Inorg. Chem. **2000,** *39,* 6067−6071 **6067**

Isolation and Structural Characterization of Triethanolaminotitanatranes:[†] X-ray Structures of Partial Hydrolysis Condensates

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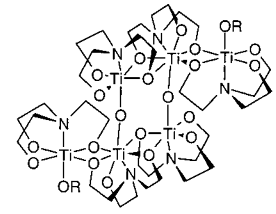
Received May 12, 2000

A family of triethanolamine complexes of titanium with varying metal/ligand ratios have been prepared from reactions of titanium tetraisopropoxide with triethanolamine. Three nonhydrolytic products, having essentially all isopropoxide ligands substituted by triethanolamine, were prepared as hygroscopic, glassy solids. Crystals of two hexameric titanatrane partial hydrolysis analogues $[Ti_3(\mu_2\text{-}O)\{(HOCH_2CH_2)_2NCH_2CH_2O\}\{(OCH_2CH_2)_2(\mu_2\text{-}OCH_2CH_2)N\}_2\{(OCH_2CH_2)(\mu_2\text{-}OCH_2CH_2)_2N\}]_2$ (**1**), and $[Ti_3(\mu_2\text{-}O)\{OCH(CH_3)_2\}\{(OCH_2CH_2)_2(\mu_2\text{-}OCH_2CH_2)N\}_2\{(OCH_2CH_2)(\mu_2\text{-}OCH_2CH_2)_2N\}]_2$ (**2**) were isolated and structurally characterized. The structures consist of a central core of two oxo-bridged dititanatranes (TEA)TiOTi(TEA) ($TEAH_3$ = triethanolamine) with the nonhydrolytic residue (TEA)Ti($TEAH_2$) included as an adduct in (**1**), analogously to (TEA)Ti(OPr^i) in (**2**).

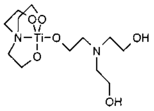
Introduction

Titanium amino alcohol complexes often exhibit improved hydrolysis and condensation characteristics[1,2] over the simple alkoxides, allowing for better control in sol−gel and chemical solution deposition (CSD) processes for the formation of monoliths and thin films. Although structural data on titanium mono-[3] and diethanolamine[4,5] complexes are rare, a number of complexes of triethanolamine have been reported in the literature prepared variously from titanium chloride,[6,7] tetraalkoxides,[8−11] and tetrakis(dimethylamide)[12] or by nucleophilic substitution in the axial position.[13] The term "titanatrane" has been used to describe these compounds, with the titanium being coordinated by all three arms of the trialkoxide and incorporating a transannular N→Ti bond. A further charged ligand is attached to the titanium to satisfy the Ti(IV) oxidation state.

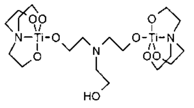
In a novel synthesis route to titanatrane compounds from inexpensive, amorphous titanium oxide,[4] the resulting products could not be isolated as single compounds, but electrospray mass spectral studies identified the titanium species **3**−**7** as derivative components in ratios determined by reaction conditions.



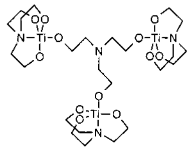
(**1**) R = $OCH_2CH_2N(CH_2CH_2OH)_2$
(**2**) R = $OCH(CH_3)_2$



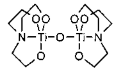
(**3**)



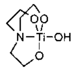
(**4**)



(**5**)



(**6**)



(**7**)

In this study we have attempted to isolate, crystallize, and structurally characterize titanatrane species containing at least one of the structural motifs **3**−**7** in the solid state. This has resulted in the formation of the complex adducts **1** and **2**, incorporating building blocks of both **3** and **6**.

Experimental Section

General Procedures. Syntheses were carried out under an atmosphere of dry nitrogen unless indicated otherwise. NMR spectra were recorded in $CDCl_3$ or d_4-MeOD on an AC300 Bruker spectrometer. Triethanolamine (Panreac Quimica), toluene, and benzene were dried and distilled before use. $Ti(OPr^i)_4$ (Lancaster Synthesis) was used as received. Representative synthetic procedures are described below.

Synthesis of Bis(2,2′-hydroxyethyl-2″-iminoethanolatotitanatrane)-bis(bis(titanatrane)oxide)·toluene Solvate (1). Triethanolamine (19.9 g, 133 mmol) was added to $Ti(OPr^i)_4$ (28.4 g, 99.9 mmol) dissolved in dry toluene (150 mL) and heated to reflux. After 30 min, distilled water (0.9 mL, 50 mmol) in 2-propanol (20 mL) was added dropwise, during which time the distillation was continued. On completion of the

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[†] Metallatrane refers to cyclic metal ethers of imino-2,2′,2″-trialkanolate: Verkade, J. G. *Acc. Chem. Res.* **1993**, *26*, 483.

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10.1021/ic000510u CCC: $19.00

addition, the 2-propanol was removed by azeotropic distillation until the distillation temperature reached 110 °C. The product separated from the residual toluene layer as a viscous syrup, which slowly crystallized on cooling. Yield = 13.3 g (50.4%). Anal. Calcd for $\mathrm{C_{62}H_{116}N_8O_{26}Ti_6}$: C, 44.4; H, 7.0; N, 6.7. Found: C, 44.7; H, 7.2; N, 6.5%. ^{1}H NMR (d$_4$-MeOD, 30 °C): δ 2.33 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{C_6H_5}$), 2.7 (br, 12H, $\mathrm{NCH_2}$), 3.23 (br, 36H, $\mathrm{TiNCH_2}$), 3.32 (br, 4H, $\mathrm{OCH_2}$), 3.62 (br, 8H, $\mathrm{C}\mathit{H}_2\mathrm{OH}$), 4.42 (m, 36H, $\mathrm{OCH_2}$) 4.83 (m, 4H, OH), 7.1−7.3 (m, 5H, $\mathrm{C_6}\mathit{H}_5\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (d$_4$-MeOD, 30 °C): δ 21.92 ($\mathit{C}\mathrm{H_3C_6H_5}$), 55−65 ($\mathrm{NCH_2}$ + $\mathrm{O}\mathit{C}\mathrm{H_2OH}$), 67−75 ($\mathrm{OCH_2}$), 126.74, 129.65, 130.36, 139.33 ($\mathrm{CH_3}\mathit{C}_6\mathrm{H_5}$).

Synthesis of Bis(isopropoxytitanatrane)bis(bis(titanatrane)oxide)·toluene Solvate (2). This was prepared similarly to **1** above using triethanolamine (14.9 g, 99.9 mmol) added to Ti(OPr^i)$_4$ (28.4 g, 99.9 mmol) dissolved in dry toluene (150 mL) and heated to reflux. After 30 min, distilled water (0.9 mL, 50 mmol) in 2-propanol (20 mL) was added dropwise, during which time the reflux was continued. On completion of the addition, the 2-propanol was removed by azeotropic distillation until the distillation temperature reached 110 °C. The product began to precipitate from the solution as a white powder as the 2-propanol was removed. When the solution was cooled, X-ray quality crystals grew on the surface of the glass flask. The product was filtered and dried. Yield = 18.4 g (78.6%). Anal. Calcd for $\mathrm{C_{49}H_{94}N_6O_{22}Ti_6}$: C, 41.8; H, 6.7; N, 6.0. Found: C, 42.0; H, 6.7; N, 5.9. ^{1}H NMR (d$_4$-MeOD, 30 °C): δ 1.16 (d, J = 6.18 Hz, 12H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 2.33 (s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{C_6H_5}$), 3.24 (br, 24H, $\mathrm{NCH_2}$), 4.43 (br, 24H, $\mathrm{OCH_2}$), 4.64 (m, 2H, $\mathrm{CH_3C}\mathit{H}$), 7.1−7.3 (m, 5H, $\mathrm{C_6}\mathit{H}_5\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (d$_4$-MeOD, 30 °C): δ 21.94 ($\mathit{C}\mathrm{H_3C_6H_5}$), 25.73 ($\mathit{C}\mathrm{H_3CH}$), 55−65 ($\mathrm{NCH_2}$), 65.11 ($\mathrm{CH_3}\mathit{C}\mathrm{H}$), 67−75 ($\mathrm{OCH_2}$), 126.75, 129.66, 130.37, 139.5 ($\mathrm{CH_3}\mathit{C}_6\mathrm{H_5}$).

Reaction of Triethanolamine with Titanium Tetraisopropoxide. Method a. Using a 2:1 TEAH$_3$/Ti Ratio (3). Triethanolamine (7.45 g, 49.9 mmol) was added to Ti(OPr^i)$_4$ (7.10 g, 25.0 mmol) in a 250 mL round-bottom flask. The reaction mixture was mixed well before being evacuated on a rotary evaporator equipped with a silicone oil bath. The reaction mixture was heated gradually to between 120 and 150 °C to ensure complete exchange and removal of the isopropoxide. Initial foaming of the reaction mixture subsided and the solid foam melted as the reaction temperature approached 120 °C. When the mixture cooled, the product solidified as brittle glasses and was not further purified. Yield: 8.53 g (99.8%). Anal. Calcd for $\mathrm{C_{12}H_{29}N_2O_{7.5}}$-Ti: C, 40.5; H, 8.2; N, 7.9. Found: C, 40.8; H, 8.5; N, 7.9. ^{1}H NMR ($\mathrm{CDCl_3}$ 30 °C): δ 5.0−3.5 (m, 14H, $\mathrm{OCH_2}$, OH), 3.3−2.5 (m, 12H, $\mathrm{NCH_2}$). ^{1}H NMR ($\mathrm{CDCl_3}$ 55 °C): δ 4.5, 4.1, 3.8, 3.6 (br, 14H,$\mathrm{OCH_2}$, OH), 2.9, 2.7 (br, 12H, $\mathrm{NCH_2}$).

Reaction of Triethanolamine with Titanium Tetraisopropoxide. Method b. Using a 3:2 TEAH$_3$/Ti Ratio (4). By use of the same technique as in method a above, triethanolamine (5.58 g, 37.4 mmol) was reacted with Ti(OPr^i)$_4$ (7.10 g, 25.0 mmol) in a 250 mL round-bottom flask. Yield: 6.78 g (101%). Anal. Calcd for $\mathrm{C_{18}H_{39}N_3O_{10}Ti_2}$: C, 39.1; H, 7.1; N, 7.6. Found: C, 39.1; H, 7.3; N, 7.5. ^{1}H NMR ($\mathrm{CDCl_3}$ 30 °C): δ 4.5, 4.4, 4.3, 3.7 (br m, 19H, $\mathrm{OCH_2}$, OH), 3.2, 2.8, 2.6 (br, 18H, $\mathrm{NCH_2}$). ^{1}H NMR ($\mathrm{CDCl_3}$ 55 °C): δ 4.4, 3.6 (br, 19H, $\mathrm{OCH_2}$, OH), 3.0, 2.6 (br, 18H, $\mathrm{NCH_2}$) (br = broad).

Reaction of Triethanolamine with Titanium Tetraisopropoxide. Method c. Using a 4:3 TEAH$_3$/Ti Ratio (5). By use of the same technique as in method a above, triethanolamine (4.97 g, 33.3 mmol) was reacted with Ti(OPr^i)$_4$ (7.10 g, 25.0 mmol) in a 250 mL round-bottom flask. Yield: 6.05 g (99.8%). Anal. Calcd for $\mathrm{C_{24}H_{48}N_4O_{12}Ti_3}$: C, 39.6; H, 6.6; N, 7.7. Found: C, 39.3; H, 7.1; N, 7.4. ^{1}H NMR ($\mathrm{CDCl_3}$ 30 °C): δ 4.5, 3.5 (m, br, 24H, $\mathrm{OCH_2}$), 3.18 (16H, $\mathrm{NCH_2}$), 2.75 (v br, 8H, $\mathrm{NCH_2}$). ^{1}H NMR ($\mathrm{CDCl_3}$ 55 °C): δ 4.4 (24H, $\mathrm{OCH_2}$), 3.1 (24H, $\mathrm{NCH_2}$).

X-ray Crystallographic Data Collection and Refinement of Structures. Crystallographic parameters are given in Table 1. Cut blocks were mounted under a nitrogen stream on a Siemens P4 SMART diffractometer with a CCD detector. Accurate cell dimensions and orientation matrices were obtained by least-squares refinements. The data were corrected for background, Lorentz and polarization factors, and crystal decay (SAINT[14]), and an empirical absorption correction was applied (SADABS[14]). The data were collected using molybdenum radiation, λ(Mo Kα) = 0.710 73 Å, with a graphite monochromator. The structures were solved by direct methods using SHELXS-90[15] and successive difference Fourier syntheses. Refinement calculations were performed using SHELXL-97.[16] Alternative conformations, with atoms labeled as a/b sets, were found for some of the five-membered TEA rings, and the two conformations were refined to a total unit occupancy. The atom labels and refined final occupancies for the larger occupied site are the following: in **1**, C12a, C16a 0.574(8); in **2**, C11a, C12a 0.64(1), C15a, C16a 0.82(1), C39a 0.70(1). In **2**, bonds were constrained to the same values for C37 to C39a and C39b, and the pairs C11a, C12a and C11b, C12b.

Table 1. Crystal Data and Structure Refinement for **1** and **2**

	1	**2**
formula	$\mathrm{C_{31}H_{58}N_4O_{13}Ti_3}$	$\mathrm{C_{24.5}H_{47}N_3O_{11}\,Ti_3}$
fw	838.5	703.35
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	9.4237(7)	10.891(2)
b, Å	19.9219(15)	12.417(3)
c, Å	20.3520(15)	12.432(3)
α, deg	90	81.996(3)
β, deg	101.280(1)	88.815(3)
γ, deg	90	73.583(2)
V, Å^3	3737.0(5)	1596.6(6)
Z	4	2
ρ, Mg m^{-3}	1.486	1.463
μ, mm^{-1}	0.691	0.790
cryst size, mm	0.48 × 0.17 × 0.17	0.72 × 0.57 × 0.41
θ range, deg	2.80−26.47	1.95−26.42
reflns collected	23 554	20 540
no. unique data	7337	5751
R_{int}	0.0434	0.0199
no. of observations[a]	5369	2283
range of abs coeff	1.0−0.805	1.0−0.8709
no. of parameters	489	408
no. of restraints	9	3
P_1, P_2 weighting parameters[b]	0.0645, 3.0521	0.0544, 2.238
goodness-of-fit on F^2	1.029	1.142
R1[c]	0.0461	0.0457
wR2[c]	0.115	0.123
largest difference Fourier peaks & holes, e Å^{-3}	0.556, −0.399	0.765, −0.705

[a] Intensities are 2.0 times their standard deviations (from counting statistics). [b] For weights w, see ref 16. [c] $\mathrm{R1} = \sum||F_o| - |F_c||/\sum|F_o|$; $\mathrm{wR2} = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

The toluene solvent of crystallization was disordered close to a crystallographic center of symmetry in both crystals. In structure **1**, two different orientations were refined to a total occupancy of 1 (four molecules per cell) although the methyl of the minor conformer (with occupancy of 0.152(6)) was not able to be refined. In **2** there is one toluene molecule per cell; the final model contains five half-atoms (C51−C53, C56−C57) and one full atom C545, with some common isotropic thermal parameters.

A summary of selected bond lengths, angles, and close contact distances are given in Tables 2 and 3. The ORTEP diagrams[17,18] illustrating the atomic numbering are shown in Figures 1 and 2. For clarity, only one of the two positions refined when conformational disorder was detected are shown and labeled with an additional “a” (e.g., C16a in Figure 1). Tables 1S−7S in Supporting Information contain atomic positional parameters, dihedral angles, mean planes, hydrogen atomic coordinates, and anisotropic thermal parameters for both structures.

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Table 2. Selected Bond Lengths [Å] and Angles (deg) for **1** and **2**

	1	**2**		**1**	**2**
Ti(1)−O(1)	1.890(2)	1.881(2)	Ti(1)−O(11)	1.872(2)	1.893(2)
Ti(1)−O(121)	2.070(2)	2.111(2)	Ti(1)−O(122)	2.051(2)	2.080(2)
Ti(1)−O(131)	2.066(2)	2.054(2)	Ti(1)−O(132)	2.116(2)	2.092(2)
Ti(1)−N(1)	2.313(3)	2.312(2)	Ti(2)−O(21)	1.872(2)	1.852(2)
Ti(2)−O(22)	1.901(2)	1.902(2)	Ti(2)−O(121)	2.050(2)	2.041(2)
Ti(2)−O(122)	2.059(2)	2.043(2)	Ti(2)−N(2)	2.319(3)	2.400(3)
Ti(2)−O(1)a	1.791(2)	1.807(2)	Ti(3)−O(32)	1.888(2)	1.870(2)
Ti(3)−O(33)	1.877(3)	1.903(2)	Ti(3)−O(34)	1.822(3)	1.819(3)
Ti(3)−O(131)	2.046(2)	2.052(2)	Ti(3)−O(132)	2.003(2)	2.028(2)
Ti(3)−N(3)	2.293(3)	2.295(3)			
	Ranges and Means (Å)				
O−C	1.374,1.394 to 1.436,1.433; means, 1.412, 1.417				
N−C	1.454,1.468 to 1.485,1.481; means, 1.473, 1.481				
C−C	1.488,1.506 to 1.536,1,534; means, 1.511, 1.523				

	1	**2**		**1**	**2**
O(1)−Ti(1)−O(11)	168.47(9)	167.55(10)	O(1)−Ti(1)−O(121)	85.53(8)	85.60(8)
O(1)−Ti(1)−O(122)	95.75(8)	93.37(8)	O(1)−Ti(1)−O(131)	100.01(9)	101.08(9)
O(1)−Ti(1)−O(132)	85.58(9)	88.53(8)	O(1)−Ti(1)−N(1)	91.60(9)	90.49(9)
O(11)−Ti(1)−O(121)	91.43(9)	87.81(9)	O(11)−Ti(1)−O(122)	93.58(9)	94.06(8)
O(11)−Ti(1)−O(131)	88.32(9)	90.19(9)	O(11)−Ti(1)−O(132)	90.19(9)	90.70(9)
O(11)−Ti(1)−N(1)	76.88(9)	77.43(9)	O(121)−Ti(1)−O(122)	69.49(8)	68.67(8)
O(121)−Ti(1)−O(131)	149.01(8)	146.80(8)	O(121)−Ti(1)−O(132)	142.73(8)	144.42(8)
O(121)−Ti(1)−N(1)	72.98(9)	72.44(8)	O(122)−Ti(1)−O(131)	79.59(8)	78.43(8)
O(122)−Ti(1)−O(132)	147.50(8)	146.81(8)	O(122)−Ti(1)−N(1)	140.97(9)	140.46(8)
O(131)−Ti(1)−O(132)	68.26(8)	68.71(8)	O(131)−Ti(1)−N(1)	136.58(9)	139.08(8)
O(132)−Ti(1)−N(1)	71.18(9)	72.55(9)	O(21)−Ti(2)−O(22)	104.6(1)	100.05(9)
O(21)−Ti(2)−O(121)	88.86(10)	91.77(9)	O(21)−Ti(2)−O(122)	143.81(9)	145.64(9)
O(21)−Ti(2)−N(2)	75.23(10)	74.53(9)	O(21)−Ti(2)−O(1)^a	100.7(1)	100.06(9)
O(22)−Ti(2)−O(121)	159.64(9)	158.64(9)	O(22)−Ti(2)−O(122)	91.05(9)	89.88(9)
O(22)−Ti(2)−N(2)	76.29(10)	74.79(8)	O(22)−Ti(2)−O(1)^a	95.49(9)	97.12(9)
O(121)−Ti(2)−O(122)	69.73(8)	70.73(8)	O(121)−Ti(2)−N(2)	92.30(9)	91.56(8)
O(121)−Ti(2)−O(1)^a	97.50(9)	98.25(8)	O(122)−Ti(2)−N(2)	76.82(9)	76.60(8)
O(122)−Ti(2)−O(1)^a	110.49(9)	111.32(9)	N(2)−Ti(2)−O(1)^a	169.4(1)	168.99(9)
O(32)−Ti(3)−O(33)	104.1(1)	105.8(1)	O(32)−Ti(3)−O(34)	99.6(1)	99.9(1)
O(32)−Ti(3)−O(131)	144.7(1)	143.72(9)	O(32)−Ti(3)−O(132)	91.36(10)	90.36(9)
O(32)−Ti(3)−N(3)	76.4(1)	76.33(9)	O(33)−Ti(3)−O(34)	89.9(1)	91.5(1)
O(33)−Ti(3)−O(131)	91.8(1)	91.38(9)	O(33)−Ti(3)−O(132)	162.6(1)	161.36(9)
O(33)−Ti(3)−N(3)	76.9(1)	77.04(9)	O(34)−Ti(3)−O(131)	111.9(1)	111.6(1)
O(34)−Ti(3)−O(132)	95.4(1)	94.8(1)	O(34)−Ti(3)−N(3)	164.5(1)	166.2(1)
O(131)−Ti(3)−O(132)	70.86(8)	69.99(8)	O(131)−Ti(3)−N(3)	76.95(9)	76.85(9)
O(132)−Ti(3)−N(3)	99.57(9)	98.45(9)	Ti(1)−O(1)−Ti(2)^a	177.8(1)	172.4(1)
Ti(1)−O(11)−C(11)	125.8(2)	121.2(3)	Ti(2)−O(21)−C(21)	125.5(2)	127.8(2)
Ti(2)−O(22)−C(25)	125.6(2)	118.4(2)	Ti(3)−O(32)−C(31)	124.0(2)	124.7(2)
Ti(3)−O(33)−C(35)	125.7(2)	124.5(2)	Ti(3)−O(34)−C(37)	133.6(3)	139.3(7)
Ti(1)−O(121)−Ti(2)	108.32(9)	106.12(12)	Ti(1)−O(121)−C(15)	121.0(2)	123.9(3)
Ti(2)−O(121)−C(15)	125.4(2)	124.0(3)	Ti(1)−O(122)−Ti(2)	108.69(9)	107.23(9)
Ti(1)−O(122)−C(23)	120.9(2)	119.5(2)	Ti(2)−O(122)−C(23)	114.7(2)	116.1(2)
Ti(1)−O(131)−Ti(3)	108.04(9)	108.32(9)	Ti(1)−O(131)−C(33)	126.3(2)	126.3(2)
Ti(3)−O(131)−C(33)	115.7(2)	115.7(2)	Ti(1)−O(132)−Ti(3)	107.73(9)	107.77(9)
Ti(1)−O(132)−C(13)	123.6(3)	123.8(2)	Ti(3)−O(132)−C(13)	125.2(3)	121.5(2)

Discussion

Electrospray mass spectral studies[4] in alcoholic solvents have detected the species **3**−**5** incorporating varying degrees of solvation, as well as the minor constituents **6** and **7**. A related study in chloroform solvent has identified analogous species without solvation.[19,20] However, the coordination requirements of titanium make it unlikely that these species exist in solution or the solid state as pentacoordinate titanatranes as drawn. Typically, titanatrane complexes coalesce via μ_2-bridging arms of the triethanoxoamine ligand in order to increase the coordination sphere. The coordination number for titanium is generally 6, although variations to this (5- and 7-coordination[10−12,21]) have been reported. Pentacoordinate titanatranes have only been reported in cases where the axial ligand has large steric bulk.

Nonhydrolytic Titanatranes 3−5. Reaction of Ti(OPr^i)$_4$ with a single equivalent of triethanolamine produces the dimeric isopropoxytitanatrane.[9] Increasing the proportion of triethanolamine to access the species **3**−**5** was carried out by removing the liberated 2-propanol in vacuo at temperatures greater than 120 °C. Thus, ratios of titanium tetraisopropoxide to triethanolamine used were 1:1.33, 1:1.5, and 1:2. When the mixture was cooled to room temperature, the products solidified as hard, pale-yellowish glasses. It was not possible to distill or recrystallize the products for purification purposes; however, under the specified reaction conditions, the yields of products were close to theoretical quantities for products corresponding to the stoichiometric species **3**−**5**. Thermogravimetric analyses were consistent with the expected weight losses from **3**−**5** to leave

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Table 3: Hydrogen Bond Contacts (Å) and Angles (deg) for Both Structures (D = Donor, A = Acceptor)

no.	D−H···A	D−H	H···A	D···A	D−H···A	A···H···A*	structure
1	O(40)−H(40)···O(32)	1.09(6)	1.91(5)	2.864(5)	144(3)		**1**
2	O(40)−H(40)···N(4)	1.09(6)	2.33(4)	2.914(5)	112(3)′	103(2)′	**1**
3	O(42)−H(42)···O(32)	0.86(6)	2.15(6)	2.939(4)	151(5)		**1**
4	O(42)−H(42)···N(4)	0.86(6)	2.40(6)	2.871(5)	115(5)′	94(2)′	**1**
5	C(26)−H(26B)···O(40)[b]	0.99	2.48	3.399(5)	153.8		**1**
6	C(36)−H(36A)···O(32)[d]	0.99	2.53	3.439(4)	152.0		**2**
7A	C(14)−H(14B)···O(22)[a]	0.99	2.27	3.239(4)	165.1		**1**
7B	C(14)−H(14B)···O(22)[c]	0.99	2.22	3.189(4)	165.8		**2**
8A	C(32)−H(32a)···O(21)[a]	0.99	2.60	3.391(4)	137.2		**1**
8B	C(32)−H(32A)···O(21)[c]	0.99	2.42	3.252(4)	141.8		**2**
9A	C(24)−H(24B)···O(11)	0.99	2.39	3.098(4)	128.1		**1**
9B	C(24)−H(24B)···O(11)	0.99	2.37	3.108(3)	130.5		**2**
10	C(31)−H(31B)···O(42)	0.99	2.59	3.212(5)	120.7		**1**
11A	C(34)−H(34B)···O(21)[a]	0.99	2.30	3.276(4)	167.0		**1**
11B	C(34)−H(34B)···O(21)[c]	0.99	2.34	3.307(4)	163.3		**2**
13	C(36)−H(36A)···O(42)	0.99	2.54	3.335(5)	136.9		**1**
14	C(37)−H(37A)···O(33)	0.99	2.37	2.936(5)	115.2		**1**

[a] Symmetry operation to bring acceptor into contact: $-x, 2 - y, -z$. [b] Symmetry operation to bring acceptor into contact: $-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$. [c] Symmetry operation to bring acceptor into contact: $1 - x, 1 - y, 2 - z$. [d] Symmetry operation to bring acceptor into contact: $2 - x, 1 - y, 1 - z$.

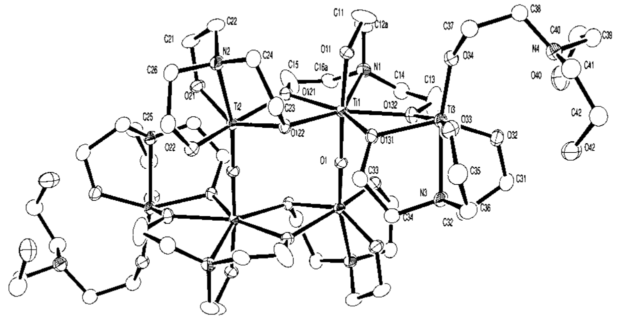

Figure 1. Molecular structure and crystallographic numbering for **1**. Thermal ellipsoids are at the 30% probability level. For clarity, hydrogen atoms are excluded and atoms related by the center of symmetry at the center of the molecule are not labeled. Atoms with an appended “a” label are in the major positions of two alternatives refined (see text).

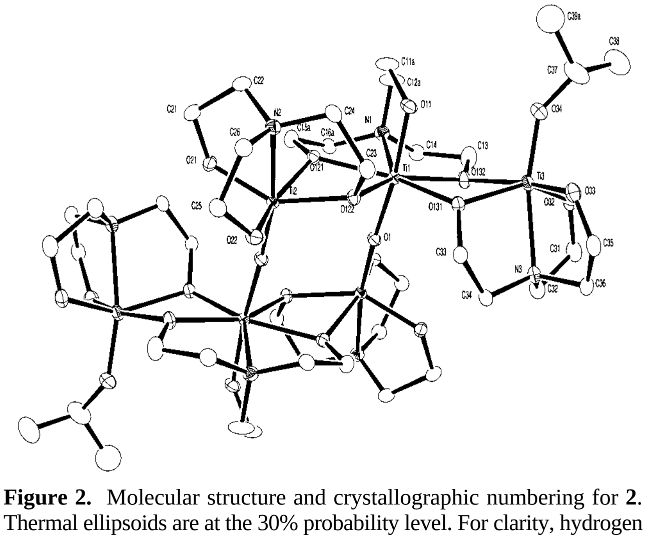

Figure 2. Molecular structure and crystallographic numbering for **2**. Thermal ellipsoids are at the 30% probability level. For clarity, hydrogen atoms are excluded and atoms related by the center of symmetry at the center of the molecule are not labeled. Atoms with an appended “a” label are in the major positions of two alternatives refined (see text).

a white residue of TiO_2.[22] Proton NMR data for the three reaction mixtures were generally complex but highly reproducible (see Supporting Information). Broad signals attributable to free and coordinated CH_2O and CH_2N groups were identifiable, with the signal positions and integral ratios changing with the reactant ratios. The hydroxyl signals, if present, were generally obscured by other overlapping signals. Running the spectra at 55 °C broadened the signals and simplified the spectra. The signals attributable to the nonchelating TEA ligand were only observable as shoulders on the main peaks. The solvent limited the ability to further increase the temperature at which the spectra could be run; however, the results suggested that the complexes fall into the second type of titanatrane structure as defined by Verkade;[11] they exhibit exchange processes dominated by an intramolecular fluxional “gearing” motion. Bridging between two titanatrane units to form dimers[11] is complicated in the current compounds because of the presence of multiple titanatrane moieties in a single residue. Thus, oligomerization or polymerization would be expected to occur, contributing to their broad NMR signals and inability to crystallize.

Microanalytical data obtained from a commercial laboratory confirmed the product from the reactant ratio $3Ti(OPr^i)_4$/$4TEAH_3$, which corresponded to the formulation of **5**. The analyses of the products from the other reaction ratios corresponded to the products **3** and **4** with 1.5 and 1.0 H_2O, respectively (see Experimental Section), reflecting the highly hydrophilic nature of the materials. It is noted that these analyses could possibly correspond to average figures representing mixtures of compounds represented by **3**−**5** and possibly other species,[4] including uncoordinated triethanolamine. The only species unequivocably identified as single compounds are the partial hydrolysis products described below.

Partial Hydrolysis Products. Preparation of partial hydrolysis products was attempted using a 0.5 molar equiv of water (with respect to Ti) added to reactions utilizing a range of titanium tetraisopropoxide/triethanolamine ratios. The products depended on the amount of triethanolamine present. A single equivalent of triethanolamine resulted in a product containing both isopropoxide and iminotriethanolate ligands. Reaction mixtures containing 1.3 equiv or more of triethanolamine resulted in a product containing iminotriethanolate ligands only. More than 1.5 equiv of triethanolamine, however, produced mainly viscous oils together with only limited amounts of the same crystalline material. Suitable crystals from the two products described were isolated for X-ray studies and produced the structures **1** and **2** containing TiOTi linear oxo bridges. The structures also contain adducted triethanolaminotitanatrane (**1**)

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and 2-propanolatotitanatrane (**2**) residues. NMR of these products was not possible in $CDCl_3$ because of low solubilities. The complexes dissolved in d_4-methanol, but it was not clear whether they maintained their molecular integrity. The ^1H and ^{13}C NMR spectra showed unresolved broad signals for the triethanolamine ligands and sharp signals for coordinated isopropoxide and residual toluene from the solvent of crystallization. Microanalytical data were collected several times in order to obtain good agreement with the crystallographic formulas. Partial loss of the toluene solvate regularly resulted in low carbon values, and attempts to completely remove the solvation resulted in hygroscopic powders that failed to yield good analytical data.

The crystal structures consist of independent centrosymmetric titanium complex aggregates Ti_6(triethanoxoamino-N,O,O′,O″)$_3$-(R), where R is monodentate triethanolamino ($TEAH_2$) (**1**) or isopropoxide (**2**), as shown in Figures 1 and 2, and a toluene solvent of crystallization. There is a single, weak interaction (C−H···O type)[23] between aggregates (hydrogen-bonding interactions are listed in Table 3). The isopropoxide ligand in **2** exhibits some disorder so that two positions are found for the methyl atom (C39). In **1** there are several strong intramolecular hydrogen bonds involving the monodentate $TEAH_2$ ligand atoms utilizing the terminal hydroxyl groups O40 and O42, the nitrogen N4 and O33, and part of an adjacent ligand bound to Ti3. The different terminal ligands (R, above), which distinguish the two structures, have only resulted in minor changes in the total structure. This is emphasized in Table 2 with often indistinguishable geometric parameters. Thus, both structures contain three unique titanium atoms, with two of them (Ti1 and Ti2) bound through an oxygen (O1) to the centrosymmetrically related other half of the molecule.

Atom Ti1 is 7-coordinate in an arrangement that is best described as a pentagonal bipyramid. The pentagon is defined by two oxygens and a nitrogen from one TEA (O121, O132, N1) and by one oxygen each from TEAs bound to Ti2 and Ti3 (O122, O131). The apexes of the bipyramid are occupied by the third oxygen of the first TEA (O11) and the oxo-bridging oxygen (O1).

The other two titaniums Ti2 and Ti3 are 6-coordinate with slightly different stereochemistries. As for Ti1, Ti2 and Ti3 are chelated by three oxygens and the nitrogen of separate TEAs. They both share TEA oxygen bridges with Ti1, while their axial ligands are the oxo bridge (Ti2) and the terminal monodentate $TEAH_2$ (**1**) or isopropoxide (**2**) (Ti3). The axial ligand on Ti3 lies trans to the nitrogen in both **1** and **2**. The oxo bridge lies trans to the nitrogen on Ti2, while it is cis to the nitrogen on Ti1. Published structures of titanatranes have examples of the axial group in both positions, dependent on their σ-donating ability. In this case, the titanium geometries are influenced by steric requirements, which allow one titanium to attain 7-coordination while the others maintain 6-coordination. The geometry at Ti2 is highly tetragonally distorted octahedral, while the geometry at Ti3 is closer to octahedral and is in fact very similar to that found in the dimeric isopropoxotitanatrane structure.[9]

The range of Ti−O bond lengths, 1.791(2)−2.116(2) Å, is similar to that observed before (1.845−2.16 Å).[9−13] The average bridging Ti−O distance for the three coordinate oxygen atoms is 2.060 Å (range 2.003(2)−2.116(2) Å) compared with the nonbridging TEA Ti−O average of 1.873 Å (range 1.822(3)−1.903(2) Å). The oxo bridges (Ti1−O1−Ti2′) are virtually linear in both structures, 177.8(6)° and 172.4(7)°, with mean bond lengths of 1.842 Å. This is comparable to the linear N−Ti−O−Si arrangement[11] but contrasts with the bent oxo bridges in the pseudo-atrane structure.[5] The Ti−N bonds are unexceptional with a mean 2.306 Å (range 2.293(3)−2.319(3) Å), excluding the longer Ti(2)−N(2) (2.400(3) Å) in structure **2**, which is still shorter than the Ti−N bonds reported in the related amino alcohol complex (2.422 Å[4]).

The apparently stable structure exhibited by these complexes lead us to suppose that many variations can be prepared, varying only in the terminal axial group on Ti3. Indeed, the so-called "trititanates" reported by Cohen[8] have strikingly similar formulations and may well share the same structural characteristics. These hexanuclear condensates represent titanium oxoalkoxides $[Ti_xO_y(OR)_{4x-2y}]$ where the degree of condensation, $y/x = 0.33$, is equal to the lowest reported values.[24,25]

Acknowledgment. This work was funded by the New Zealand Foundation for Research in Science and Technology, Contract No. CO8810. We thank the staff of the University of Canterbury Crystallography Laboratory for the X-ray data collection.

Supporting Information Available: Anisotropic thermal parameters and hydrogen coordinates (Tables 1S−7S) and selected NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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