DALTON FULL PAPER

Polynuclear tantalum oxoalkoxides. Crystal structures of $[Ta_8O_{10}(OEt)_{20}]$, $[Ta_7O_9(OPr^i)_{17}]$ and $[Ta_5O_7(OBu^t)_{11}]\cdot C_6H_5Me$ †

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By controlled hydrolysis of the parent pentaalkoxides of tantalum $[Ta(OR)_5$, R = Et, Pr^i or $Bu^t]$ in mixed alcohol–toluene solutions the following crystalline oxoalkoxides were obtained and their structures determined by single crystal X-ray diffraction: $[Ta_8(\mu_3\text{-O})_2(\mu\text{-O})_8(\mu\text{-OEt})_6(OEt)_{14}]$ **1**, $[Ta_7(\mu_3\text{-O})_3(\mu\text{-O})_6(\mu\text{-OPr}^i)_4(OPr^i)_{13}]$ **3** and $[Ta_5(\mu_3\text{-O})_4(\mu\text{-O})_3(\mu\text{-OBu}^t)(OBu^t)_{10}]\cdot C_6H_5Me$ **4**. Each compound contained all of its tantalum atoms in distorted octahedral co-ordination. Using ^{17}O-enriched (10 atom%) water these compounds were obtained with ^{17}O-enriched oxo atoms and their ^{17}O NMR spectra measured in toluene solution and related to their molecular structures. Structural aspects of these tantalum oxoalkoxides are discussed in terms of the steric effects of the alkoxo ligands and π-electron donation of terminal alkoxo ligands.

Structurally, metal oxoalkoxides, $[MO_h(OR)_{(x-2h)}]_m$, are of interest by bridging the transition from the oligomeric metal alkoxides, $[M(OR)_x]_n$, to the macromolecular metal oxides, M_2O_x. As intermediates in the hydrolysis of metal alkoxides they are of special technical significance in the conversion of the metal alkoxide into metal oxide by either the sol–gel process or the MOCVD technique.[1] Our earlier research on the controlled hydrolysis of metal alkoxides[2] was limited to ebulliometric studies in boiling alcohol solutions which provided data on the number average degree of polymerization, m, as a function of the degree of hydrolysis, h (eqn. 1).

$$(m/n)\,[M(OR)_x]_n + mh(H_2O) \longrightarrow [MO_h(OR)_{(x-2h)}]_m + 2mh(ROH) \quad (1)$$

For a number of metals the reciprocal m^{-1} was a linear function of h in the early stages of hydrolysis (before precipitation of insoluble products) and the results were interpreted in terms of structural models related to the molecularity n of the original metal alkoxide. However, in the case of titanium tetraethoxide the readily obtained crystalline product, corresponding to $[Ti_6O_4(OEt)_{16}]$ in the ebulliometric studies,[3] was shown, by X-ray crystallography, to be the heptanuclear molecule, $[Ti_7O_4(OEt)_{20}]$.[4] In recent years Klemperer and co-workers[5] have demonstrated the value of ^{17}O labelling of the oxo-atom in titanium oxoalkoxides using ^{17}O-enriched water in the hydrolysis (eqn. 1) by relating the ^{17}O chemical shifts to the different oxo-environments as deduced from crystal structures.

We have now applied this technique in studies on the hydrolysis of some tantalum pentaalkoxides.

Results and discussion

Hydrolysis of tantalum pentaethoxide $[Ta_2(OEt)_{10}]$

Tantalum pentaethoxide has an edge shared bioctahedral structure with bridging μ-OEt ligands and the earlier ebulliometric studies in boiling ethanol[6] gave results suggesting that the tantalum oxoethoxides conformed approximately to a structural series based on a linear condensation of binuclear units bridged by μ_4- and μ-oxo atoms. We have now isolated a crystalline compound, $[Ta_8(\mu_3\text{-O})_2(\mu\text{-O})_8(\mu\text{-OEt})_6(OEt)_{14}]$ **1**, which has a centrosymmetric structure (Fig. 1) analogous to that previously found for niobium, $[Nb_8O_{10}(OEt)_{20}]$.[7] The degree of hydrolysis h for **1** is 1.25 and for that value m_{obs} in the ebulliometric work was 8.05 ± 0.6. There the similarity ends because the structure of **1** does not conform to the binuclear series. Instead it involves two trinuclear units, $Ta_3(\mu_3\text{-O})(\mu\text{-OEt})_3(OEt)_5$, each linked to two $Ta(\mu\text{-O})_4(OEt)_2$ octahedra by four μ-oxo atoms. All of the tantalums involve distorted octahedral configurations, with six of them bonded to *cis* pairs of terminal ethoxo ligands. The other two tantalums are bonded to single ethoxo ligands and all terminal ligands are *trans* to μ_3- or μ-oxo atoms. There are three different tantalum environments with two metals having one terminal ethoxo *trans*

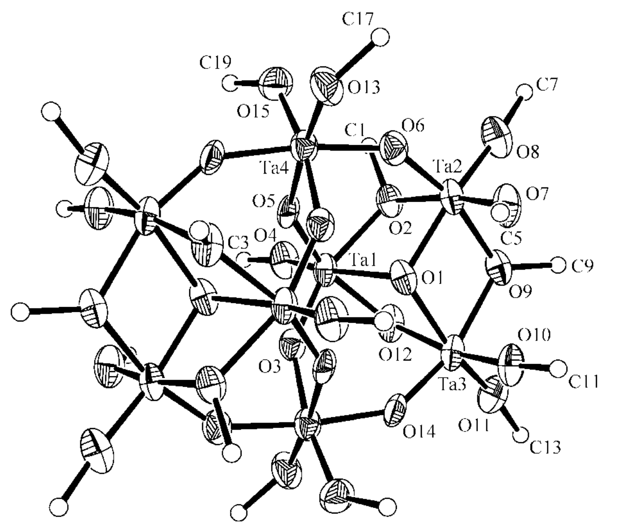

Fig. 1 Structure of compound **1** showing thermal ellipsoids (30% probability) for Ta and O atoms and spheres for C. Hydrogen and terminal carbon atoms are omitted for clarity.

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b001797n/

Table 1 Some bond lenghts (Å) and angles (°) in $[Ta_8(\mu_3\text{-}O)_2(\mu\text{-}O)_8(\mu\text{-}OEt)_6(OEt)_{14}]$ **1**

Ta–O				
Terminal EtO–Ta	Ta(1)–O(4)	1.851(11)	Ta(2)–O(7)	1.891(14)
	Ta(2)–O(8)	1.881(16)	Ta(3)–O(10)	1.875(15)
	Ta(3)–O(11)	1.848(14)	Ta(4)–O(13)	1.858(15)
	Ta(4)–O(15)	1.857(16)		
Bridging EtO	Ta(1)–O(2)	2.174(13)	Ta(1)–O(12)	2.154(13)
	Ta(2)–O(2)	2.074(12)	Ta(2)–O(9)	2.109(15)
	Ta(3)–O(9)	2.166(14)	Ta(3)–O(12)	2.108(12)
Bridging oxo	Ta(1)–O(3)	1.891(13)	Ta(1)–O(5)	1.842(12)
	Ta(2)–O(6)	1.838(14)	Ta(3)–O(14)	1.848(13)
	Ta(4)–O(3)	1.974(13)	Ta(4)–O(5)	2.038(13)
	Ta(4)–O(6)	1.997(13)	Ta(4)–O(14)	1.981(12)
Triple bridging oxo	Ta(1)–O(1)	2.047(11)	Ta(2)–O(1)	2.022(12)
	Ta(3)–O(1)	2.076(13)		
Ta–O–Ta				
μ_3-oxo	Ta(1)–O(1)–Ta(2)	108.5(6)	Ta(2)–O(1)–Ta(3)	112.3(5)
	Ta(1)–O(1)–Ta(3)	107.7(5)		
μ-oxo	Ta(1)–O(3)–Ta(4)	146.5(6)	Ta(1)–O(5)–Ta(4)	143.4(5)
	Ta(2)–O(6)–Ta(4)	144.6(8)	Ta(3)–O(14)–Ta(4)	145.9(7)
μ-OEt	Ta(1)–O(2)–Ta(2)	102.0(5)	Ta(2)–O(9)–Ta(3)	105.5(5)
	Ta(1)–O(12)–Ta(3)	102.8(5)		
Ta–O–C				
Terminal Et–O–Ta	Ta(1)–O(4)–C(3)	166(2)	Ta(2)–O(7)–C(5)	136.5(16)
	Ta(2)–O(8)–C(7)	175(2)	Ta(3)–O(10)–C(11)	175(2)
	Ta(3)–O(11)–C(13)	168(2)	Ta(4)–O(13)–C(17)	133(3)
	Ta(4)–O(15)–C(19)	134(2)		
Bridging Et–O	Ta(1)–O(2)–C(1)	121.6(11)	Ta(2)–O(2)–C(1)	122.1(12)
	Ta(2)–O(9)–C(9)	128.8(14)	Ta(3)–O(9)–C(9)	123.7(15)
	Ta(1)–O(12)–C(15)	125.5(14)	Ta(3)–O(12)–C(15)	131.7(14)

O–Ta–O			
O(1)–Ta(1)–O(4)	155.7(5)	O(2)–Ta(1)–O(3)	161.1(5)
O(5)–Ta(1)–O(12)	162.7(5)	O(1)–Ta(1)–O(2)	71.0(5)
O(1)–Ta(1)–O(3)	92.1(5)	O(1)–Ta(1)–O(5)	93.5(5)
O(1)–Ta(1)–O(12)	71.5(4)	O(2)–Ta(1)–O(4)	90.9(6)
O(2)–Ta(1)–O(5)	87.5(5)	O(2)–Ta(1)–O(12)	79.6(5)
O(3)–Ta(1)–O(4)	102.7(6)	O(3)–Ta(1)–O(5)	102.2(5)
O(3)–Ta(1)–O(12)	87.3(5)	O(4)–Ta(1)–O(5)	102.0(6)
O(4)–Ta(1)–O(12)	89.8(6)		
O(1)–Ta(2)–O(8)	156.2(6)	O(2)–Ta(2)–O(7)	170.5(7)
O(6)–Ta(2)–O(9)	165.3(5)	O(1)–Ta(2)–O(2)	73.6(5)
O(1)–Ta(2)–O(6)	94.0(5)	O(1)–Ta(2)–O(7)	96.9(6)
O(1)–Ta(2)–O(9)	71.5(5)	O(2)–Ta(2)–O(6)	87.3(5)
O(2)–Ta(2)–O(8)	89.8(6)	O(2)–Ta(2)–O(9)	86.4(5)
O(6)–Ta(2)–O(7)	93.0(6)	O(6)–Ta(2)–O(8)	102.3(7)
O(7)–Ta(2)–O(8)	99.4(7)	O(7)–Ta(2)–O(9)	91.1(6)
O(8)–Ta(2)–O(9)	91.0(7)		
O(1)–Ta(3)–O(11)	155.1(6)	O(9)–Ta(3)–O(14)	162.4(5)
O(10)–Ta(3)–O(12)	169.7(7)	O(1)–Ta(3)–O(9)	69.4(5)
O(1)–Ta(3)–O(10)	99.2(6)	O(1)–Ta(3)–O(12)	71.8(5)
O(1)–Ta(3)–O(14)	93.1(5)	O(9)–Ta(3)–O(10)	88.2(7)
O(9)–Ta(3)–O(11)	93.4(6)	O(9)–Ta(3)–O(12)	83.9(6)
O(10)–Ta(3)–O(11)	98.0(7)	O(10)–Ta(3)–O(14)	95.9(7)
O(11)–Ta(3)–O(12)	89.1(6)	O(11)–Ta(3)–O(14)	103.0(7)
O(12)–Ta(3)–O(14)	89.8(5)		
O(3)–Ta(4)–O(15)	169.7(6)	O(5)–Ta(4)–O(13)	175.2(6)
O(6)–Ta(4)–O(14)	172.6(5)	O(3)–Ta(4)–O(5)	84.5(5)
O(3)–Ta(4)–O(6)	91.6(5)	O(3)–Ta(4)–O(13)	92.8(6)
O(3)–Ta(4)–O(14)	83.7(5)	O(5)–Ta(4)–O(6)	84.4(5)
O(5)–Ta(4)–O(14)	89.5(5)	O(5)–Ta(4)–O(15)	89.6(6)
O(6)–Ta(4)–O(13)	91.7(6)	O(6)–Ta(4)–O(15)	96.2(7)
O(13)–Ta(4)–O(14)	94.2(6)	O(13)–Ta(4)–O(15)	93.7(8)
O(14)–Ta(4)–O(15)	87.8(7)		

to a μ_3-oxo, two *cis* μ-oxo and two *cis* μ-ethoxo ligands. Four metals each have a μ_3-oxo *trans* to a terminal ethoxo, one μ-ethoxo *trans* to a terminal ethoxo and the other μ-ethoxo *trans* to a μ-oxo ligand. The two metals bridging the trinuclear units each have two *cis* terminal ethoxo ligands *trans* to μ-oxo ligands and two other *trans* μ-oxo ligands.

Some bond length and bond angle data are presented in Table 1. As expected the Ta–O bond lengths are shorter for terminal ethoxo ligands (av. 1.866 Å) than those to bridging ethoxo ligands (av. 2.131 Å). The μ-oxo bridges are unsymmetrical (av. shorter length, 1.855; av. longer length 1.998 Å) and are generally shorter than the Ta–μ_3-O bond lengths (av.

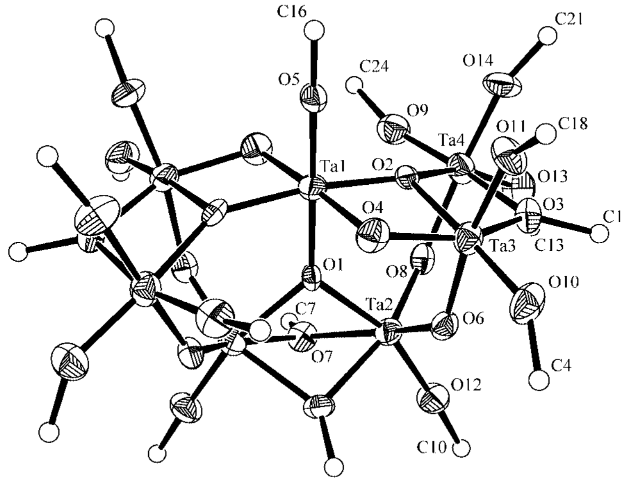

Fig. 2 Structure of compound **3**. Details as in Fig. 1.

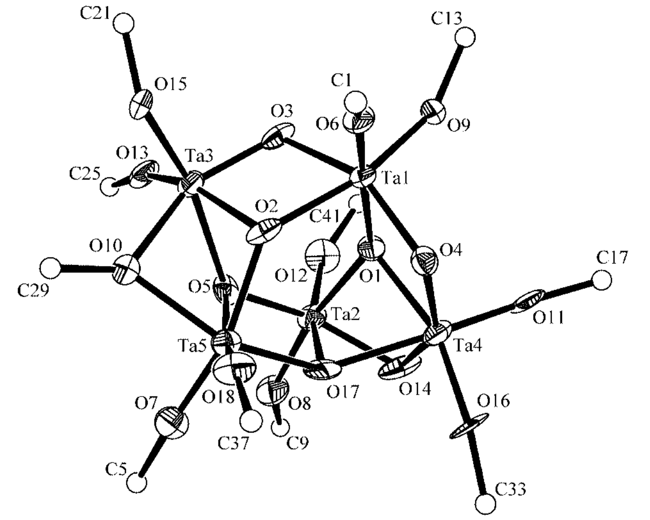

Fig. 3 Structure of compound **4**. Details as in Fig. 1.

2.048 Å). The μ_3-oxo atom, O(1), is pyramidally bonded to three tantalums (av. Ta–O–Ta, 109.5°). The Ta–O bond length averages for the four tantalum sites probably reflect the differences in environments discussed above (Ta(1)–O, av. 1.993; Ta(2)–O, av. 1.969; Ta(3)–O, av. 1.987; Ta(4)–O, av. 1.951 Å). The distorted nature of all of the TaO_6 octahedra is seen in the divergence of the O–Ta–O angles from those of a regular octahedron, 180 (155.1–175.2) and 90° (69.4–103.0°). Also of interest are the wide angles (Ta–O–C; 133–175°) of the terminal ethoxo ligands which suggest significant π-electron donation to the tantalum d orbitals. The preference of π-donating alkoxo ligands to be *cis* rather than *trans* to one another and to be *trans* to μ_3-oxo atoms may well be of significance in generating the observed structure of compound **1**. The ^{17}O-enriched sample of **1** gave three peaks (*δ* 377; 374; 282) in the ^{17}O NMR spectrum in the ratio 3 : 3 : 2. Perusal of the crystal structure of **1** shows the presence of three symmetrically non-equivalent types of oxo atoms, but in a 4 : 4 : 2 ratio. This discrepancy in the oxo atom ratios may indicate some structural differences between the crystalline compound and its solution in toluene. The alternative possibility of selective enrichment of the μ_3-oxo positions relative to the μ-oxo positions seems unlikely.

Hydrolysis of tantalum pentaisopropoxide

Whilst our research was in progress Turova and co-workers[8] reported the isolation of $[Ta_2(\mu\text{-O})(\mu\text{-OPr}^i)(\text{OPr}^i)_7(\text{Pr}^i\text{OH})]$ **2** from either the anodic oxidation of tantalum in Pr^{i}OH or by refluxing a solution of tantalum pentaisopropoxide in boiling Pr^{i}OH. Prolonged storage of Pr^{i}OH solutions led to the formation of the heptanuclear compound $[Ta_7(\mu_3\text{-O})_3(\mu\text{-O})_6(\mu\text{-OPr}^i)_4(\text{OPr}^i)_{13}]$ **3**. The structures of **2** and **3** were determined by X-ray crystallography and the formation of these oxo species was attributed to elimination of ether molecules from the alkoxides although detection of diisopropyl ether was not reported. In attempting to repeat the preparation of **2** by prolonged refluxing of tantalum pentaisopropoxide in Pr^{i}OH solution we found that no reaction occurred and the pentaalkoxide was recovered quantitatively. Presumably **2** and **3** resulted from inadvertent ingress of moisture causing hydrolysis. Furthermore, we found that **3** could be prepared directly by controlled hydrolysis and determined its crystal structure and confirmed its heptanuclear composition (Fig. 2).

The unique tantalum atom in this remarkable structure is linked to three binuclear units by three μ_3- and two μ-oxo atoms. The three binuclear units are in turn linked to one another by two μ-oxo atoms. The terminal isopropoxo ligands are all *trans* to either μ_3- or μ-oxo atoms. Some bond length and angle data are presented in Table 2. The terminal isopropoxo–tantalum bonds are shorter (Ta–O, 1.838–1.905 Å) than the μ-OPr^i bridges (Ta–O, 2.083–2.179 Å), whilst the Ta–O–C angles of the terminal groups bonded to the unique Ta(1) are linear and the other angles are also wide (Ta–O–C, 141.0–175.9°) suggesting significant π-electron donation to the vacant tantalum d orbitals. The μ_3-oxo atom bridging the isosceles triangle of Ta(1), Ta(2), Ta(2′) is in a trigonal planar configuration whereas the other μ_3-oxo atoms linking Ta(1) to Ta(3) and Ta(4) are slightly out of the plane of the three metals. The distortions from the regular octahedral configurations for the TaO_6 units are evident in the data on the O–Ta–O angles (wide angles: 146.6–180.0; small angles: 69.8–107.0°). Interestingly the ^{17}O NMR spectrum of **3** in toluene solution gave four peaks (*δ* 470.4, 452.1, 442.0, 301.5) in the ratio 2 : 2 : 2 : 3, consistent with the structure containing three pairs of distinguishable μ-oxo atoms and three μ_3-oxo atoms. By symmetry the μ_3-O(1) atom is non-equivalent to the two equivalent μ_3-O(2) atoms, but the linewidth precluded resolution into two peaks.

Hydrolysis of tantalum penta*tert*-butoxide

Whereas normal alkoxides of tantalum are binuclear $[Ta_2(\mu\text{-OR})_2(\text{OR})_8]$ with octahedral tantalum and the isopropoxide shows a dimer–monomer equilibrium, the penta*tert*-butoxide is monomeric due to the steric hindrance of the bulky *tert*-butoxo groups[9] and it was therefore of interest to explore its hydrolysis. Controlled hydrolysis in a toluene–Bu^{t}OH solvent led to isolation of the crystalline $[Ta_5(\mu_3\text{-O})_4(\mu\text{-O})_3(\mu\text{-OBu}^t)(\text{OBu}^t)_{10}]\cdot C_6H_5Me$ **4**. It is evident from the analytical results that the bulk sample was only partially solvated, with values lying between the calculated ones for the solvated and non-solvated formulae. The molecular structure (Fig. 3) shows a very compact $[Ta_5(\mu_3\text{-O})_4(\mu\text{-O})_3(\mu\text{-OBu}^t)]$ core in which all of the octahedrally co-ordinated tantalums are non-equivalent, but each one is bonded to two terminal Bu^{t}O ligands which are in the *cis* configuration. Some relevant bond length and bond angle data are given in Table 3. The terminal Bu^{t}O ligands (Ta–O, 1.813–1.905; av. 1.865 Å) subtend wide angles at oxygen (Ta–O–C, 144–168.3°) suggesting ligand to metal π-electron donation. The configurations about the μ_3-oxo ligands are distorted T shaped, with one wide Ta–O–Ta angle (140.7, 134.2, 131.9, 143.7°) one intermediate angle (100.7, 101.1, 109.0, 101.5°) and a third smaller angle (92.9, 96.9, 90.9, 81.6° for O(1), O(2), O(5) and O(17) respectively). The sums of the three angles (334.3, 332.2, 331.8, 326.8°) show substantial deviations from planarity at the μ_3-oxo atoms. Two of the μ-oxo bridges are also unsymmetrical (O(3) and O(14)), whereas the third μ-oxo atom and the bridging μ-OBu^t are close to symmetrical. The distorted nature of each TaO_6 unit is seen in the O–Ta–O bond angles (wide angles: 141.2–170.0; small angles: 71.3–109.1°). It is also evidenced in

Table 2 Some bond lengths (Å) and angles (°) in $[Ta_7(\mu_3\text{-}O)_3(\mu\text{-}O)_6(\mu\text{-}OPr^i)_4(OPr^i)_{13}]$ **3**

Ta–O				
Terminal Pr^iO–Ta	Ta(1)–O(5)	1.880(15)	Ta(2)–O(12)	1.866(12)
	Ta(3)–O(10)	1.886(13)	Ta(3)–O(11)	1.892(11)
	Ta(4)–O(9)	1.838(13)	Ta(4)–O(13)	1.874(15)
	Ta(4)–O(14)	1.905(12)		
Bridging Pr^iO	Ta(2)–O(7)	2.143(11)	Ta(2′)–O(7)	2.145(12)
	Ta(3)–O(3)	2.083(12)	Ta(4)–O(3)	2.179(11)
Bridging oxo	Ta(1)–O(4)	1.972(11)	Ta(3)–O(4)	1.897(12)
	Ta(2)–O(6)	1.863(11)	Ta(3)–O(6)	2.020(11)
	Ta(2)–O(8)	1.845(12)	Ta(4)–O(8)	2.019(12)
Triple bridging oxo	Ta(1)–O(1)	2.007(14)	Ta(2)–O(1)	2.092(9)
	Ta(2′)–O(1)	2.092(9)	Ta(1)–O(2)	1.955(10)
	Ta(3)–O(2)	2.118(9)	Ta(4)–O(2)	2.100(11)
Ta–O–Ta				
μ_3-oxo	Ta(1)–O(1)–Ta(2)	131.8(3) × 2	Ta(2)–O(1)–Ta(2′)	96.4(6)
	Ta(1)–O(2)–Ta(3)	99.7(4)	Ta(1)–O(2)–Ta(4)	145.5(5)
	Ta(3)–O(2)–Ta(4)	109.2(4)		
μ-oxo	Ta(1)–O(4)–Ta(3)	107.2(5)	Ta(2)–O(6)–Ta(3)	129.3(5)
	Ta(2)–O(8)–Ta(4)	138.6(6)		
μ-OPr^i	Ta(2)–O(7)–Ta(2′)	93.3(4)	Ta(3)–O(3)–Ta(4)	107.6(5)
Ta–O–C				
Terminal Pr^i–O–Ta	Ta(1)–O(5)–C(16)	180.0(−)	Ta(2)–O(12)–C(10)	175.9(18)
	Ta(3)–O(10)–C(4)	145.1(14)	Ta(3)–O(11)–C(18)	141.0(16)
	Ta(4)–O(9)–C(24)	164(2)	Ta(4)–O(13)–C(13)	145.9(18)
	Ta(4)–O(14)–C(21)	162.0(17)		
O–Ta–O				
	O(1)–Ta(1)–O(5)	180.0(−)	O(2)–Ta(1)–O(2′)	170.4(5)
	O(4)–Ta(1)–O(4′)	175.9(7)	O(1)–Ta(1)–O(2)	85.2(3) × 2
	O(1)–Ta(1)–O(4)	87.9(3) × 2	O(2)–Ta(1)–O(4)	102.3(5) × 2
	O(2)–Ta(1)–O(4′)	77.3(5) × 2	O(2)–Ta(1)–O(5)	94.8(3) × 2
	O(4)–Ta(1)–O(5)	92.1(3) × 2		
	O(1)–Ta(2)–O(12)	161.7(5)	O(6)–Ta(2)–O(7)	159.2(5)
	O(7′)–Ta(2)–O(8)	162.8(4)	O(1)–Ta(2)–O(6)	88.6(4)
	O(1)–Ta(2)–O(7)	73.2(4) × 2	O(1)–Ta(2)–O(8)	95.2(4)
	O(6)–Ta(2)–O(7′)	95.6(4)	O(6)–Ta(2)–O(8)	96.7(5)
	O(6)–Ta(2)–O(12)	100.0(5)	O(7)–Ta(2)–O(7′)	69.8(5)
	O(7)–Ta(2)–O(8)	95.0(5)	O(7)–Ta(2)–O(12)	94.9(5)
	O(7′)–Ta(2)–O(12)	89.8(5)	O(8)–Ta(2)–O(12)	99.7(5)
	O(2)–Ta(3)–O(10)	174.7(5)	O(3)–Ta(3)–O(4)	146.6(4)
	O(6)–Ta(3)–O(11)	170.2(5)	O(2)–Ta(3)–O(3)	71.9(4)
	O(2)–Ta(3)–O(4)	75.1(4)	O(2)–Ta(3)–O(6)	90.4(4)
	O(2)–Ta(3)–O(11)	95.0(5)	O(3)–Ta(3)–O(6)	82.9(5)
	O(3)–Ta(3)–O(10)	105.5(5)	O(3)–Ta(3)–O(11)	91.1(5)
	O(4)–Ta(3)–O(6)	92.4(5)	O(4)–Ta(3)–O(10)	107.0(6)
	O(4)–Ta(3)–O(11)	96.9(5)	O(6)–Ta(3)–O(10)	84.6(5)
	O(10)–Ta(3)–O(11)	89.7(6)		
	O(2)–Ta(4)–O(13)	159.5(5)	O(3)–Ta(4)–O(9)	165.3(5)
	O(8)–Ta(4)–O(14)	172.9(5)	O(2)–Ta(4)–O(3)	70.3(4)
	O(2)–Ta(4)–O(8)	82.0(4)	O(2)–Ta(4)–O(9)	95.0(5)
	O(2)–Ta(4)–O(14)	93.7(5)	O(3)–Ta(4)–O(8)	86.9(4)
	O(3)–Ta(4)–O(13)	92.0(5)	O(3)–Ta(4)–O(14)	86.4(5)
	O(8)–Ta(4)–O(9)	92.5(5)	O(8)–Ta(4)–O(13)	86.8(6)
	O(9)–Ta(4)–O(13)	102.7(6)	O(9)–Ta(4)–O(14)	93.5(5)
	O(13)–Ta(4)–O(14)	95.6(7)		

the case of Ta(2) where the distance to O(17) at 2.40(2) Å is significantly longer than the other Ta–O bonds.

A sample of compound **4** obtained by hydrolysis with ^{17}O-enriched water gave an ^{17}O NMR spectrum in toluene solution exhibiting six peaks (δ 470.7, 454.1, 435.1, 421.1, 314.7, 290.7) with the ratios 1 : 1 : 1 : 1 : 1 : 2, whereas on the grounds of lack of symmetry a seven line spectrum would have been predicted indicating accidental degeneracy in the δ 290.7 peak. Similarly an eleven line ^1H NMR spectrum might have been expected but the complex spectrum showed eight peaks over the range δ_H 1.86–1.49.

It is evident that replacement of *tert*-butoxo ligands in the 5-co-ordinated $Ta(OBu^t)_5$ by smaller μ-oxo atoms has allowed the tantalum to achieve distorted octahedral co-ordination in the highly condensed molecule **4**.

In comparing the three crystalline oxoalkoxides $[Ta_8(\mu_3\text{-}O)_2(\mu\text{-}O)_8(\mu\text{-}OEt)_6(OEt)_{14}]$ **1**, $[Ta_7(\mu_3\text{-}O)_3(\mu\text{-}O)_6(\mu\text{-}OPr^i)_4(OPr^i)_{13}]$ **3** and $[Ta_5(\mu_3\text{-}O)_4(\mu\text{-}O)_3(\mu\text{-}OBu^t)(OBu^t)_{10}]\cdot C_6H_5Me$ **4** reported here it is noteworthy in Table 4 that on progressing from the less bulky ethoxide ligand to the more bulky *tert*-butoxide (*i.e.* from **1** to **3** to **4**) there is an increase in the degree of hydrolysis *h* (1.25, 1.285, 1.40), an increase in the ratio of μ_3-oxo : Ta (0.25, 0.43, 0.80), a decrease in the ratio of μ-oxo atoms (1.0, 0.86, 0.60), a marked decrease in the ratio of bridging alkoxo groups (0.75, 0.57, 0.20), a slight increase in the ratio of terminal alkoxo ligands : Ta (1.75, 1.86, 2.00) and a decrease

Table 3 Some bond lengths (Å) and angles (°) in $[Ta_5(\mu_3\text{-}O)_4(\mu\text{-}O)_3(\mu\text{-}OBu^t)(OBu^t)_{10}]\cdot C_6H_5Me$ **4**

Ta–O				
Terminal Bu^{t}O–Ta	Ta(1)–O(6)	1.866(14)	Ta(1)–O(9)	1.865(15)
	Ta(2)–O(8)	1.893(18)	Ta(2)–O(12)	1.905(19)
	Ta(3)–O(13)	1.856(17)	Ta(3)–O(15)	1.900(15)
	Ta(4)–O(11)	1.840(18)	Ta(4)–O(16)	1.884(16)
	Ta(5)–O(7)	1.813(18)	Ta(5)–O(18)	1.832(18)
Bridging Bu^{t}O	Ta(3)–O(10)	2.151(17)	Ta(5)–O(10)	2.172(15)
Bridging oxo	Ta(1)–O(4)	1.940(15)	Ta(1)–O(3)	2.026(15)
	Ta(2)–O(14)	1.906(17)	Ta(3)–O(3)	1.819(18)
	Ta(4)–O(4)	1.923(14)	Ta(4)–O(14)	1.993(16)
Triple bridging oxo	Ta(1)–O(1)	2.028(13)	Ta(1)–O(2)	2.049(17)
	Ta(2)–O(1)	2.034(14)	Ta(2)–O(5)	1.960(14)
	Ta(2)–O(17)	2.40(2)	Ta(3)–O(2)	2.076(15)
	Ta(3)–O(5)	2.186(15)	Ta(4)–O(1)	2.103(15)
	Ta(4)–O(17)	2.18(2)	Ta(5)–O(2)	2.060(16)
	Ta(5)–O(5)	2.158(17)	Ta(5)–O(17)	1.911(18)
Ta–O–Ta				
μ_3-oxo	Ta(1)–O(1)–Ta(2)	140.7(8)	Ta(1)–O(1)–Ta(4)	100.7(6)
	Ta(2)–O(1)–Ta(4)	92.9(6)	Ta(1)–O(2)–Ta(3)	101.1(6)
	Ta(1)–O(2)–Ta(5)	134.2(7)	Ta(3)–O(2)–Ta(5)	96.9(7)
	Ta(2)–O(5)–Ta(3)	131.9(8)	Ta(2)–O(5)–Ta(5)	109.0(7)
	Ta(3)–O(5)–Ta(5)	90.9(5)	Ta(2)–O(17)–Ta(4)	81.6(7)
	Ta(2)–O(17)–Ta(5)	101.5(9)	Ta(4)–O(17)–Ta(5)	143.7(8)
μ-oxo	Ta(1)–O(3)–Ta(3)	111.7(8)	Ta(1)–O(4)–Ta(4)	110.9(7)
	Ta(2)–O(14)–Ta(4)	100.6(7)		
μ-OBu^t	Ta(3)–O(10)–Ta(5)	91.4(6)		
Ta–O–C				
Terminal Bu^t–O–Ta	Ta(1)–O(6)–C(1)	158.7(15)	Ta(1)–O(9)–C(13)	151.9(14)
	Ta(2)–O(8)–C(9)	144(2)	Ta(2)–O(12)–C(41)	150.0(17)
	Ta(3)–O(13)–C(25)	165.1(16)	Ta(3)–O(15)–C(21)	144.9(16)
	Ta(4)–O(11)–C(17)	161.1(19)	Ta(4)–O(16)–C(33)	152.5(19)
	Ta(5)–O(7)–C(5)	168.3(18)	Ta(5)–O(18)–C(37)	157.9(18)

O–Ta–O			
O(1)–Ta(1)–O(6)	170.0(7)	O(2)–Ta(1)–O(9)	165.5(6)
O(3)–Ta(1)–O(4)	151.9(6)	O(1)–Ta(1)–O(2)	88.6(6)
O(1)–Ta(1)–O(3)	83.1(6)	O(1)–Ta(1)–O(4)	74.9(6)
O(1)–Ta(1)–O(9)	92.5(6)	O(2)–Ta(2)–O(3)	71.7(6)
O(2)–Ta(1)–O(4)	90.2(6)	O(2)–Ta(1)–O(6)	88.0(6)
O(3)–Ta(1)–O(6)	104.7(6)	O(3)–Ta(1)–O(9)	94.1(7)
O(4)–Ta(1)–O(6)	95.7(6)	O(4)–Ta(1)–O(9)	104.0(6)
O(6)–Ta(1)–O(9)	93.2(7)		
O(1)–Ta(2)–O(8)	169.6(7)	O(5)–Ta(2)–O(14)	141.2(7)
O(12)–Ta(2)–O(17)	160.1(7)	O(1)–Ta(2)–O(5)	88.4(6)
O(1)–Ta(2)–O(12)	88.8(7)	O(1)–Ta(2)–O(14)	77.9(6)
O(1)–Ta(2)–O(17)	71.3(6)	O(5)–Ta(2)–O(8)	98.3(7)
O(5)–Ta(2)–O(12)	109.1(8)	O(5)–Ta(2)–O(17)	71.2(7)
O(8)–Ta(2)–O(12)	96.4(8)	O(8)–Ta(2)–O(14)	92.0(7)
O(8)–Ta(2)–O(17)	103.2(7)	O(12)–Ta(2)–O(14)	106.7(8)
O(14)–Ta(2)–O(17)	70.0(7)		
O(2)–Ta(3)–O(13)	158.1(6)	O(3)–Ta(3)–O(10)	148.7(6)
O(5)–Ta(3)–O(15)	164.0(7)	O(2)–Ta(3)–O(3)	75.3(6)
O(2)–Ta(3)–O(5)	72.8(6)	O(2)–Ta(3)–O(10)	73.4(6)
O(2)–Ta(3)–O(15)	103.0(6)	O(3)–Ta(3)–O(5)	97.1(6)
O(3)–Ta(3)–O(13)	104.7(7)	O(3)–Ta(3)–O(15)	96.6(7)
O(5)–Ta(3)–O(10)	72.7(6)	O(5)–Ta(3)–O(13)	85.6(6)
O(10)–Ta(3)–O(13)	103.9(7)	O(10)–Ta(3)–O(15)	91.4(7)
O(13)–Ta(3)–O(15)	98.8(7)		
O(1)–Ta(4)–O(16)	161.9(7)	O(4)–Ta(4)–O(14)	146.0(6)
O(11)–Ta(4)–O(17)	169.7(9)	O(1)–Ta(4)–O(4)	73.5(6)
O(1)–Ta(4)–O(11)	99.3(6)	O(1)–Ta(4)–O(14)	74.4(6)
O(1)–Ta(4)–O(17)	74.9(7)	O(4)–Ta(4)–O(16)	106.5(7)
O(4)–Ta(4)–O(11)	99.0(7)	O(4)–Ta(4)–O(17)	87.5(6)
O(11)–Ta(4)–O(14)	96.7(9)	O(11)–Ta(4)–O(16)	98.6(8)
O(14)–Ta(4)–O(16)	100.6(7)	O(14)–Ta(4)–O(17)	73.7(8)
O(16)–Ta(4)–O(17)	87.0(8)		
O(2)–Ta(5)–O(7)	162.1(7)	O(5)–Ta(5)–O(18)	166.3(7)
O(10)–Ta(5)–O(17)	149.4(8)	O(2)–Ta(5)–O(5)	73.7(6)
O(2)–Ta(5)–O(10)	73.3(6)	O(2)–Ta(5)–O(17)	90.3(6)
O(2)–Ta(5)–O(18)	92.6(7)	O(5)–Ta(5)–O(7)	93.7(6)
O(5)–Ta(5)–O(10)	72.8(6)	O(5)–Ta(5)–O(17)	78.0(8)
O(7)–Ta(5)–O(10)	91.1(7)	O(7)–Ta(5)–O(17)	99.6(7)
O(7)–Ta(5)–O(18)	99.6(8)	O(10)–Ta(5)–O(18)	103.4(7)
O(17)–Ta(5)–O(18)	103.0(9)		

Table 4 Ligand to tantalum ratios in the crystalline tantalum oxoalkoxides $[TaO_h(OR)_{(5-2h)}]_m$

Compound	*h*	*m*	μ$_3$-O : Ta	μ-O : Ta	μ-OR : Ta	term.-OR : Ta
$[Ta_8O_{10}(OEt)_{20}]$ **1**	1.25	8	0.25 : 1	1.00 : 1	0.75 : 1	1.75 : 1
$[Ta_7O_9(OPr^i)_{17}]$ **3**	1.285	7	0.43 : 1	0.86 : 1	0.57 : 1	1.86 : 1
$[Ta_5O_7(OBu^t)_{11}]$ **4**	1.40	5	0.80 : 1	0.60 : 1	0.20 : 1	2.00 : 1

(a)

(b)

(c)

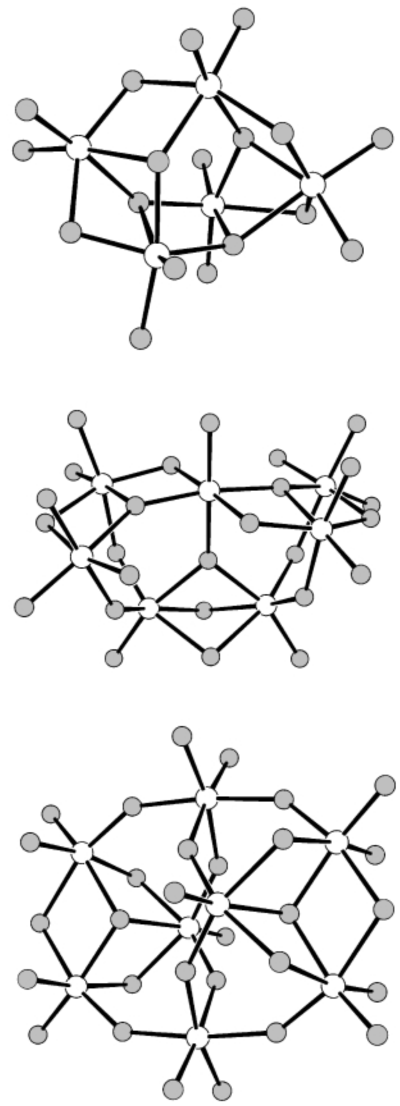

Fig. 4 Polynuclear core structures showing (a) Ta_5O_{18} of **4**, (b) Ta_7O_{26} of **3** and (c) Ta_8O_{30} of **1**. Open and shaded circles represent Ta and O atoms respectively.

in the nuclearity (8, 7, 5) of the molecule. It is also of interest that neither hydroxo ligands nor co-ordinated alcohols are present in these molecules although the interesting binuclear compound $[Ta_2(\mu\text{-O})(\mu\text{-OPr}^i)(OPr^i)_7(Pr^iOH)]$ **2** obtained by Turova and co-workers[8] contains one Pr^iOH ligand hydrogen bonded to an adjacent terminal isopropoxo ligand. A common structural feature of compounds **1**, **3** and **4** is the presence of terminal $Ta(OR)_2$ groups in the *cis* configuration with wide Ta–O–C angles, implying significant oxygen to tantalum π-electron donation. The tantalum–oxygen cores are summarised in Fig. 4. Those of both **1** and **3** have point group symmetry C_2 while that of **4** is asymmetric with point group C_1.

Experimental

All manipulations were carried out under dry nitrogen using Schlenk/vacuum line techniques and a controlled atmosphere glove box. The tantalum pentaalkoxides were prepared by reaction of $TaCl_5$ and the appropriate alcohol with an excess of ammonia together, in the case of the *tert*-butoxide, with pyridine,[10] and purified by distillation *in vacuo*.

^1H NMR spectra in C_6D_6 solutions were obtained using Bruker WM 250 or WH 400 FT spectrometers and referenced to TMS, ^{17}O NMR on enriched ^{17}O-oxo (10 atom%) compounds at 33.9 MHz in mixed solvent ($C_6D_5CD_3$–C_6H_5Me; 1 : 2 ratio) and referenced to D_2O at room temperature. Estimated uncertainty on ^{17}O integrations is 15%. Infrared spectra (Nujol mulls) in the 4000–200 cm^{-1} range were obtained with a Perkin-Elmer FT 1720 spectrophotometer.

The C and H analyses were obtained commercially from either Butterworth Microanalytical Labs. or University College, London and Ta was determined gravimetrically as Ta_2O_5.

Crystal structures of compounds 1, 3 and 4

Single crystals were grown from toluene solutions and mounted and sealed under dry N_2 in Lindemann tubes. Data collection and structure refinement parameters are given in Table 5. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) with ω–2θ scans. Owing to rapid sample decomposition, data for compounds **1** and **4** were collected on two and three similar sized crystals respectively. Data for **3** were initially corrected for absorption by empirical methods (Ψ scan).[11] The structures were solved by Patterson methods using the SHELXS 97 program[12] and developed by Fourier difference techniques with subsequent refinement on F^2 by full matrix least squares using SHELXL 97.[12] Initial refinements of **1** and **4** were carried out using individual batch scale factors with no merging of equivalent reflections. In the final stages of refinement, data were corrected for absorption against a refined isotropic model with the program DIFABS.[13] In all cases merging of equivalent reflections was carried out after absorption correction. The H atoms were calculated geometrically and isotropic thermal parameters refined with a riding model. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Molecular graphics were obtained using ORTEP 3.[14] WINGX[15] was used to prepare material for publication.

CCDC reference number 186/2067.

See http://www.rsc.org/suppdata/dt/b0/b001797n/ for crystallographic files in .cif format.

Hydrolyses

$Ta_2(OEt)_{10}$. Ethanol (15 cm^3) containing water (0.16 cm^3) was slowly added dropwise to a solution of $Ta_2(OEt)_{10}$ (7.0 g) in a mixture of ethanol (50 cm^3) and toluene (20 cm^3) at room temperature and left for 1 week when it was shown by NMR that hydrolysis was incomplete. More aqueous ethanol was gradually added until $h = 1.25$ (mol H_2O per Ta atom) was reached and the solution kept at room temperature for 10 days. The volume was then reduced to 30 cm^3 by vacuum evaporation and the solution cooled to −20 °C to cause deposition of colourless crystals (1.08 g; mp 245–247 °C) of **1**. Recrystallisation from ethanol gave X-ray quality crystals (Found: C, 19.15; H, 4.02; Ta, 57.28. $C_{20}H_{50}O_{15}Ta_4$ requires: C, 19.15; H, 4.02; Ta, 57.70%). ^1H NMR (C_6D_6): δ 1.31, 1.45, 1.50, 1.56, 1.60 (t, CH_3); 4.49, 4.65, 4.73, overlapping 4.88–5.02, 5.16, 5.20 (q, CH_2). IR: 1261w, 1159s, 1121s, 1073s, 1054s, 918m, 901w, 862s, 819s, 747s, 550s, 483m, 389w, 302w and 275w cm^{-1}. The preparation was repeated using ^{17}O-enriched (10 atom%) water to label the oxo

Table 5 Crystal data and structure refinement for $[Ta_8O_{10}(OEt)_{20}]$ **1**, $[Ta_7O_9(OPr^i)_{17}]$ **3** and $[Ta_5O_7(OBu^t)_{11}]\cdot C_6H_5Me$ **4**

	1	**3**	**4**
Formula	$C_{40}H_{100}O_{30}Ta_8$	$C_{51}H_{119}O_{26}Ta_7$	$C_{44}H_{99}O_{18}Ta_5\cdot C_7H_8$
M	2508.80	2415.11	1913.12
T/K	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$C2/c$	$P\bar{1}$
a/Å	16.956(2)	21.847(9)	12.421(3)
b/Å	14.131(1)	13.626(5)	12.854(2)
c/Å	14.927(2)	27.917(9)	22.921(4)
α/°			78.78(9)
β/°	90.09(1)	98.56(6)	79.79(2)
γ/°			80.63(3)
U/Å^3	3576.6(7)	8218.0(53)	3501.4(12)
Z	2	4	2
μ(Mo-Kα)/mm^{-1}	12.252	9.341	7.839
Reflections collected	6535	7433	12901
Independent reflections	6277	7228	12284
R_{int}	0.0534	0.0341	0.0727
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0688, 0.1799	0.0643, 0.1409	0.0876, 0.2345
(all data)	0.1150, 0.2045	0.1425, 0.1584	0.1546, 0.2645

atoms and the product submitted to ^{17}O NMR spectroscopy ($C_6D_5CD_3$–toluene, 1:2 ratio): δ 377.5 ($\omega_{1/2}$ 68), 373.6 (68) and 282.2 (102 Hz) in ratio 3:3:2.

$Ta_2(OPr^i)_{10}$/$Ta(OPr^i)_5$. Isopropyl alcohol (40 cm^3) containing water (0.04 cm^3) was slowly added dropwise to a solution of tantalum pentaisopropoxide (1.90 g) in a mixture of Pr^{i}OH (40 cm^3) and toluene (40 cm^3), corresponding to $h = 0.5$ (mol H_2O per Ta atom), and left at room temperature for 1 week. The solution was then evaporated *in vacuo* and the residue crystallised from Pr^{i}OH (20 cm^3) giving colourless crystals (0.71 g, mp 209–213 °C) of compound **3**. Repetition of the hydrolysis with a higher h value (1.0) gave the same product (Found: C, 24.04; H, 4.55; Ta, 51.96. $C_{51}H_{119}O_{26}Ta_7$ requires: C, 25.36; H, 4.97; Ta, 52.45%). ^{1}H NMR (solvent C_6D_6): several overlapping doublets δ 1.39–1.58, and at 1.66, 1.72, 1.77, 1.80, 1.86 (d, CH_3); 4.85, 5.04, 5.22 overlapping 5.31–5.64 (sept, CH). IR: 1363m, 1355w, 1261w, 1168s, 1129s, 1016s, 999s, 954w, 851m, 808s, 734s, 631m, 586s, 525w, 462m, 372w, 329w and 296w cm^{-1}. A ^{17}O-labelled compound was obtained as above using ^{17}O-enriched (10 atom%) water and its ^{17}O NMR spectrum obtained ($C_6D_5CD_3$–toluene, 1:2 ratio): δ 470.4 ($\omega_{1/2}$ 68), 452.1 (68), 442.0 (68) and 301.5 (170 Hz) in the ratio 2:2:2:3.

$Ta(OBu^t)_5$. $Ta(OBu^t)_5$ (4.45 g) dissolved in a mixture of Bu^{t}OH (35 cm^3) and toluene (35 cm^3) was treated very gradually with water (0.16 cm^3, corresponding to $h = 1.0$) over a period of 2 weeks at room temperature. After removal of volatiles *in vacuo* the residue was dissolved in warm toluene (5 cm^3) and left to deposit colourless crystals (0.84 g, mp 235 °C decomp.) of compound **4**. Recrystallisation from toluene gave X-ray quality crystals (Found: C, 28.98; H, 5.51; Ta, 47.86. $C_{44}H_{99}O_{18}Ta_5$ requires: C, 29.02; H, 5.48; Ta, 49.68%. $C_{51}H_{107}O_{18}Ta_5$ requires: C, 32.02; H, 5.64; Ta, 47.29%). ^{1}H NMR (C_6D_6): complex spectrum δ 1.49–1.86; main peaks 1.59, 1.62, 1.63, 1.67, 1.68, 1.71, 1.73 and 1.81 (s, CH_3). IR: 1362s, 1261w, 1237m, 1193s, 1024s, 998s, 896w, 792m, 734s, 690m, 636m, 553s, 486m, 386w and 282w cm^{-1}. A ^{17}O-labelled compound was obtained as above using ^{17}O-enriched (10 atom%) water and its ^{17}O NMR spectrum obtained ($C_6D_5CD_3$–toluene 1:2 ratio): δ 470.7 ($\omega_{1/2}$ 68), 454.1 (85), 435.1 (68), 421.1 (68), 314.7 (170) and 290.7 (102 Hz) in the ratio 1:1:1:1:1:2.

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