 0.96 Å.

5. Supplementary material

Listings of thermal parameters, atomic coordinates, and bond lengths and angles for **1** have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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