

# Polyoxotitanates join the Keggin family: synthesis, structure and reactivity of $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}^\dagger$

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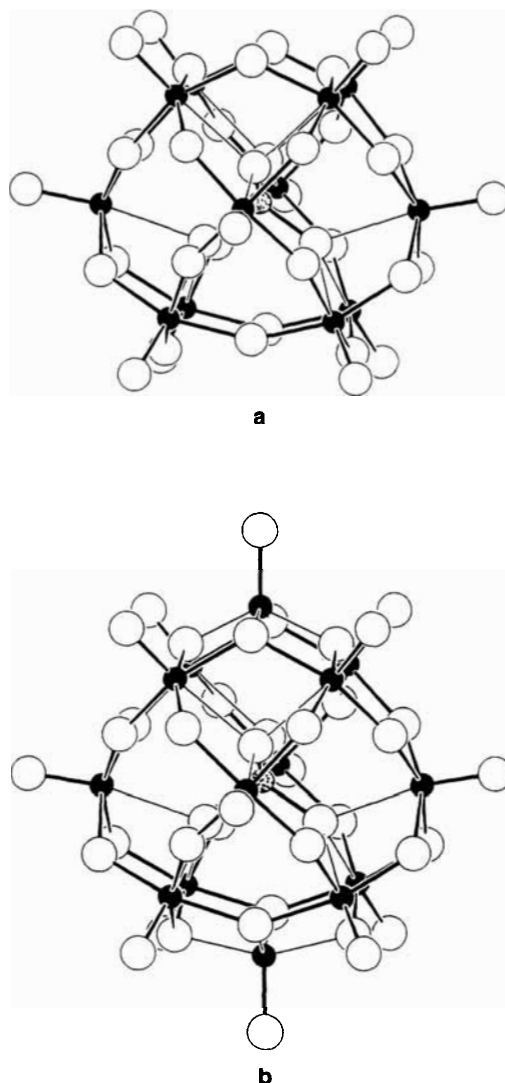
Reaction of  $\text{Ti}(\text{OBU}^t)_4$  with about 1 equivalent of water in *tert*-butyl alcohol for 5 d at 100 °C yielded the polytitanate complex  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$ . A single-crystal X-ray diffraction study of its  $\text{Bu}^t\text{OH}$  solvate [ $a = 15.789(4)$ ,  $b = 29.544(5)$ ,  $c = 27.496(5)$  Å,  $\beta = 91.85(5)^\circ$ ;  $Z = 4$ ; space group  $P2_1/c-C_{2h}^5$ ] revealed a  $\text{Ti}_{18}\text{O}_{45}$  metal–oxygen framework having a pentacapped Keggin structure, *i.e.* a  $\text{Ti}_{13}\text{O}_{40}$  Keggin unit capped by five  $\text{TiO}$  moieties which lie above five of the six approximately square faces of the  $T_d$ -distorted cuboctahedron defined by the metals in the Keggin unit. All seventeen of the terminal oxygen atoms are bonded to *tert*-butyl groups. This complex is the most highly condensed titanium alkoxide hydrolysis product isolated to date and showed good stability in solution, retaining its structure and showing no decomposition after 24 h at ambient temperature in toluene–*tert*-butyl alcohol solution, according to NMR spectroscopy. Reactions of the complex with water, 2-methylbutan-2-ol and triethylamine are also reported.

In 1933 Keggin<sup>1</sup> determined the crystal structure of 12-tungstophosphoric acid, revealing the  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  anion structure shown in **a** where a tetrahedral oxoanion ( $\text{PO}_4^{3-}$ ) is encapsulated by a metal–oxygen cage ( $\text{W}_{12}\text{O}_{36}$ ) whose twelve metal centres lie at the vertices of a  $T_d$ -distorted cuboctahedron. This Keggin structure, the first structure ever definitively assigned to a large early-transition-metal polyoxoanion, proved to be of central importance in heteropolyanion chemistry in that numerous stable polyoxo-tungstate and -molybdate complexes have been shown to adopt this or closely related structures.<sup>2</sup> The Keggin structure was not, however, observed in Group 5 polyoxoanion chemistry until 1980, when the 14-vanadophosphate structure was reported.<sup>3</sup> Several isostructural polyvanadates have since been reported.<sup>4</sup> As shown in **b**, the  $[\text{PV}_{14}\text{O}_{42}]^{9-}$  anion has a bicapped Keggin structure in which two  $\text{VO}^{3+}$  units lie above *trans* 'square' faces of the distorted metal cuboctahedron in a  $[\text{PV}_{12}\text{O}_{40}]^{15-}$  Keggin anion. Alternatively, the  $[\text{PV}_{14}\text{O}_{42}]^{9-}$  anion can be derived from the 'superkeggin' structure **c** in which all six square faces of the Keggin metal cuboctahedron have been capped with metal oxide moieties. Indeed, this superkeggin structure was subsequently observed for the 18-vanadosulfate ion and an isostructural isopolyvanadate.<sup>5</sup> In this paper we report a new polytitanate complex,  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$ , which is the first example of a Group 4 Keggin complex. As shown in **d**, this complex has a  $[\text{Ti}_{18}\text{O}_{45}]^{18-}$  metal–oxygen core structure that can be viewed either as a  $[\text{Ti}_{13}\text{O}_{40}]^{28-}$  Keggin complex capped by five  $\text{TiO}^{2+}$  units or as a defective superkeggin complex, *i.e.* a  $[\text{Ti}_{19}\text{O}_{46}]^{16-}$  superkeggin lacking one  $\text{TiO}^{2+}$  moiety.

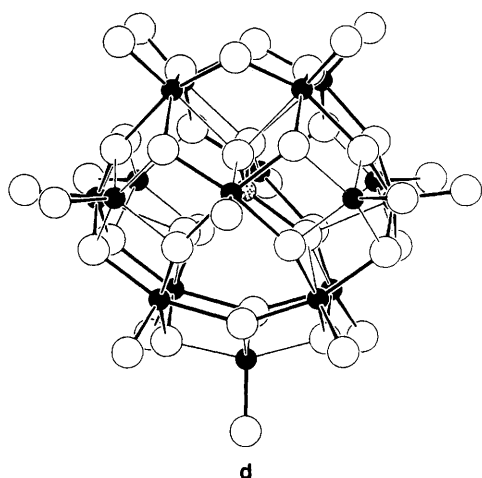
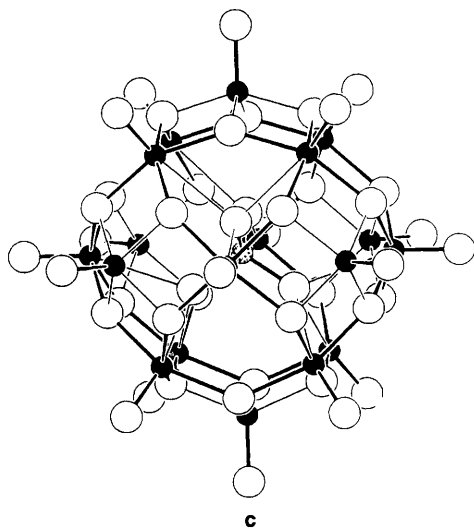
## Experimental

### Reagents, solvents and general procedures

The following reagents were purchased from commercial sources and used without further purification: titanium(IV) isopropoxide (Aldrich), anhydrous *tert*-butyl acetate (Aldrich)



<sup>†</sup> Basis of the presentation given at Dalton Discussion No. 1, 3rd–5th January 1996. University of Southampton, UK.



and 10 atom %  $^{17}\text{O}$  isotope-enriched water (Aldrich). All manipulations of titanium alkoxides and oxoalkoxides were carried out under a nitrogen or argon atmosphere using standard Schlenk and dry-box techniques.

All solvents were of reagent grade and were dried prior to use, unless specified otherwise. Toluene (Fisher), *tert*-butyl alcohol (Fisher) and 2-methylbutan-2-ol (Aldrich) were refluxed over sodium and freshly distilled prior to use. Acetonitrile (Aldrich) was dried over 3 Å molecular sieves and then distilled over  $\text{CaH}_2$  prior to use.  $[^2\text{H}_8]\text{Toluene}$  and  $\text{C}_6\text{D}_6$  (all Cambridge Isotope Laboratories) were dried over 3 Å molecular sieves (Linde) prior to use. Molecular sieves were activated by heating at 250 °C for at least 24 h and cooling under vacuum.

All glassware was washed in an ethanolic KOH bath, rinsed with dilute HCl and deionized water and then oven-dried before use.

#### Analytical procedures

Oxygen-17 solution NMR spectra were recorded at 40.7 MHz in 10 mm vertical sample tubes without sample spinning on an unlocked General Electric GN-300NB spectrometer and  $^{17}\text{O}$  magic angle spinning (MAS) solid-state NMR spectra were recorded at 40.7 MHz on a General Electric GN-300WB spectrometer. The chemical shifts were externally referenced to fresh tap water ( $\delta$  0.00) by the sample replacement method. The  $^{13}\text{C}\{-^1\text{H}\}$  NMR were recorded in 5 mm vertical sample tubes either at 75.6 MHz on a General Electric QE-300 spectrometer or at 125.8 MHz on a General Electric GN-500 spectrometer, chemical shifts were referenced internally to  $[^2\text{H}_8]\text{toluene}$  ( $\delta$  137.50) or  $\text{C}_6\text{D}_6$  ( $\delta$  128.00).

#### Preparation of $\text{Ti}(\text{O}^i\text{Bu})_4$

This is a modified version of the procedure reported by Mehrotra.<sup>6</sup> To a 500 cm<sup>3</sup> three-necked flask fitted with a reflux condenser and an argon inlet, titanium isopropoxide (48 g, 169 mmol) and *tert*-butyl acetate (86 g, 740 mmol) were added *via* a syringe. The solution was then heated with an oil-bath at 120 °C and the isopropyl acetate generated in the reaction was removed by distillation at 95 °C. After the solution had cooled to room temperature, *tert*-butyl acetate (43 g, 370 mmol) was added to the flask and the solution heated (oil-bath 120 °C) to remove isopropyl acetate and an excess of *tert*-butyl acetate at 95–98 °C. The resulting solution was then fractionally distilled under reduced pressure (*ca.* 0.5 Torr, 70 Pa) at 82–83 °C to yield 55 g (162 mmol) of colourless oil. Yield: 96%.  $^{17}\text{O}$  NMR (40.7 MHz, toluene–MeCN, 3:1 v/v, 20 °C):  $\delta$  304.  $^{13}\text{C}\{-^1\text{H}\}$  NMR (75.6 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta$  79.92 and 32.46.  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta$  1.28.

#### Hydrolysis of $\text{Ti}(\text{O}^i\text{Bu})_4$

A solvent solution was prepared from  $\text{Bu}^i\text{OH}$  (10 cm<sup>3</sup>) and toluene (30 cm<sup>3</sup>), and a water solution was then prepared by adding 10 atom %  $^{17}\text{O}$ -enriched water (116  $\mu\text{l}$ , 6.44 mmol) to the solvent solution (10 cm<sup>3</sup>). The following volumes of solvent solution and water solution were then added to three 10 mm NMR sample tubes containing  $\text{Ti}(\text{O}^i\text{Bu})_4$  (136 mg, 0.40 mmol) dissolved in the solvent solution (1.5 cm<sup>3</sup>): (i) 375  $\mu\text{l}$  of solvent solution: 125  $\mu\text{l}$  of water solution, (ii) 187:313 and (iii) 0:500. In this fashion, water to  $\text{Ti}(\text{O}^i\text{Bu})_4$  ratios of (i) 0.2, (ii) 0.5 and (iii) 0.8:1.0 were obtained.

Solid materials were isolated from solutions of partially hydrolysed  $\text{Ti}(\text{O}^i\text{Bu})_4$  as follows. A solution of 10 atom %  $^{17}\text{O}$ -enriched water (50  $\mu\text{l}$ , 2.8 mmol) in MeCN (10 cm<sup>3</sup>) was added dropwise to a solution of  $\text{Ti}(\text{O}^i\text{Bu})_4$  (2 g, 5.9 mmol) in toluene (10 cm<sup>3</sup>) with vigorous stirring. After 10 min, the volatiles were removed under vacuum and the resulting colourless oil was dissolved in MeCN (10 cm<sup>3</sup>) and cooled at –15 °C for 12 h to yield white crystals. The crystals were separated from the solution at low temperature but reverted to an oil when warmed to room temperature.  $^{17}\text{O}$  NMR (40.7 MHz, MeCN, 20 °C):  $\delta$  543 and 304.  $^{13}\text{C}\{-^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta$  80.59, 79.91, 32.46 and 32.41.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta$  1.32 and 1.28.

#### Preparation of $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{O}^i\text{Bu}]_{17}\cdot 0.25\text{C}_6\text{H}_5\text{Me}$

A screw-top flask was charged with  $\text{Ti}(\text{O}^i\text{Bu})_4$  (28 g, 82 mmol). Then a solution of water (1700  $\mu\text{l}$ , 94 mmol) in *tert*-butyl alcohol (100 cm<sup>3</sup>) was added slowly *via* a cannula while swirling the flask vigorously. The solution was clear after the completion of the water addition. The flask was then screw-capped tightly and left in an oven (100 °C) for 5 d. Generally, several small crystals were observed on the wall of the reaction vessel after 2 d, and the quantity of crystals increased slightly with time but did not change significantly after 5 d. The solution was then cooled to *ca.* 60 °C, and all volatiles were removed under vacuum at 60 °C. The remaining sticky solid was washed with MeCN (2  $\times$  30 cm<sup>3</sup>) and then crystallized from heptane (50 cm<sup>3</sup>) at –15 °C. This material was then recrystallized in the same fashion from toluene (25 cm<sup>3</sup>), yielding 2.78 g (1.1 mmol) of product (32% based on water, 24% based on Ti). The sample used for  $^{17}\text{O}$  NMR measurements was prepared using 10 atom %  $^{17}\text{O}$ -enriched water (Found: C, 32.85; H, 6.30; Ti, 33.70. Calc. for  $\text{C}_{69.75}\text{H}_{156}\text{O}_{45}\text{Ti}_{18}$ : C, 32.50; H, 6.15; Ti, 33.45%). IR (KBr, 480–1370 cm<sup>-1</sup>): 480m, 526m, 596s, 642s (br), 750s (br), 796m, 840m, 1028s (br), 1190s, 1235m and 1362m.  $^{17}\text{O}$  NMR (40.7 MHz, 0.039 mol dm<sup>-3</sup> in toluene– $\text{Bu}^i\text{OH}$ , 3:1 v/v, 3 atom %  $^{17}\text{O}$ -enriched sample, 20 °C; see Fig. 4):  $\delta$  760, 699, 578, 554, 543 (sh), 532, 440, 439 and 407.  $^{13}\text{C}\{-^1\text{H}\}$  NMR {125.8 MHz, 0.023 mol dm<sup>-3</sup> in  $[^2\text{H}_8]\text{toluene}$ ,

20 °C; see Figs. 5(b) and 6(b)}:  $\delta$  88.16, 87.78, 87.58, 87.17, 86.92, 84.59, 84.06, 84.01, 83.93 and 83.70 (OCMe<sub>3</sub>); 33.00, 32.91, 32.83, 32.00, 31.84, 31.78, 31.68 (sh), 31.65 and 31.46 (OCMe<sub>3</sub>). <sup>13</sup>C-<sup>1</sup>H} NMR {125.8 MHz, 0.023 mol dm<sup>-3</sup> in [<sup>2</sup>H<sub>8</sub>]toluene, -70 °C; see Fig. 6(a)}:  $\delta$  88.51, 88.03, 87.88, 87.21, 86.89, 85.02, 84.22, 84.02, 83.86 and 83.74 (OCMe<sub>3</sub>); 32.78, 32.71, 32.65, 31.78, 31.72, 31.55, 31.48, 31.26, 31.14 and 31.11 (OCMe<sub>3</sub>). <sup>13</sup>C-<sup>1</sup>H} NMR spectra of a 0.023 mol dm<sup>-3</sup> [<sup>2</sup>H<sub>8</sub>]toluene solution, 0.0035 mol dm<sup>-3</sup> in NEt<sub>3</sub>, prepared as follows were also measured. The compound [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub> (0.03 g, 0.012 mmol) was dissolved in [<sup>2</sup>H<sub>8</sub>]toluene in a 5 mm NMR tube. A stock solution was made by mixing NEt<sub>3</sub> (8  $\mu$ l, 0.0575 mmol) with [<sup>2</sup>H<sub>8</sub>]toluene (792  $\mu$ l), and 24  $\mu$ l of this solution was added to the NMR tube *via* a syringe. The solution was mixed well by shaking the tube. <sup>13</sup>C-<sup>1</sup>H} NMR [125.8 MHz, 20 °C; methyl region only, see Fig. 6(c)}:  $\delta$  32.90, 31.91, 31.75, 31.64 and 31.45.

#### [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub> stability studies

A 10 mm NMR sample tube was charged with 3 atom % <sup>17</sup>O-enriched [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub> (0.20 g, 0.078 mmol) and capped with a rubber septum. A solution of Bu<sup>t</sup>OH (0.5 cm<sup>3</sup>) in toluene (1.5 cm<sup>3</sup>) was then added. This solution (0.039 mol dm<sup>-3</sup>) was used for stability tests at ambient temperature; a 0.020 mol dm<sup>-3</sup> solution prepared in the same fashion using 0.10 g (0.039 mmol) of alkoxide was used for the stability test at 80 °C.

#### Reaction of [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub> with 2-methylbutan-2-ol

To a solution of [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub> (1.0 g, 0.39 mmol) in toluene (15 cm<sup>3</sup>), 2-methylbutan-2-ol (10 cm<sup>3</sup>, 91 mmol) was added with stirring. After 10 min at room temperature, volatiles were removed under vacuum. The toluene-2-methylbutan-2-ol treatment just described was then repeated twice at room temperature and once at 80 °C. The resulting white solid was crystallized from toluene (15 cm<sup>3</sup>) at -15 °C. Yield: 0.67 g (0.26 mmol, 65%). <sup>17</sup>O NMR (40.7 MHz, 0.021 mol dm<sup>-3</sup> in toluene, 20 °C):  $\delta$  759, 698, 579, 556, 543 (sh), 532, 439 and 408. <sup>13</sup>C-<sup>1</sup>H} NMR {125.8 MHz, 0.038 mol dm<sup>-3</sup> in [<sup>2</sup>H<sub>8</sub>]toluene, 20 °C; see Fig. 5(c)}:  $\delta$  88.19, 87.81, 87.58, 87.47, 87.18, 87.01, 86.96, 86.61, 84.04 and 83.90 (OCMe<sub>3</sub> and OCETMe<sub>2</sub>); 38.32, 38.29 and 38.16 [OC(CH<sub>2</sub>CH<sub>3</sub>)Me<sub>2</sub>]; 32.00, 31.83 (sh), 31.79, 31.65 and 31.49 (OCMe<sub>3</sub>); 30.06, 30.00 and 29.85 (OCETMe<sub>2</sub>); 10.21 and 10.13 [OC(CH<sub>2</sub>CH<sub>3</sub>)Me<sub>2</sub>].

#### Preparation of Ti(OBu<sup>t</sup>)<sub>4</sub>- and [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub>-derived xerogels for <sup>17</sup>O MAS NMR studies

The Ti(OBu<sup>t</sup>)<sub>4</sub>-derived xerogel was prepared as follows. A solution of 10% <sup>17</sup>O-enriched water (200  $\mu$ L, 11.1 mmol) and HCl (12 mol dm<sup>-3</sup>, 10  $\mu$ l, 0.012 mmol) in Bu<sup>t</sup>OH (5 cm<sup>3</sup>) was added dropwise *via* a syringe under argon to a solution of Ti(OBu<sup>t</sup>)<sub>4</sub> (1.3 g, 3.8 mmol) in tetrahydrofuran (thf) (5 cm<sup>3</sup>) with vigorous stirring. The solution was stirred for 5 min, and then left undisturbed under Ar at ambient temperature for 45–60 min to form a translucent gel which was then dried under vacuum. The [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub>-derived xerogel samples were prepared in a similar fashion. A solution of water (360  $\mu$ l, 20.0 mmol) and HCl (10  $\mu$ l, 12 mol dm<sup>-3</sup>, 0.012 mmol) in Bu<sup>t</sup>OH (5 cm<sup>3</sup>) was added dropwise *via* a syringe to a solution of [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub> (0.55 g, 0.22 mmol) in thf (5 cm<sup>3</sup>) with vigorous stirring under an argon atmosphere. The solution was stirred for 30 min, and then left undisturbed for 1.5–2 d at ambient temperature under Ar to form a translucent gel which was then dried under vacuum. Three [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub>-derived xerogel samples for solid state NMR were prepared by following the procedure just described, using different levels of <sup>17</sup>O enrichment. The <sup>17</sup>O enrichment employed for each sample was (i) 10% <sup>17</sup>O-enriched [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub> plus 10% <sup>17</sup>O-enriched water; (ii) unenriched [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub> plus 10% <sup>17</sup>O-enriched water; (iii) 10% <sup>17</sup>O-enriched [Ti<sub>18</sub>O<sub>28</sub>H]-

[OBu<sup>t</sup>]<sub>17</sub> plus unenriched water. In each case, xerogel samples were ground to fine powders with an aluminium oxide mortar and pestle under an open atmosphere before packing in the spinner. All MAS NMR spectra were recorded at 20 °C.

#### Crystal structure determinations

Two different crystallized forms of [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub> were obtained and structurally characterized using single crystal X-ray diffraction techniques.

[Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub>. The first crystals to be examined were obtained directly from the walls of the reaction vessel (see above). The lattice for this crystalline form contained no solvent of crystallization and utilized a primitive tetragonal unit cell with  $a = 19.461(6)$ ,  $c = 16.131(5)$  Å,  $U = 6109(5)$  Å<sup>3</sup>,  $Z = 2$ , and space group  $P4/nmm-D_{4h}^7$  (no. 129). Room-temperature data were collected as previously described,<sup>7</sup> using 1.20° wide  $\omega$  scans and graphite-monochromated Mo-K $\alpha$  radiation with a conventional computer-controlled four-circle Nicolet diffractometer, yielding 2357 unique reflections having  $2\theta(\text{Mo-K}\alpha) \leq 45.9^\circ$ . Although structure solution and refinement (based on  $F$ ) using this data with the Siemens SHELXTL PC software package<sup>8a</sup> gave  $R_1$  (unweighted, based on  $F$ ) = 0.14 for 634 reflections having  $I > 2\sigma(I)$ , it also indicated the unlikely formulation [Ti<sub>18</sub>O<sub>28</sub>][OBu<sup>t</sup>]<sub>18</sub>. The structure appeared to be highly disordered and based on an  $\alpha$ -Keggin metal oxide core with all six metal 'squares' capped by [Ti<sup>IV</sup>(OBu<sup>t</sup>)<sub>3</sub>]<sup>3+</sup> units. While not unusual for crystals of polyoxotitanates, the fact that the diffracted intensities dropped rapidly with increasing scattering angle was consistent with a highly disordered structure. When all attempts to model the disorder or refine the structure in lower-symmetry space groups failed to provide a more reasonable result, recrystallization attempts were begun in the hope that a crystalline solvate free from disorder might be obtained.

[Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub>-Bu<sup>t</sup>OH. Large, well-shaped, colourless crystals of the *tert*-butyl alcohol solvate of [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub> could be grown reproducibly from a toluene-*tert*-butyl alcohol solvent mixture by cooling a solution of [Ti<sub>18</sub>O<sub>28</sub>H][OBu<sup>t</sup>]<sub>17</sub>·0.25C<sub>6</sub>H<sub>5</sub>Me (0.5 g) in toluene (5 cm<sup>3</sup>) and *tert*-butyl alcohol (1 cm<sup>3</sup>) to 4 °C for about 2 weeks. Unfortunately, preliminary examination of nearly two dozen of these crystals on a four-circle diffractometer with both Cu- and Mo-K $\alpha$  radiation always failed to yield a reasonable unit cell, even when samples from several different crystallizations were examined. Each crystal produced axial photographs indicating the presence of diminished diffraction intensities at high scattering angles, at least one very long (> 50 Å) axis, a large (> 25 000 Å<sup>3</sup>) unit cell volume, and intensity profiles which suggested twinning. Given the possibility of large lattice constants and relatively poor diffraction for these crystals, Cu-K $\alpha$  radiation appeared to be the best choice for eventually making intensity measurements using a conventional diffractometer. Unfortunately, Cu-K $\alpha$  radiation was absorbed rather strongly by the large crystals being studied. In fact, some intensities were lower when measured at the same X-ray tube wattage with Cu-K $\alpha$  radiation than with Mo-K $\alpha$  radiation.

When all attempts to grow better crystals under different conditions failed, the decision was made to proceed with the study using the possibly twinned crystals grown from toluene-*tert*-butyl alcohol. This decision was prompted by the availability of the Siemens Molecular Analysis Research Tool Charge Coupled Device (SMART CCD) area detector which was being developed for small molecule use with Mo-K $\alpha$  radiation by Siemens Analytical Instruments. For each of the three different crystals obtained from toluene-*tert*-butyl alcohol, a full hemisphere of diffraction data (1270 10 s frames with an  $\omega$  scan width of 0.30°) was measured to 0.91 Å resolution

using graphite-monochromated Mo-K $\alpha$  radiation. X-Rays were provided by a sealed X-ray tube at 50 kV and 40 mA. All three crystals were twinned. For the third crystal, centres for a set of 300 reflections were obtained. These were then sorted into two groups corresponding to the two twin components. This was done with a version of the conventional Siemens Autoindexing program<sup>8b</sup> which was modified to obtain reflection indices, orientation matrices and lattice parameters for twinned crystalline samples. This program systematically generates combinations of three reflections at a time. For each combination of three reflections it tries to generate integer indices for a large fraction (default = 0.40) of all 300 of the centred reflections. This procedure is successful if the three reflections are all derived from one of the major components of the twinned sample. An orientation matrix, lattice parameters and integer indices were obtained in this fashion for a large number of the initial reflections. These reflections were designated set 1. The set 1 reflections were then deleted from the original set and the procedure was repeated for the set of remaining reflections. A second set (set 2) of reflections was thus generated, producing a second orientation matrix with corresponding lattice parameters and integer indices for the reflections. Nearly all of the original 300 reflections were thus assigned to set 1 or set 2, with some reflections appearing in both sets. Next, those reflections in set 1 but not in set 2 were used to obtain a least-squares orientation matrix and lattice parameters. Likewise, those reflections in set 2 but not in set 1 were used to obtain a second least-squares orientation matrix and lattice parameters. These two sets of lattice parameters gave the same unit cell dimensions to within 0.02 Å and were seen to correspond to a 180° rotation of the reciprocal lattice about the  $c^*$  axis.

With the orientation matrix for the first twin component and the 1270 frames of collected CCD data, the Siemens program SAINT<sup>8c</sup> was used to obtain a set of integrated reflection intensities for the first twin. With the same frames of data but the orientation matrix for the second twin component, SAINT was then used to obtain a second set of integrated reflection intensities for the second twin. Each reflection in the first twin intensity data set was classified into one of three categories: (i) no overlap with any reflection in the second data set, (ii) almost complete overlap with a reflection from the second data set or (iii) partial overlap with a reflection from the second data set. Only reflections from the first two categories were used for an initial structure solution and refinement. An initial structure solution and refinement was also obtained from the second twin data set following the same procedure. Unfortunately, it was not possible to assign the correct space group at this point since the reflections in category (ii) could obscure the glide plane extinctions which were present in the correct space group. However, the monoclinic screw-axis extinction was not obscured and the structure was initially solved in the non-centrosymmetric space group  $P2_1$ . This solution yielded two separate molecules in the asymmetric unit which, when combined with their screw-axis related mates, were shown to be related by the symmetry operations present in the centrosymmetric space group  $P2_1/c-C_{2h}^5$  (no. 14). Both molecules were then translated in the unit cell for proper alignment with the symmetry elements of  $P2_1/c$  and the second molecule was discarded.

The final stages of refinement were conducted using the SHELXL 92<sup>8d</sup> software package, space group  $P2_1/c$ , and a final set of twin-resolved intensity data obtained from the two sets of integrated intensity data and both orientation matrices described above. Only those reflections belonging to the first two categories defined above were retained; this resulted in a final data set which contained integrated intensity measurements for only 69% (12 068 of 17 600) of the unique reflections having  $2\theta(\text{Mo-K}\alpha) < 45.8^\circ$ . Non-overlapping reflections for each twin component were assigned indices and a scale-factor

parameter ( $K1$  or  $K2$ ) associated with that twin component. Reflections which almost completely overlapped were assigned two sets of indices and two associated scale-factor parameters ( $K1$  and  $K2$ ). It was assumed that the measured intensity of an overlapped reflection is a linear combination of the intensities of the individual reflections from the two twins. Letting  $K2 = 1.0 - K1$ , the scale-factor parameter  $K1$  was refined with all of the other parameters normally refined by SHELXL. This scale-factor parameter refined to a final value of 0.469(3), indicating relative volumes of 1.000:1.132 for the two twin components.

The lattice constants reported in the crystal data summary of Table 1 were derived from a least-squares refinement of the intensity profiles for 50 reflections of the first twin which were totally resolved from those of the second twin. The initial and final stages of structure refinement used a common set of geometrical restraints for all *tert*-butoxide groups and the *tert*-butyl alcohol solvent molecule of crystallization. Removal of these restraints for intermediate refinement cycles did not produce major structural differences or dramatic changes in the  $R$  values. Methyl hydrogen atoms were included in the refinement at idealized positions and refined using a riding model; they were assigned isotropic thermal parameters equal to 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded.

Selected bond lengths from the structure determination of  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}']_{17}\cdot\text{Bu}'\text{OH}$  are given with estimated standard deviations in Table 2.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

## Results

### Synthesis

The complex  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}']_{17}$  was prepared by treating  $\text{Ti}(\text{OBu}')_4$  with slightly more than 1 equivalent of water in  $\text{Bu}'\text{OH}$  solution for 3–5 d at 100 °C. Removal of volatiles followed by washing with acetonitrile and recrystallizing twice, first from heptane and then from toluene, yielded pure, crystalline material as a toluene solvate in modest yield. Given the formulation  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}']_{17}\cdot 0.25\text{C}_6\text{H}_5\text{Me}$ , based on elemental analysis, NMR spectroscopy and X-ray crystallography (see Experimental section), the overall yield was 32% based on water and 24% based on titanium.

According to  $^{17}\text{O}$  solution NMR measurements, synthesis of  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}']_{17}$  required the high reaction temperature and long reaction time employed. At ambient temperature,  $^{17}\text{O}$  NMR spectra measured from 0.2 mol dm<sup>-3</sup> solutions of  $\text{Ti}(\text{OBu}')_4$  in toluene– $\text{Bu}'\text{OH}$  (3:1 v/v) hydrolysed with 0.2–0.8 equivalent of  $^{17}\text{O}$ -enriched water showed only a narrow  $\delta$  547 triply-bridging oxide oxygen ( $\text{OTi}_3$ ) resonance† plus a broad band at about  $\delta$  525. Solids isolated from solutions of partially hydrolysed  $\text{Ti}(\text{OBu}')_4$  showed  $^{17}\text{O}$ ,  $^{13}\text{C}\{-^1\text{H}\}$  and  $^1\text{H}$  NMR resonances in benzene solution assigned to  $\text{Ti}(\text{OBu}')_4$  by comparison with an authentic sample plus a single  $\delta$  543  $^{17}\text{O}$  resonance in the  $\text{OTi}_3$  region, single  $^{13}\text{C}\{-^1\text{H}\}$  NMR resonances in the tertiary carbon and methyl carbon regions, and a single  $^1\text{H}$  NMR resonance in the methyl region (see Experimental section). Solution  $^{17}\text{O}$  NMR spectra of *tert*-butyl alcohol solutions prepared in a similar fashion but kept at 100 °C for at least 3 d showed resonances assigned to  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}']_{17}$  (see below), partially obscured by a large, broad  $\delta$  534 resonance, plus a sharp  $\delta$  547 resonance.

† Oxygen-17 chemical shift observed for titanium oxoalkoxides are:<sup>9</sup>  $\text{OTi}_2$  oxygens,  $\delta$  650–850;  $\text{OTi}_3$  oxygens,  $\delta$  450–650;  $\text{OTi}_4$  oxygens,  $\delta$  250–450.

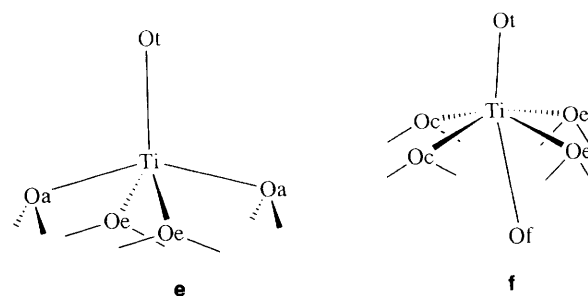
**Table 1** Crystal data and structure refinement for  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^+]_{17}\cdot\text{Bu}^+\text{OH}$ 

Formula	$\text{C}_{72}\text{H}_{164}\text{O}_{46}\text{Ti}_{18}$
<i>M</i>	2628.23
<i>T</i> /K	293(2)
$\lambda/\text{\AA}$	0.710 73
Crystal system	Monoclinic
Space group	$P2_1/c-C_{2h}^5$ (no. 14)
<i>a</i> /\AA	15.789(4)
<i>b</i> /\AA	29.544(5)
<i>c</i> /\AA	27.496(5)
$\beta/^\circ$	91.85(5)
<i>U</i> /\AA <sup>3</sup>	12 819(5)
<i>Z</i>	4
<i>D<sub>c</sub></i> /Mg m <sup>-3</sup>	1.362
$\mu/\text{mm}^{-1}$	1.120
<i>F</i> (000)	5 440
Crystal size/mm	0.54 × 0.60 × 0.72
$\theta$ range for data collection/ $^\circ$	1.89–22.90
Index ranges	$-17 \leq h \leq 17, -32 \leq k \leq 32, -30 \leq l \leq 30$
Independent reflections	12 068
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup>
Data, parameters	11 496, 1 087
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.048
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>7</sup>	<i>R</i> 1 = 0.1193, <i>wR</i> 2 = 0.2961
<i>R</i> indices (all data) <sup>7</sup>	<i>R</i> 1 = 0.1441, <i>wR</i> 2 = 0.3391
Largest difference peak, hole/e \AA <sup>-3</sup>	0.626, -0.622

### Solid-state structure

The solid-state structure of  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^+]_{17}\cdot\text{Bu}^+\text{OH}$  is shown in Figs. 1 and 2; its metal–oxygen core structure is shown in Fig. 3. Even though hydrogen atoms could not be located directly from Fourier-difference syntheses, the protonation site could be inferred from indirect evidence. Oxygen atom O(1a) is the protonation site as indicated by the fact that this  $\mu\text{-OH}^-$  ligand is hydrogen bonded in the lattice to the oxygen of the *tert*-butyl alcohol solvent molecule of crystallization. Although the specific details of this hydrogen-bonding interaction are unclear since hydrogen atoms could not be located directly, the O(1a)···O(1s) separation of 2.77 \AA and the Ti(1)–O(1a)–O(1s), Ti(2)–O(1a)–O(1s) and C(1s)–O(1s)–O(1a) angles of 104°, 141° and 132°, respectively, are consistent with its existence. The 3.01 \AA O(15)···O(1) separation is similarly accounted for by weak hydrogen bonding between the Bu<sup>+</sup>OH hydroxyl proton and O(1). The average Ti–O(1a) bond length of 1.996(13,1,1,2) \AA is also significantly longer than the 1.825(12,51,90,6) \AA\* average Ti–O bond length to the other oxygen atoms bonded to two titanium centres, O(2a), O(3a) and O(4a). Although the  $\text{Ti}_{18}\text{O}_{45}$  metal–oxygen framework of  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^+]_{17}$  could ideally possess  $C_{2v}$  symmetry, protonation of O(1a) effectively reduces the symmetry to  $C_s$ , with an idealized mirror plane containing Ti(6), Ti(10), Ti(17), Ti(18), O(6), O(10), O(17), O(1a), O(3a), O(17b), O(19b), O(1c) and O(2c). These atoms are coplanar to within 0.05 \AA. Atoms Ti(8), Ti(12), Ti(17), Ti(18), O(2a), O(4a), O(18b), O(20b), O(3c), O(4c), O(8), O(12) and O(17) would lie in the second mirror plane of a  $C_{2v}$  species and are coplanar to within 0.02 \AA.

The 18 Ti<sup>IV</sup> ions utilize three distinctly different co-ordination geometries: one [Ti(18)] is tetrahedral, five [Ti(5), Ti(7), Ti(9), Ti(11), Ti(17)] have distorted trigonal-bipyramidal co-ordination, and 12 [Ti(1), Ti(2), Ti(3), Ti(4), Ti(6), Ti(8), Ti(10), Ti(12), Ti(13), Ti(14), Ti(15), Ti(16)] have distorted octahedral co-ordination. The 28 oxo or hydroxy ligands all serve as bridges between Ti atoms and have the following



distribution among three distinct structural types: four serve as  $\mu$  bridges between two octahedral Ti centres and are designated as *a*-type bridges; 20 serve as *b*-type  $\mu_3$  bridges between two octahedral Ti centres and one trigonal-bipyramidal Ti centre and four serve as *c*-type  $\mu_4$  bridges between the central tetrahedral Ti and three octahedral Ti centres. The central Ti<sup>IV</sup> is tetrahedrally co-ordinated to four O<sup>2-</sup> ligands: the Ti–O distances and O–Ti–O angles average 1.812(12,22,43,4) \AA and 109.5(6,8,14,6)°, respectively.

The detailed co-ordination geometries at the five 'capping' five-co-ordinate titanium centres and the twelve 'Keggin' six-co-ordinate titanium centres are shown in e and f, respectively. Each of the five 'capping' titanium centres adopts a distorted trigonal-bipyramidal co-ordination geometry. An alkoxide oxygen (O<sub>i</sub> in e) occupies one of the equatorial positions with an average Ti–O distance of 1.78(1,2,4,5) \AA. The average Ti–O bond distances to the other equatorial oxygens (O<sub>e</sub> in e) and the axial oxygens (O<sub>a</sub> in e) are 1.87(1,2,5,10) and 1.96(1,4,7,10) \AA, respectively. Average bond angles follow, using the labelling scheme shown in e: O<sub>a</sub>–Ti–O<sub>a</sub> 151.8(6,10,17,5), O<sub>a</sub>–Ti–O<sub>e</sub> 82.4(6,14,41,20), O<sub>a</sub>–Ti–O<sub>i</sub> 104.4(6,13,25,10), O<sub>e</sub>–Ti–O<sub>e</sub> 115.8(6,7,18,5) and O<sub>e</sub>–Ti–O<sub>i</sub> 122.0(7,9,23,10)°. Each of the 12 six-co-ordinate titanium centres in the outer shell of the Keggin framework is bonded to one  $\mu_4$  oxygen ligand (O<sub>f</sub> in f), four  $\mu$  or  $\mu_3$  oxygen ligands (O<sub>c</sub> and O<sub>e</sub> in f) and one terminal *tert*-butoxide ligand (O<sub>i</sub> in f). The *tert*-butoxide is *trans* to a  $\mu_4$  oxygen ligand and has an average Ti–O<sub>i</sub> bond length of 1.76(1,2,6,12) \AA; the Ti–O<sub>f</sub> bonds to the  $\mu_4$  oxygen atoms have an average bond length of 2.25(1,2,4,12) \AA. Bonds to the remaining O<sub>c</sub> and O<sub>e</sub> oxygens generally have lengths intermediate between these values. As illustrated in f, the O<sub>c</sub> oxygens link octahedral titanium centres in the Keggin framework by corner sharing

\* The first number in parentheses following an average value of a bond length or angle is the root-mean-square estimated standard deviation 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) in crystalline  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}^t]_{17}\text{Bu}^t\text{OH}$ 

Ti(1)–O(1)	1.819(10)	Ti(10)–O(10)	1.762(12)
Ti(2)–O(2)	1.717(13)	Ti(11)–O(11)	1.759(13)
Ti(3)–O(3)	1.771(11)	Ti(12)–O(12)	1.740(12)
Ti(4)–O(4)	1.782(11)	Ti(13)–O(13)	1.756(11)
Ti(5)–O(5)	1.794(13)	Ti(14)–O(14)	1.746(11)
Ti(6)–O(6)	1.787(11)	Ti(15)–O(15)	1.735(11)
Ti(7)–O(7)	1.801(13)	Ti(16)–O(16)	1.756(13)
Ti(8)–O(8)	1.745(11)	Ti(17)–O(17)	1.735(14)
Ti(9)–O(9)	1.784(12)		
Ti(1)–O(1a)	1.997(14)	Ti(2)–O(1a)	1.995(12)
Ti(2)–O(2a)	1.739(12)	Ti(3)–O(2a)	1.915(13)
Ti(3)–O(3a)	1.810(11)	Ti(4)–O(3a)	1.820(13)
Ti(1)–O(4a)	1.779(11)	Ti(4)–O(4a)	1.887(12)
Ti(1)–O(1b)	2.142(13)	Ti(4)–O(11b)	2.114(14)
Ti(5)–O(1b)	1.90(2)	Ti(10)–O(11b)	1.916(13)
Ti(6)–O(1b)	1.900(12)	Ti(11)–O(11b)	1.91(2)
Ti(5)–O(2b)	1.886(12)	Ti(10)–O(12b)	2.025(14)
Ti(6)–O(2b)	2.066(14)	Ti(11)–O(12b)	1.886(13)
Ti(13)–O(2b)	1.917(14)	Ti(16)–O(12b)	1.956(13)
Ti(2)–O(3b)	2.170(13)	Ti(4)–O(13b)	2.073(14)
Ti(6)–O(3b)	1.94(2)	Ti(11)–O(13b)	1.865(13)
Ti(7)–O(3b)	1.897(12)	Ti(12)–O(13b)	1.993(12)
Ti(6)–O(4b)	1.986(12)	Ti(11)–O(14b)	1.993(13)
Ti(7)–O(4b)	1.92(2)	Ti(12)–O(14b)	1.929(13)
Ti(14)–O(4b)	1.979(13)	Ti(16)–O(14b)	1.939(12)
Ti(2)–O(5b)	1.994(12)	Ti(1)–O(15b)	2.02(2)
Ti(7)–O(5b)	1.860(12)	Ti(5)–O(15b)	1.854(12)
Ti(8)–O(5b)	1.973(12)	Ti(12)–O(15b)	1.98(2)
Ti(7)–O(6b)	2.028(13)	Ti(5)–O(16b)	1.96(2)
Ti(8)–O(6b)	2.019(12)	Ti(12)–O(16b)	1.965(13)
Ti(14)–O(6b)	1.96(2)	Ti(13)–O(16b)	1.938(12)
Ti(3)–O(7b)	2.132(12)	Ti(13)–O(17b)	1.987(12)
Ti(8)–O(7b)	1.970(12)	Ti(14)–O(17b)	1.989(13)
Ti(9)–O(7b)	1.821(13)	Ti(17)–O(17b)	1.891(14)
Ti(8)–O(8b)	1.97(2)	Ti(14)–O(18b)	1.982(13)
Ti(9)–O(8b)	2.008(12)	Ti(15)–O(18b)	1.994(12)
Ti(15)–O(8b)	1.96(2)	Ti(17)–O(18b)	1.97(2)
Ti(3)–O(9b)	2.05(2)	Ti(15)–O(19b)	1.933(13)
Ti(9)–O(9b)	1.971(12)	Ti(16)–O(19b)	2.056(12)
Ti(10)–O(9b)	1.92(2)	Ti(17)–O(19b)	1.875(12)
Ti(9)–O(10b)	1.88(2)	Ti(13)–O(20b)	1.98(2)
Ti(10)–O(10b)	2.002(12)	Ti(16)–O(20b)	2.007(13)
Ti(15)–O(10b)	1.963(13)	Ti(17)–O(20b)	1.972(13)
Ti(1)–O(1c)	2.222(12)	Ti(8)–O(3c)	2.271(14)
Ti(2)–O(1c)	2.287(13)	Ti(14)–O(3c)	2.228(12)
Ti(6)–O(1c)	2.254(12)	Ti(15)–O(3c)	2.218(12)
Ti(3)–O(2c)	2.276(13)	Ti(12)–O(4c)	2.259(11)
Ti(4)–O(2c)	2.276(12)	Ti(13)–O(4c)	2.238(12)
Ti(10)–O(2c)	2.264(12)	Ti(16)–O(4c)	2.261(12)
Ti(18)–O(1c)	1.814(12)	Ti(18)–O(3c)	1.836(12)
Ti(18)–O(2c)	1.769(12)	Ti(18)–O(4c)	1.830(12)

and the  $\text{O}_e$  oxygens link them by edge sharing. If only those  $\text{O}_e$  and  $\text{O}_c$  that are triply bridging are considered, fairly regular geometry is observed: the average  $\text{Ti}_{\text{oct}}\text{--O}_c\text{--Ti}_{\text{oct}}$  angle is  $146.2(7,16,44,10)$ , the average  $\text{Ti}_{\text{oct}}\text{--O}_e\text{--Ti}_{\text{oct}}$  angle is  $114.1(6,14,32,10)^\circ$  and the average Ti–O bond length for  $\text{O}_c$  and  $\text{O}_e$  oxygens at octahedral Ti centres not bonded to the doubly bridging oxygens O(1a), O(2a), O(3a) and O(4a) (see Fig. 3) is  $1.97(1,3,9,32)$  Å. Bond lengths involving titanium centres bonded to these doubly bridging oxygens are shown in Scheme 1. Here, the effect of protonation at O(1a) is apparent: bond lengths at O(1a) are long compared to those at O(3a), and this bond weakening is compensated for largely by strengthening the Ti(2)–O(2a) and Ti(1)–O(4a) bonds and to a lesser extent by strengthening the Ti(2)–O(5b) and Ti(1)–O(15b) bonds. The Ti(1)–O(1b) and Ti(2)–O(3b) bonds are actually slightly longer than the corresponding Ti(4)–O(11b) and Ti(3)–O(9b) bonds, presumably owing to a *trans* influence induced by the very short Ti(1)–O(4a) and Ti(2)–O(2a) bonds.

### Solution structure and stability

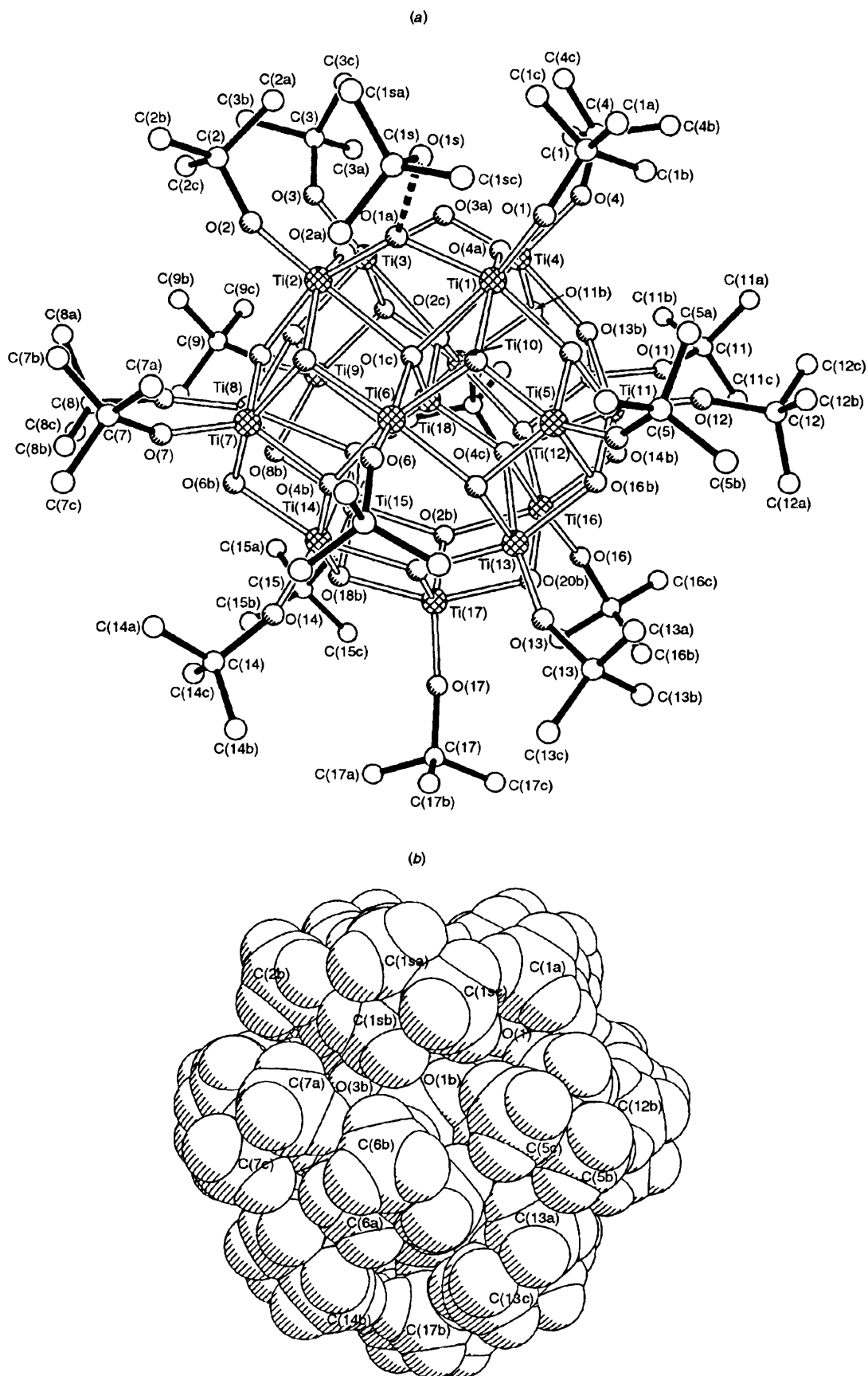
The  $^{17}\text{O}$  NMR spectrum shown in Fig. 4 was measured from a toluene-*tert*-butyl alcohol solution of a  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}^t]_{17}$  sample prepared by hydrolysis of  $\text{Ti}(\text{OBu}^t)_4$  with  $^{17}\text{O}$ -enriched water. The sample was therefore enriched in  $^{17}\text{O}$  at the oxide and hydroxide oxygen sites but not at the alkoxide oxygen sites.<sup>9</sup> The  $^{17}\text{O}$  NMR spectrum obtained is consistent with the  $\text{C}_s$   $\text{Ti}_{18}\text{O}_{28}$  metal oxide core structure observed in the solid state (see Fig. 3). Two resonances are observed for the two types of doubly bridging oxygens, the O(3a) resonance appearing at  $\delta$  760 and the resonance for the symmetry-equivalent O(2a) and O(4a) oxygens appearing at  $\delta$  699. Three resonances are observed for the three types of four-fold bridging oxygens: the barely-resolved  $\delta$  440 and 439 resonances are assigned to the two  $\text{OTi}_4$  oxygens near the open face of the molecule, O(1c) and O(2c); the remaining  $\delta$  407 resonance is assigned to the symmetry-equivalent O(3c) and O(4c) oxygens further removed from the open face. The remaining resonances lie in the  $\delta$  500–600 region and are assigned to the  $\text{OTi}_3$  and  $\text{OTi}_2\text{H}$  oxygens labelled O(1b)–O(20b) and O(1a), respectively, in Fig. 3. Given that the  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}^t]_{17}$  structure contains twelve symmetry-non-equivalent types of triply bridging  $\text{OTi}_3$  and  $\text{OTi}_2\text{H}$  oxygens, the poor resolution obtained in this region is not surprising.

Fully-resolved  $^{13}\text{C}\text{--}\{^1\text{H}\}$  NMR spectra provide further support for retention of the solid-state  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}^t]_{17}$  structure in solution. This  $\text{C}_s$  structure contains ten types of Bu<sup>t</sup>O groups labelled A–J in Fig. 5(a), and  $^{13}\text{C}\text{--}\{^1\text{H}\}$  NMR spectra in the methine carbon region [Fig. 5(b)] and the methyl carbon region [Fig. 6(a)] both show ten distinct resonances. Note that the methyl carbon chemical shift values are quite temperature dependent and that all ten resonances are resolved at  $-70^\circ\text{C}$  [Fig. 6(a)] but not at  $20^\circ\text{C}$  [Fig. 6(b)]. The manner in which the resonances overlap at  $20^\circ\text{C}$  could however be delineated by measuring spectra at intermediate temperatures.

The  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}^t]_{17}$  molecule is quite stable in solution according to  $^{17}\text{O}$  NMR studies of toluene–Bu<sup>t</sup>OH (0.020 mol  $\text{dm}^{-3}$ , 3:1 v/v) solutions; no decomposition could be detected after 24 h at ambient temperature. Spectra measured before and after heating to  $80^\circ\text{C}$  for 1 h were also virtually indistinguishable, implying no significant decomposition of the metal oxide core under these conditions.

**Alkoxide exchange.** Reaction of  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}^t]_{17}$  with 2-methylbutan-2-ol in toluene solution yielded alkoxide exchange, and  $^{17}\text{O}$  NMR spectra measured before and after exchange were virtually identical, indicating that the  $\text{Ti}_{18}\text{O}_{28}$  oxide core structure was retained during alkoxide exchange (see Experimental section). Comparison of the tertiary carbon  $^{13}\text{C}\text{--}\{^1\text{H}\}$  NMR spectrum measured after exchange [Fig. 5(c)] with the spectrum measured before [Fig. 5(b)], showed that the alkoxide exchange was regioselective. Seven of the ten original *tert*-butoxide resonances were still observed after exchange. These resonances are labelled with dots in Fig. 5(b) and 5(c). Three of the ten resonances disappeared during exchange, and three new ones appeared afterwards. These resonances are labelled with crosses in Fig. 5(b) and 5(c). The same behaviour was observed for methyl carbon resonances. Only the three resonances labeled D, F and J in Fig. 6(a) and 6(b) disappeared during exchange, and three new  $\text{OCe}t\text{Me}_2$  resonances appeared in the  $\delta$  29.5–30.5 region.

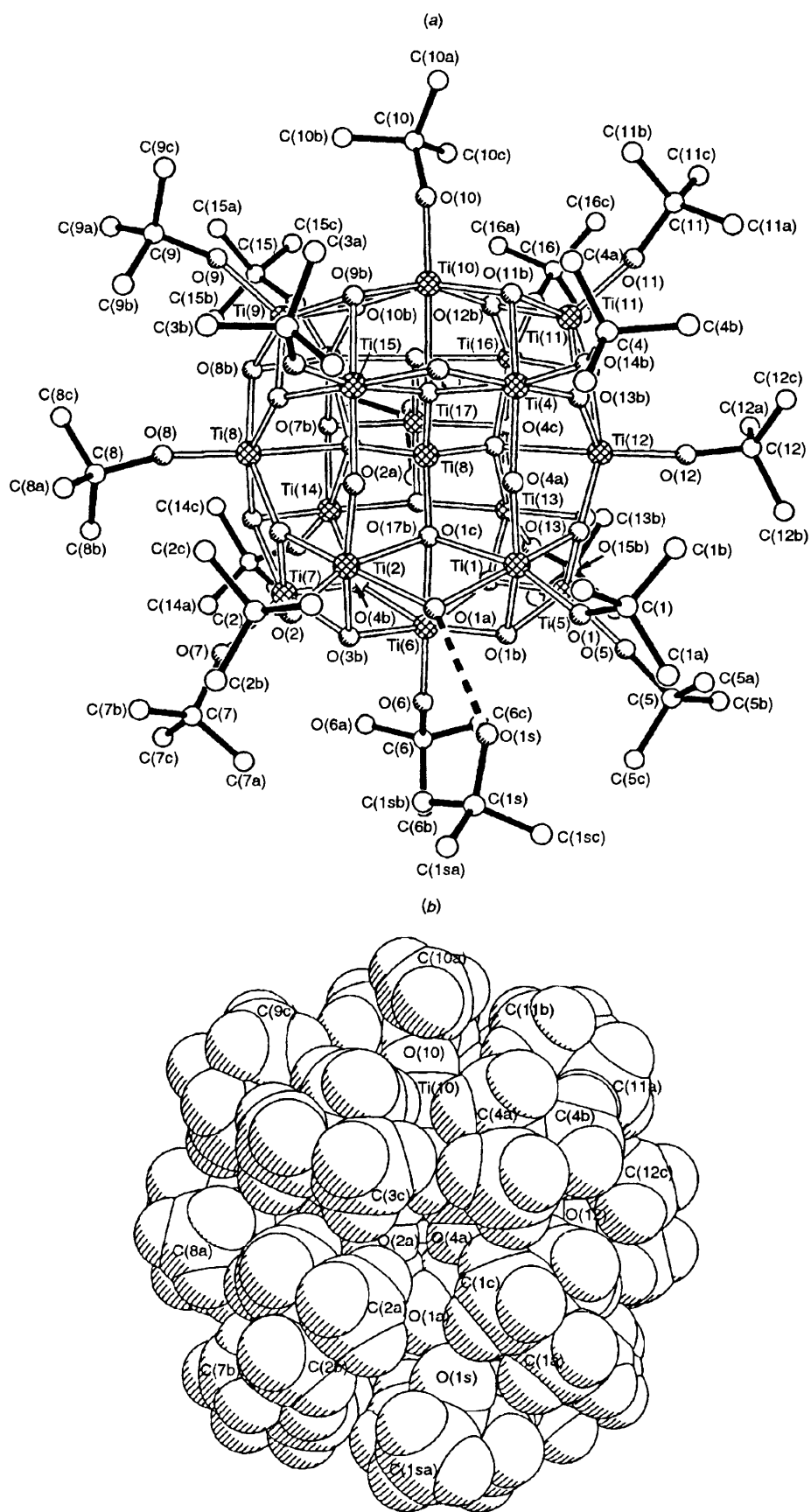
**Proton exchange.** Deprotonation of  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}^t]_{17}$  to yield the  $[\text{Ti}_{18}\text{O}_{28}][\text{OBu}^t]_{17}^-$  anion would involve conversion of a  $\text{C}_s$  symmetric molecule into a  $\text{C}_{2v}$  symmetric anion if the metal–oxygen framework of Fig. 3 were retained. Addition of a proton-transfer catalyst might therefore, in the fast-exchange limit, yield NMR spectral simplification. Such simplification could in fact be achieved for  $^{13}\text{C}\text{--}\{^1\text{H}\}$  NMR spectra in the



**Fig. 1** Perspective (a) and space-filling (b) drawing of the solid-state structure for the Bu'OH solvated  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}']_{17}$  molecule. This view is nearly parallel to the protonated 'square' face of the  $\text{Ti}_{12}$  cuboctahedron at the top of the molecule

methyl carbon region: addition of 0.15 equivalent of triethylamine to a solution of  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}']_{17}$  in toluene caused the spectrum shown in Fig. 6(b) to simplify into the spectrum shown in Fig. 6(c). Three of the resonances observed

before base addition, those labelled J, E and HI in Fig. 6(b), reappeared in spectra measured after addition of base, and are labelled J, E and H/I in Fig. 6(c). Three pairs of resonances labelled DF, AB and CG in Fig. 6(b), disappeared after



**Fig. 2** Perspective (a) and space-filling (b) drawing of the solid-state structure for the Bu'OH solvated  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}']_{17}$  molecule. This view is nearly perpendicular to the protonated 'square' face of the  $\text{Ti}_{12}$  cuboctahedron at the front of the molecule

addition of base, and resonance intensity appeared at three new positions [see Fig. 6(c)], each with chemical shift values equal within experimental error to the average of those of one of these pairs: the  $\delta$  32.90 chemical shift for resonance D/F in Fig. 6(c) is

the average of the chemical shifts of the pair of resonances DF in Figure 6(b) at  $\delta$  33.00 and 32.83;  $\delta$  31.90 for A/B in Fig. 6(c) is the average for the AB pair in Fig. 6(b) at  $\delta$  32.00 and 31.78 and  $\delta$  31.75 for C/G in Fig. 6(c) is the average for the CG pair in Fig.



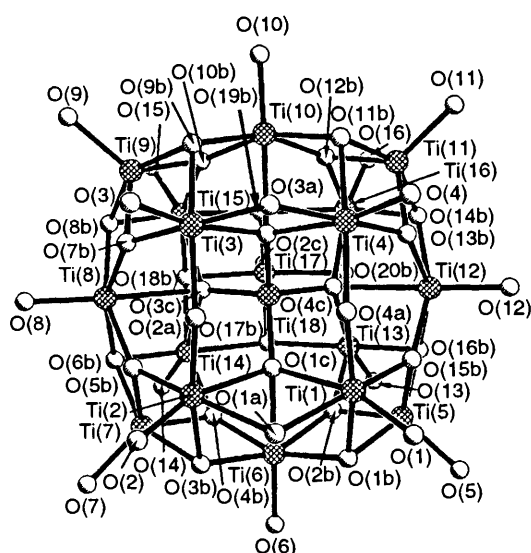
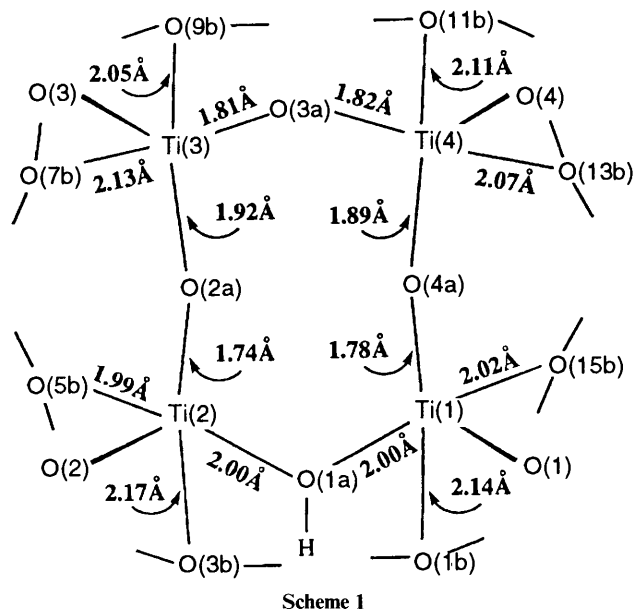


Fig. 3 Perspective drawing of the  $Ti_{18}O_{45}$  metal-oxygen core in  $[Ti_{18}O_{28}H][OBu]_{17}$



Scheme 1

6(b) at 31.84 and 31.68. A mechanistic interpretation of this result is provided below in the Discussion section.

### Sol-gel polymerization

Having demonstrated the stability of the  $Ti_{18}O_{28}$  metal oxide core of  $[Ti_{18}O_{28}H][OBu]_{17}$  during alkoxide exchange (see above), the stability of the core toward alkoxide hydrolysis and condensation was examined under sol-gel polymerization conditions. Two sets of experiments were performed to this end.

The first set of sol-gel polymerization reactions to be performed was a comparative study of  $Ti(OBu)_4$  and  $[Ti_{18}O_{28}H][OBu]_{17}$  hydrolysis/condensation under similar reaction conditions. Both sol-gel polymerizations were performed in  $thf-Bu'OH$  (1:1 v/v) solution with a total titanium concentration of  $0.38 \text{ mol dm}^{-3}$  and a  $0.024 \text{ mol dm}^{-3}$  HCl concentration. Since  $Ti(OBu)_4$  solutions gelled much faster than those of  $[Ti_{18}O_{28}H][OBu]_{17}$  upon addition of water, lower water concentrations were employed for the former in order to obtain reasonably similar gel times. Specifically,  $Ti(OBu)_4$  was hydrolysed with 2.9 equivalents of water yielding a gel time of 45–60 min, and  $[Ti_{18}O_{28}H][OBu]_{17}$  was hydrolysed with 91 equivalents of water, corresponding to 5.1 equivalents per mol Ti, yielding a gel time of about 2 d. Solid-state  $^{17}O$  MAS NMR spectra of the  $Ti(OBu)_4$ -derived

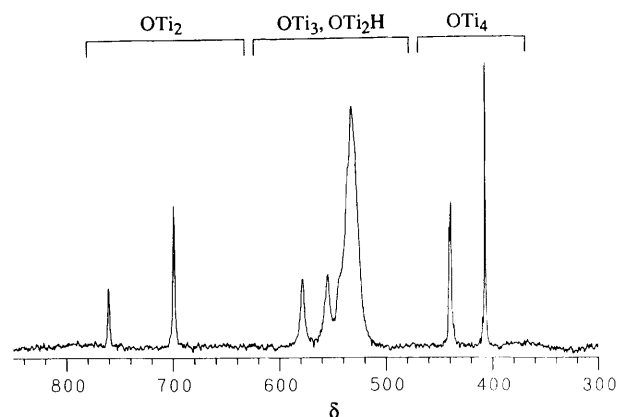


Fig. 4 40.7 MHz  $^{17}O$  solution FT-NMR spectrum of  $0.039 \text{ mol dm}^{-3}$   $[Ti_{18}O_{28}H][OBu]_{17}$  in  $Bu'OH$ -toluene (1:3 v/v) at  $20^\circ C$

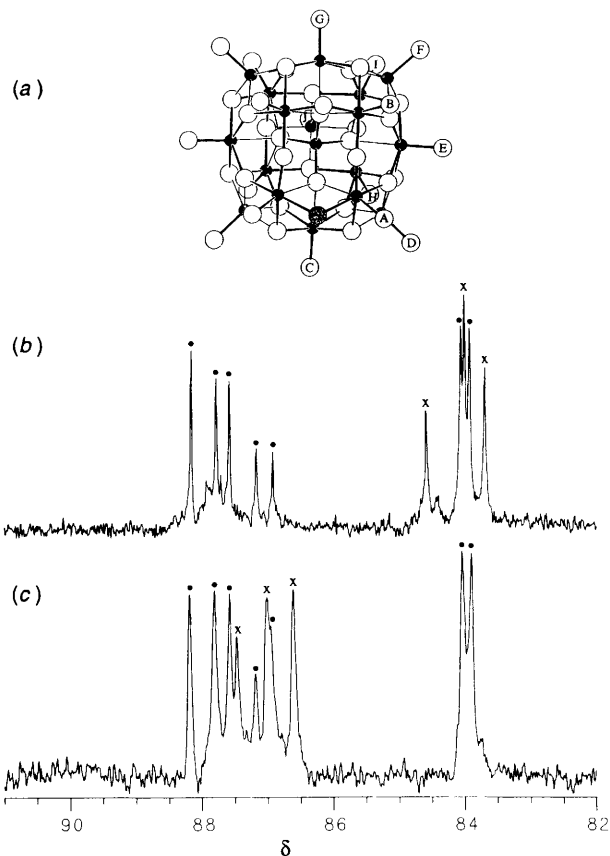
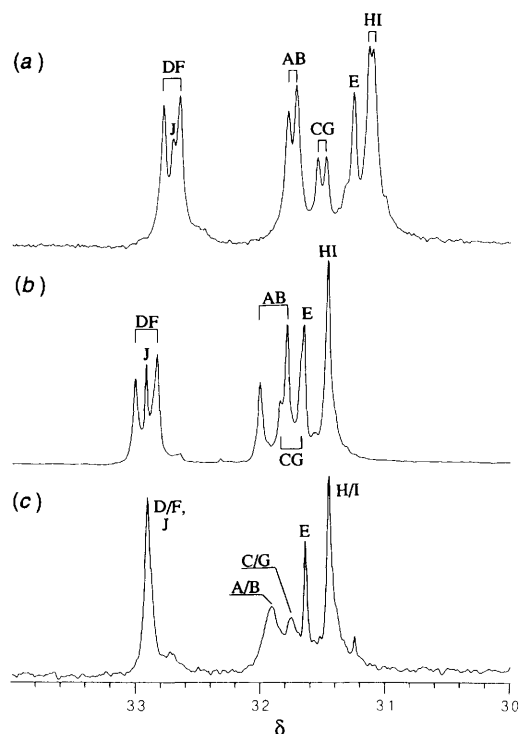


Fig. 5 (a) The  $C_5$   $Ti_{18}O_{45}$  metal-oxygen framework of  $[Ti_{18}O_{28}H][OBu]_{17}$  with titanium atoms represented by small filled circles, oxide and alkoxide oxygen atoms represented by large open circles, and the hydroxide oxygen atom represented by a large shaded circle.<sup>10</sup> One member of each symmetry-equivalent set of alkoxide oxygen atoms is labelled. 125.8 MHz  $^{13}C$  solution FT-NMR spectra at  $20^\circ C$  of (b)  $[Ti_{18}O_{28}H][OBu]_{17}$  and (c)  $[Ti_{18}O_{28}H][OBu]_{12}[OC(OMe)_2]_5$  in the methine carbon chemical shift region

gels prepared using 10 atom %  $^{17}O$ -enriched water displayed a large  $\delta$  517  $OTi_3$  resonance plus a smaller  $\delta$  375  $OTi_4$  resonance having about one third of its integrated intensity. Spectra of gels prepared by hydrolysis of 10 atom %  $^{17}O$ -enriched  $[Ti_{18}O_{28}H][OBu]_{17}$  with 10 atom %  $^{17}O$ -enriched water were quite different, displaying a large  $\delta$  534  $OTi_3$  resonance plus two much smaller resonances at about  $\delta$  710 ( $OTi_2$ ) and  $\delta$  425 ( $OTi_4$ ). These latter resonances each had intensities less than 10% of the  $OTi_3$  resonance, and were difficult to resolve accurately due to overlap with spinning sidebands of the  $OTi_3$  resonance.

The second set of experiments involved repeating the



**Fig. 6** 125.8 MHz  $^{13}\text{C}$  solution NMR spectra of  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}]_{17}$  in toluene solution at (a)  $-70\text{ }^\circ\text{C}$  and (b)  $+20\text{ }^\circ\text{C}$ . The spectrum shown in (c) was recorded at  $20\text{ }^\circ\text{C}$  from a solution of  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}]_{17}$  in toluene containing 0.15 equivalent of  $\text{NEt}_3$

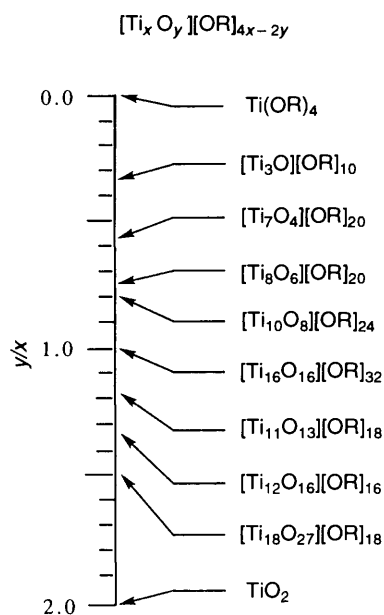
$[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}]_{17}$  sol-gel polymerization just described but with two modifications, the first employing unenriched water but still using enriched polytitanate precursor and the second employing unenriched polytitanate precursor but still using enriched water. The first modification had no measurable effect, *i.e.* the  $^{17}\text{O}$  MAS NMR spectrum was still dominated by a  $\delta$  534  $\text{OTi}_3$  resonance accompanied by small but nonetheless detectable  $\delta$  710  $\text{OTi}_2$  and  $\delta$  425  $\text{OTi}_4$  resonances. The second modification, however, had a dramatic effect in that the  $\delta$  534  $\text{OTi}_3$  resonance lost intensity to the point that no single resonance dominated the spectra, but it proved impossible to determine chemical shift values for the remaining resonances due to phasing problems associated with multiple broad resonances accompanied by multiple spinning sidebands.

## Discussion

The present study brings the number of structurally characterized titanium alkoxide partial hydrolysis products to eight, including  $[\text{Ti}_7\text{O}_4][\text{OEt}]_{20}$ ,<sup>9,11,12</sup>  $[\text{Ti}_{16}\text{O}_{16}][\text{OEt}]_{32}$ ,<sup>12,13</sup>  $[\text{Ti}_8\text{O}_6][\text{OCH}_2\text{Ph}]_{20}$ ,<sup>9</sup>  $[\text{Ti}_{10}\text{O}_8][\text{OEt}]_{24}$ ,<sup>9</sup>  $[\text{Ti}_{11}\text{O}_{13}][\text{OPr}^i]_{18}$ ,<sup>14</sup>  $\alpha_1\text{-}[\text{Ti}_{12}\text{O}_{16}][\text{OPr}^i]_{16}$ ,<sup>14</sup>  $[\text{Ti}_3\text{O}][\text{OMe}][\text{OPr}^i]_9$ ,<sup>15</sup> and the compound  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}]_{17}$ . When arranged as in Fig. 7 according to their degree of condensation,  $y/x$  for  $[\text{Ti}_x\text{O}_y][\text{OR}]_{4x-2y}$  (R = H or alkyl), the  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}]_{17}$  molecule is seen to be the most highly condensed species structurally characterized to date. Since previous studies<sup>15</sup> have shown a correlation between degree of condensation and stability in this series of compounds and since the course of titania sol-gel polymerization parallels the increasing degree of condensation culminating in  $\text{TiO}_2$  as shown in Fig. 7, discussion here will focus on the relationship between  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}]_{17}$  and the other species listed in Fig. 7.

## Synthesis

The complex first formed upon hydrolysis of  $\text{Ti}(\text{OBu})_4$  in *tert*-butyl alcohol at ambient temperature could not be isolated in



**Fig. 7** Formulae of structurally characterized titanium(IV) alkoxide hydrolysis products (R = H or alkyl) arranged in order of their degrees of condensation  $y/x$

pure form, but is proposed to be  $[\text{Ti}_3\text{O}][\text{OBu}]_{10}$ , the *tert*-butoxide analogue of the  $\text{Ti}(\text{OPr}^i)_4$  hydrolysis product  $[\text{Ti}_3\text{O}][\text{OPr}^i]_{10}$ , on the basis of NMR data. This primary hydrolysis product displays an  $\text{OTi}_3$   $^{17}\text{O}$  NMR peak at  $\delta$  547 in *tert*-butyl alcohol solution, a chemical shift value quite close to the  $\delta$  553 value observed for  $[\text{Ti}_3\text{O}][\text{OPr}^i]_{10}$  in propan-2-ol.<sup>15</sup> As in the case of  $[\text{Ti}_3\text{O}][\text{OPr}^i]_{10}$ ,  $^{13}\text{C}\{-^1\text{H}\}$  and  $^1\text{H}$  solution NMR spectra show only one type of alkoxide group, even at  $-40\text{ }^\circ\text{C}$ , even though the  $\text{Ti}_3(\mu_3\text{-OR})(\mu\text{-OR})_3(\text{OR})_6$  structure contains more than one type of alkoxide group.<sup>15</sup> Here, as in the isopropoxide complex, rapid ligand exchange is presumably responsible for the equivalence of the alkoxide ligands on the NMR time-scale.

Oxygen-17 solution NMR provides evidence for only two primary hydrolysis products of  $\text{Ti}(\text{OBu})_4$  in  $\text{Bu}'\text{OH}$  and in toluene- $\text{Bu}'\text{OH}$ :  $[\text{Ti}_3\text{O}][\text{OBu}]_{10}$ , formed at ambient temperature and also after prolonged heating at  $100\text{ }^\circ\text{C}$ , and  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}]_{17}$ , formed only after prolonged heating of the hydrolysis solution. Note, however, that spectra measured under these conditions also display a large, broad  $\text{OTi}_3$  resonance centred at  $\delta$  520–530 that contains most of the total  $^{17}\text{O}$  NMR intensity under all time and temperature conditions after addition of  $\geq 0.2$  equivalent of water to  $\text{Ti}(\text{OBu})_4$  in  $\text{Bu}'\text{OH}$  or toluene- $\text{Bu}'\text{OH}$ . Higher molecular weight polymers are presumed to be responsible for this resonance. This behaviour differs markedly from that of primary alkoxides such as  $\text{Ti}(\text{OEt})_4$ . Hydrolysis of  $\text{Ti}(\text{OEt})_4$  in  $\text{C}_6\text{H}_5\text{Me-EtOH}$  with  $\leq 0.5$  equivalent of  $^{17}\text{O}$ -enriched water yields solutions whose  $^{17}\text{O}$  NMR spectra show several sets of narrow resonances characteristic of low molecular weight primary hydrolysis products, and no intense, broad bands arising from high molecular weight polymers.<sup>9</sup> Presumably, the low molecular weight ethoxide complexes observed, such as  $[\text{Ti}_7\text{O}_4][\text{OEt}]_{20}$  and  $[\text{Ti}_8\text{O}_6][\text{OEt}]_{20}$ , are unstable as *tert*-butoxide complexes due to the steric bulk of the *tert*-butyl groups; the steric crowding well documented between isopropoxy groups in  $[\text{Ti}_3\text{O}][\text{OMe}][\text{OPr}^i]_9$ <sup>15</sup> should be still greater between *tert*-butoxy groups in similar structural environments (see below).

## Structure and stability

The observation of a pentacapped Keggin structure for  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBu}]_{17}$  is not surprising, since Group 5 and 6 polymetalates are known to adopt Keggin structures and

Group 4 polymetalates are known to adopt other structures also observed for Group 5 and 6 complexes:  $[\text{Ti}_7\text{O}_4][\text{OEt}]_{20}$ <sup>9,11,12</sup> has the  $\text{Mo}_7\text{O}_{24}$ <sup>6-16</sup> metal-oxygen framework structure;  $\text{Ti}_4(\text{OEt})_{16}$ <sup>17</sup> and related simple alkoxides<sup>18</sup> have the  $\text{C}_{2v}\text{-W}_4\text{O}_{16}$ <sup>8-19</sup> metal-oxygen framework. Moreover, the  $[\text{Zr}_{13}\text{O}_8][\text{OMe}]_{36}$  structure<sup>20</sup> contains a  $\text{Zr}_{13}\text{O}_{44}$  framework in which a cubic  $\text{ZrO}_8$  unit is encapsulated by a  $\text{Zr}_{12}\text{O}_{36}$  cage having the same structure as the  $\text{M}_{12}\text{O}_{36}$  Keggin cage (see a), but idealized to  $O_h$  symmetry.

The  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$  molecule has a surprisingly regular core structure despite its low symmetry. The distances from the central tetrahedral titanium centre to the 12 peripheral octahedral titanium centres range from 3.490 to 3.581 Å (average 3.557 Å) while the corresponding distances to the five capping trigonal-bipyramidal titanium centres range from 4.054 to 4.082 Å (average 4.068 Å). Very similar average distances are observed in the hexacapped Keggin anion  $[\text{V}_{19}\text{O}_{46}\text{H}_9]^{6-}$ ,<sup>5</sup> but a wider range of distances reflects a less regular structure;  $\text{V}_{\text{tet}} \cdots \text{V}_{\text{oct}}$  distances range from 3.437 to 3.683 Å (average 3.599 Å);  $\text{V}_{\text{tet}} \cdots \text{V}_{\text{tbp}}$  distances range from 3.947 to 4.029 Å (average 4.001 Å).

The observed stability of the  $\text{Ti}_{18}\text{O}_{28}$  core of  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$  towards  $\text{Bu}^t\text{OH}$  is consistent with a trend noted earlier, where the  $\text{Ti}_x\text{O}_y$  core structures of polytitanates  $[\text{Ti}_x\text{O}_y][\text{OR}]_{4x-2y}$  show increasing kinetic stability as the degree of condensation  $y/x$  increases.<sup>15</sup> In reference 15, the possibility was raised that this trend might arise at least in part from steric repulsion, *i.e.* that the greater stability associated with higher degrees of condensation might originate in part from lower degrees of steric repulsion between alkoxide ligands. If true, comparison of the two extreme cases cited in Fig. 7,  $[\text{Ti}_3\text{O}][\text{OR}]_{10}$  and  $[\text{Ti}_{18}\text{O}_{27}][\text{OR}]_{18}$ , should be instructive. In crystalline  $[\text{Ti}_3\text{O}][\text{OMe}][\text{OPr}^i]_9$ , there are eight intramolecular  $\text{C} \cdots \text{C}$  separations less than 4.00 Å, the van der Waals diameter of a methyl group,<sup>21</sup> between the 19 methyl groups on the surface of the molecule. In crystalline  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17} \cdot \text{Bu}^t\text{OH}$ , there are only four intramolecular  $\text{C} \cdots \text{C}$  separations less than 4.00 Å between the 51 alkoxide methyl groups on the surface, and the number of short contacts is bound to be less in the unsolvated molecule. In this case, a higher degree of condensation clearly implies less steric crowding.

### Alkoxide exchange

Alkoxide exchange experiments described in the Results section showed that three of the ten types of *tert*-butoxide groups in  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$  were replaced by 2-methylbutoxide groups upon reaction with excess 2-methylbutan-2-ol. We propose that the three types of alkoxide groups that are exchanged are those groups bonded to five-co-ordinate titanium centres, *i.e.* those labelled Ti(5), Ti(7), Ti(9), Ti(11) and Ti(17) in Fig. 3. Note that since Ti(5) and Ti(7) as well as Ti(9) and Ti(11) are symmetry equivalent, there are only three different types of five-co-ordinate titanium in  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$ . The proposal is based on precedent provided by the  $[\text{Ti}_{11}\text{O}_{13}][\text{OEt}]_5[\text{OPr}^i]_{13}$  and  $\alpha_1\text{-}[\text{Ti}_{12}\text{O}_{16}][\text{OEt}]_6[\text{OPr}^i]_{10}$  molecules, obtained by reaction of ethanol with  $[\text{Ti}_{11}\text{O}_{13}][\text{OPr}^i]_{18}$  and  $\alpha_1\text{-}[\text{Ti}_{12}\text{O}_{16}][\text{OPr}^i]_{16}$ , respectively.<sup>14</sup> In both cases, single-crystal X-ray diffraction studies showed that the compounds contained five- and six-co-ordinate titanium centres, and that alkoxide exchange occurred at the five-, but not at the six-co-ordinate, titanium centres.

Carbon-13 NMR spectroscopy provides further support for selective alkoxide exchange at five-co-ordinate titanium centres. As shown in Fig. 6(a), the  $^{13}\text{C}\text{-}\{^1\text{H}\}$  NMR spectrum of methyl groups in  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$  displays seven intense resonances (E and the DF, AB, and HI pairs), and three other resonances that are about one half as intense (J and the CG pair). Using the alkoxide oxygen labelling scheme of Fig. 5(a), three *tert*-butoxy groups in  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$  lie on its

molecular symmetry plane, namely, those whose oxygens are labelled C, G and J. The remaining 14 *tert*-butoxy groups are present as seven symmetry-equivalent pairs, and the oxygen atom of one group in each pair is labelled, yielding types A, B, D, E, F, H and I. The alkoxide groups co-ordinated to five-co-ordinate titanium are a pair of type D groups, a pair of type F groups, and a unique type J group. Exchange of *tert*-butoxy groups should therefore lead to the loss of two intense resonances and one weak resonance from the spectrum shown in Fig. 6(a). As explained in the Results section, this is precisely the case; the pair of intense resonances labelled DF and the weak resonance J are lost upon alkoxide exchange.

### Proton exchange

The effect on the  $^{13}\text{C}\text{-}\{^1\text{H}\}$  NMR spectrum of methyl groups in  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$  of adding catalytic amounts of triethylamine is shown in Fig. 6(b) and 6(c), and is described in detail in the Results section. We discuss here how this effect can be attributed to rapid proton exchange between doubly bridging oxygen atoms as shown in Fig. 8. Here, the protonated oxygen has been shaded, and the *tert*-butoxide oxygen atoms in the structure at the top of the figure are labelled as in Fig. 5(a). These labels are preserved as proton transfer generates the structure at the bottom of the figure.

Analysis of Fig. 8 shows that proton exchange implies the following site exchange scheme for *tert*-butoxy groups in  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$ : types A and B, C and G, D and F and H and I become equivalent, whereas types E and J do not undergo site exchange. With this information, the spectral simplification observed in Fig. 6(c) can be explained. First, resonances for the three types of *tert*-butoxide groups bonded to five-co-ordinate titanium centres can be assigned, since one type (J) does not undergo site exchange whereas the other two (D and F) become equivalent. Next, the remaining two low-intensity resonances

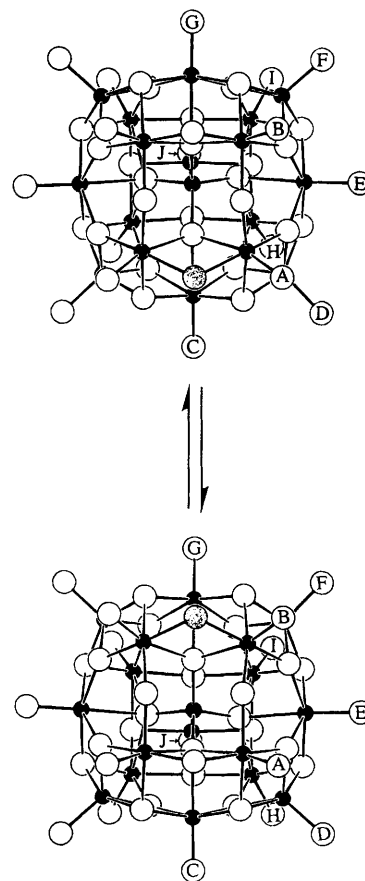


Fig. 8 Site exchange scheme for *tert*-butoxide groups in  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}^t]_{17}$  implied by proton transfer (see text)<sup>10</sup>

assigned to types C and G are seen to coalesce as predicted by Fig. 8. The intense resonance unaffected by proton exchange can then be assigned to type E *tert*-butoxy groups, leaving two pairs of resonances in Fig. 6(a) and 6(b) yet to be assigned to the two remaining pairs of *tert*-butoxy groups that become equivalent under conditions of fast proton exchange (the AB and HI pairs). These have been somewhat arbitrarily assigned in Fig. 6 on the assumption that the chemical shift difference between types A and B *tert*-butyl methyl groups is larger than that between types H and I *tert*-butyl methyl groups since types A and B are closer to the symmetry breaking protonation site.

### Sol-gel polymerization

The  $^{17}\text{O}$  MAS NMR spectra of  $\text{Ti}(\text{OBU})_4$ - and  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}]_{17}$ -derived gels described in the Results section are significantly different, suggesting that the  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}]_{17}$  core structure is sufficiently stable to at least partially retain its identity during sol-gel polymerization. By performing  $[\text{Ti}_{18}\text{O}_{28}\text{H}][\text{OBU}]_{17}$  polymerizations using either  $^{17}\text{O}$ -enriched polytitanate precursor or  $^{17}\text{O}$ -enriched water and comparing  $^{17}\text{O}$  MAS NMR of the resulting xerogels, an effort was made to support this suggestion by identifying two separate sets of oxygens in the titania gels, a set of  $\text{Ti}_{18}\text{O}_{28}$  'core' oxide oxygens and a set of water-derived oxygens that can link the  $\text{Ti}_{18}\text{O}_{28}$  cores together. Although an analogous experiment has been successfully implemented for  $[\text{Ti}_{16}\text{O}_{16}][\text{OEt}]_{32}$ -derived gels,<sup>22</sup> the labelling experiments failed to yield definitive results here (see Results section). Presumably, the small number of water-derived oxygens present in the gels relative to the number of polytitanate core oxide oxygens was at least in part responsible for the failure to observe resonances that could be assigned to water-derived oxygens in the gels.

### Acknowledgements

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