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# Synthesis and X-ray single crystal study of the bi- and trimetallic alkoxides of molybdenum(VI) and tantalum, $\text{Mo}_2\text{Ta}_4\text{O}_8(\text{OMe})_{16}$ , $\text{Mo}_4\text{Ta}_4\text{O}_{16}(\text{O}^i\text{Pr})_{12}$ and $\text{LiMo}_4\text{Ta}_3\text{O}_{14}(\text{O}^i\text{Pr})_9(\text{OC}_2\text{H}_4\text{OMe})_3$

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## Abstract

The partial hydrolysis of a mixture of molybdenum and tantalum methoxides (Mo:Ta = 1:2) with stoichiometric amounts of water yields a new bimetallic complex  $\text{Mo}_2\text{Ta}_4\text{O}_8(\text{OMe})_{16}$  (**I**) on crystallization from toluene. The molecules of **I** appear to be a combination of two  $\text{MoO}(\text{O}^i\text{Pr})_2$  units with the earlier described  $\text{Ta}_4\text{O}_4(\text{O}^i\text{Pr})_{12}$  core. The thermal reduction of a mixture of  $\text{MoO}(\text{O}^i\text{Pr})_4$  and  $\text{Ta}_2(\text{O}^i\text{Pr})_{10}$  (in a 1:1 Mo:Ta ratio) followed by oxidation of the products by dry oxygen, provides access to  $\text{Mo}_4\text{Ta}_4\text{O}_{16}(\text{O}^i\text{Pr})_{12}$  (**II**). The same procedure, using  $\text{LiMo}_2\text{O}_4(\text{O}^i\text{Pr})_4(\text{OC}_2\text{H}_4\text{OMe})$  instead of  $\text{MoO}(\text{O}^i\text{Pr})_4$ , yielded trimetallic  $\text{LiMo}_4\text{Ta}_3\text{O}_{14}(\text{O}^i\text{Pr})_9(\text{OC}_2\text{H}_4\text{OMe})_3$  (**III**) in minor yields. The molecular structure of **II** can be described as a distorted cube, the corners of which are occupied in turn by  $[(^i\text{PrO})_3\text{Ta}(\mu\text{-O})_3]$  octahedra and  $[\text{MoO}(\mu\text{-O})_3]$  tetrahedra sharing common vertexes. The molecular structure of **III** can be derived from that of **II** by replacing one  $[(^i\text{PrO})_3\text{Ta}(\mu\text{-O})_3]$  octahedron with an  $[\text{Li}(\mu, \eta^2\text{-OC}_2\text{H}_4\text{OMe})_3]$  trigonal prism (the coordination number of the three Mo atoms is then increased to six). © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Molybdenum; Tantalum; Trimetallic alkoxides; Crystal structures

## 1. Introduction

Heterometallic alkoxides of heavy transition elements appear to be potent precursors of fine powders of the mixed-metal oxides and corresponding metal alloys having a broad range of applications [1,2]. We have reported earlier the isolation and characterization of the mixed-metal molybdenum(VI) and Group 4, e.g.  $\text{Zr}_3\text{Mo}_8\text{O}_{24}(\text{O}^i\text{Pr})_{12}(\text{O}^i\text{PrOH})_4$  [3], and Group 7, e.g.  $\text{ReMoO}_2(\text{OMe})_7$  [4], derivatives. It appeared challenging to extend this study to the Group 5 derivatives and we report here the isolation and structural characterization of the bimetallic alkoxides of molybdenum(VI) and tantalum and of the related trimetallic complex of these elements and lithium. A preliminary communication reporting the isolation and a short description of the molecular structure of  $\text{Mo}_2\text{Ta}_4\text{O}_8(\text{OMe})_{16}$  has been published [5].

## 2. Experimental

All manipulations were carried out in a dry nitrogen atmosphere using the Schlenk technique or a dry box. The alcohols were purified by distillation over  $\text{Al}(\text{O}^i\text{Pr})_3$  or  $\text{Mg}(\text{OMe})_2$  under argon. IR spectra of Nujol mulls were registered with a Bruker IFS-55 spectrometer. The  $^1\text{H}$  NMR spectra were obtained with a Varian 400 MHz spectrometer, using dry deaerated toluene as solvent (using TMS as internal and 20 vol% solution of  $\text{CDCl}_3$  as external standards). The metal ratio in the samples was determined, exploiting the facilities of Arrhenius Laboratory, Stockholm University, Sweden, on a JEOL-820 scanning electron microscope (SEM), supplied with a Link AN-10000 energy dispersive spectrometer (EDS). The total contents of the incombustible residues for the samples was determined using Perkin–Elmer TGA-7 device (in air,  $10^\circ\text{C min}^{-1}$ , final temperature  $800^\circ\text{C}$ ).

The starting reagents used in this work ( $\text{MoO}(\text{OMe})_4$  and  $\text{LiMo}_2\text{O}_4(\text{O}^i\text{Pr})_4(\text{OC}_2\text{H}_4\text{OMe})$  [6]  $\text{Ta}(\text{OMe})_5$ , and

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Ta(O<sup>*i*</sup>Pr)<sub>5</sub> [7]) were prepared by anodic oxidation of metals in alcohols and purified according to conventional techniques. An alcohol interchange reaction with isopropanol was used to obtain MoO(O<sup>*i*</sup>Pr)<sub>4</sub> and was performed by repeated (three times) dissolution of a measured quantity of methoxide in an excess of <sup>*i*</sup>PrOH with subsequent evaporation to dryness.

### 2.1. Preparation of Mo<sub>2</sub>Ta<sub>4</sub>O<sub>8</sub>(OMe)<sub>16</sub> (**I**)

MoO(OMe)<sub>4</sub> (0.584 g, 2.47 mmol) and Ta(OMe)<sub>5</sub> (1.734 g, 5.16 mmol) were dissolved in 20 ml MeOH and then a solution of H<sub>2</sub>O (0.13 ml, 7.2 mmol) in 20 ml MeOH was added dropwise to the bright yellow solution over a period of 1 h. The transparent colorless solution formed was then evaporated to dryness in vacuo and the glassy residue was redissolved in 5 ml of toluene and left to crystallize at –30°C for 2 days. The colorless crystals obtained were separated by decantation, washed with 1 ml toluene and dried in vacuo. Yield: 1.353 g (71%). IR (cm<sup>-1</sup>): 1160 s, 1155 s, 1146 s, 1133 s, 1059 s br, 1035 sh, 1028 s, 935 s, 912 s, 837 sh, 826 s br, 732 w, 616 s br, 578 m, 547 s, 540 s, 527 s br, 502 s, 494 s, 449 m br. The <sup>1</sup>H NMR spectrum of **I** is shown in Fig. 1.

### 2.2. Preparation of Mo<sub>4</sub>Ta<sub>4</sub>O<sub>16</sub>(O<sup>*i*</sup>Pr)<sub>12</sub> (**II**)

MoO(O<sup>*i*</sup>Pr)<sub>4</sub> (0.472 g, 1.36 mmol) and Ta(O<sup>*i*</sup>Pr)<sub>5</sub> (0.674 g, 1.41 mmol) were dissolved in 5 ml of toluene and the bright yellow solution obtained was refluxed for 30 min. The brownish–orange viscous liquid thus formed was left at room temperature (r.t.) for 2 weeks

in a flask covered by a serum cup and it changed color slowly to light brown. The solvent was evaporated in vacuo and the light-brown glassy residue redissolved in 3 ml of hexane and left overnight to crystallize. The colorless transparent crystals formed were separated by filtration and dried in vacuo. Yield: 0.127 g (18%). IR (cm<sup>-1</sup>): 1381 m, 1367 m, 1337 w, 1262 w, 1179 s, 1168 m, 1120 s br, 1007 s br, 966 w, 904 sh, 877 s, 840 s, 810 s br, 684 sh, 583 s br, 565 sh, 455 m br. <sup>1</sup>H NMR (ppm): 5.28 septet (1H, CH), 1.56 doublet (6H, CH<sub>3</sub>).

### 2.3. Preparation of LiMo<sub>4</sub>Ta<sub>3</sub>O<sub>14</sub>(O<sup>*i*</sup>Pr)<sub>9</sub>(OC<sub>2</sub>H<sub>4</sub>OMe)<sub>3</sub> (**III**)

The procedure used was analogous to that for the preparation of **II** except that LiMo<sub>2</sub>O<sub>4</sub>(O<sup>*i*</sup>Pr)<sub>4</sub>-(OC<sub>2</sub>H<sub>4</sub>OMe) was used instead of MoO(O<sup>*i*</sup>Pr)<sub>4</sub>. The crystals of **III** were obtained in minor yields after prolonged storage in toluene solution in contact with dry air (about 2 months) of the products of thermal reduction.

### 2.4. Crystallography

#### 2.4.1. Crystal data for C<sub>16</sub>H<sub>48</sub>O<sub>24</sub>Mo<sub>2</sub>Ta<sub>4</sub> (**I**)

*M* = 1450.22, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 9.3422(18), *b* = 9.455(2), *c* = 22.621(6) Å, β = 99.94(3)°, *V* = 1968.3(8) Å<sup>3</sup>, *D*<sub>calc</sub> = 2.599 g cm<sup>-3</sup> for *Z* = 2, λ(Mo Kα) = 0.71073 Å, 4414 [*R*<sub>int</sub> = 0.1053] independent reflections with *I* > 2σ(*I*) were collected at 22°C up to 2θ<sub>max</sub> = 56.58° with a Bruker SMART CCD 1K diffractometer. The structure was solved by standard direct methods; the coordinates of tantalum and molybdenum

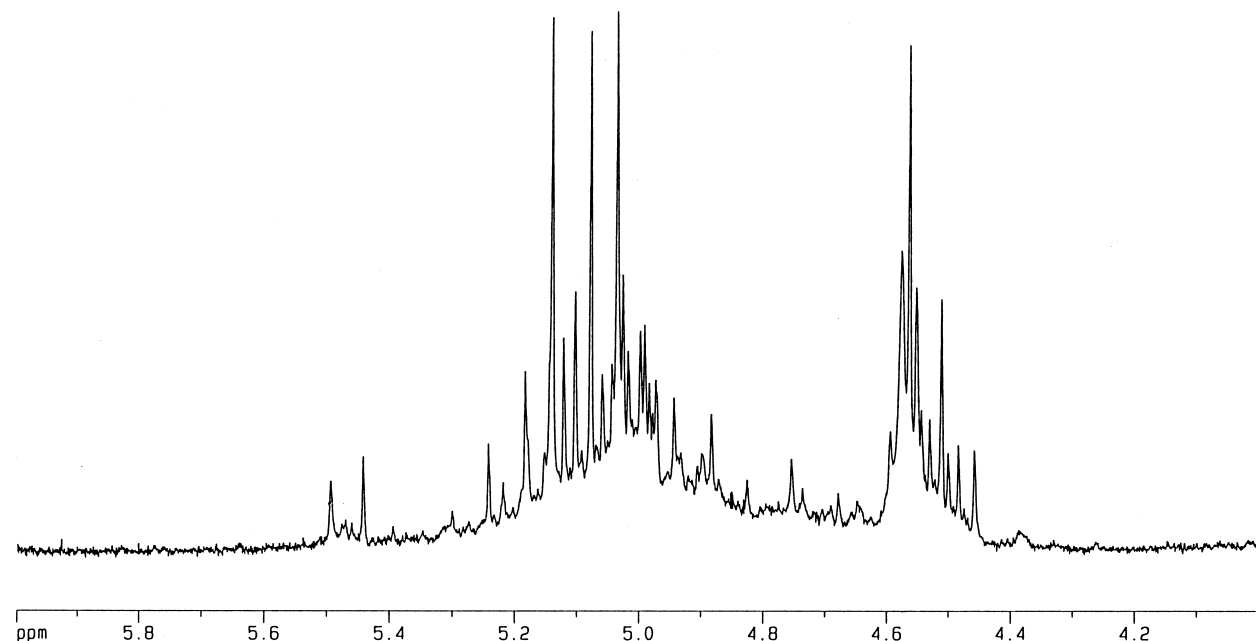


Fig. 1. The <sup>1</sup>H NMR spectrum of Mo<sub>2</sub>Ta<sub>4</sub>O<sub>8</sub>(OMe)<sub>16</sub> (**I**) (toluene, 300 K).

atoms were taken from the initial solution and the other non-hydrogen atoms were located in subsequent Fourier syntheses. The structure was refined by full-matrix least-squares in an isotropic and then anisotropic approximation. Final discrepancy factors are  $R = 0.0501$  and  $wR_2 = 0.0711$ .

#### 2.4.2. Crystal data for $C_{36}H_{84}O_{28}Mo_4Ta_4$ (II)

$M = 2072.59$ , tetragonal, space group  $I\bar{4}$ ,  $a = b = 14.998(6)$ ,  $c = 14.974(8)$  Å,  $V = 3368(3)$  Å<sup>3</sup>,  $D_{\text{calc}} = 2.044$  g cm<sup>-3</sup> for  $Z = 2$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å, 785 [ $R_{\text{int}} = 0.0000$ ] independent reflections with  $I > 2\sigma(I)$  were collected at 22°C up to  $2\theta_{\text{max}} = 41.58^\circ$  with a Bruker SMART CCD 1K diffractometer. The structure was solved by direct methods, applying HKLF 5 option for the experimental data file because of the presence of two twinning domains (creating a pseudo 3-fold axis and a pseudo-symmetry plane, the crystal thus having six individual components with an ideal crystallographic symmetry). The coordinates of tantalum and molybdenum atoms were taken from the initial solution and refined anisotropically. The other non-hydrogen atoms were located in subsequent Fourier syntheses and refined isotropically, the geometrical restraints being applied to conserve the idealized geometry for the Pr-radicals (subjected to rotational disorder at r.t.). Final discrepancy factors are  $R_1 = 0.0766$  and  $wR_2 = 0.1933$ .

#### 2.4.3. Crystal data for $C_{36}H_{84}O_{29}Mo_4Ta_3Li$ (III)

$M = 1914.58$ , triclinic, space group  $P\bar{1}$ ,  $a = 14.628(4)$ ,  $b = 14.721(4)$ ,  $c = 17.238(6)$  Å,  $\alpha = 90.620(17)$ ,  $\beta = 95.908(18)$ ,  $\gamma = 118.354(9)^\circ$ ,  $V = 3241.6(17)$  Å<sup>3</sup>,  $D_{\text{calc}} = 1.962$  g cm<sup>-3</sup> for  $Z = 2$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å, 8399 [ $R_{\text{int}} = 0.0534$ ] independent reflections with  $I > 2\sigma(I)$  were collected at 22°C up to  $2\theta_{\text{max}} = 45.00^\circ$  with a Bruker SMART CCD 1K diffractometer. The coordinates of tantalum and molybdenum atoms were taken from the initial solution and refined anisotropically. The coordinates of all other non-hydrogen atoms were located in subsequent Fourier syntheses and refined in anisotropic approximation for the oxygen atoms and isotropically for the carbon atoms. Final discrepancy factors are  $R_1 = 0.0636$  and  $wR_2 = 0.1516$ .

The positions of the hydrogen atoms in the structures I–III were calculated geometrically and included in the final cycles of the refinement in isotropic approximation. All calculations were performed with an IBM PC using SHELXTL-NT programs [8].

### 3. Results and discussion

Taking into account the absence of complex formation between the monooxoalkoxides of molybdenum(VI),  $\text{MoO}(\text{OR})_4$ , and tantalum alkoxides,

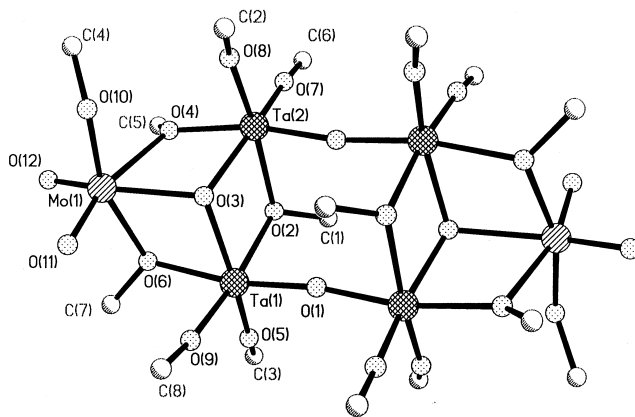


Fig. 2. The molecular structure of  $\text{Mo}_2\text{Ta}_4\text{O}_8(\text{OMe})_{16}$  (I).

$\text{Ta}(\text{OR})_5$ , [9] we decided to apply the microhydrolysis as the latter leads to oxoalkoxide species [10,11] that might have unsaturated coordination and thus be prone to aggregation with the formation of heterometallic products. The Mo:Ta = 1:2 ratio was chosen initially taking into account the existence of a bimetallic oxoalkoxotantalate of  $\text{I}_2\text{Zn}_2\text{Ta}_4\text{O}_4(\text{O}^i\text{Pr})_{14}$  [12] composition, in which molecular structure the  $\text{ZnI}(\mu\text{-OR})_2(\mu_3\text{-O})$  tetrahedra appeared to be as sterically demanding as should be necessary for the  $\text{MoO}_2(\text{OR})(\mu\text{-OR})_2(\mu_3\text{-O})$  octahedra. When the hydrolysis of a mixture of methoxides with stoichiometric amounts of water was carried out in MeOH and the transparent solution obtained was left overnight to crystallize, the amorphous solid product collected did not contain tantalum (according to EDS analysis) and displayed an IR spectrum identical with that described for  $\text{MoO}_2(\text{OMe})_2$  [13]. To enhance the formation of heterometallic species, which could occur only via the Lewis acid–base interaction mechanism, a non-donor solvent was used (thus removing the concurrent Lewis base, MeOH). Evaporation of the reaction mixture produced by the hydrolytic treatment, to dryness and redissolution of the residue in toluene produced a clear solution from which the expected heterometallic complex,  $\text{Mo}_2\text{Ta}_4\text{O}_8(\text{OMe})_{16}$  (I), was obtained by crystallization at low temperatures.

The molecular structure of I, determined by an X-ray single crystal study (see Fig. 2 and Tables 1 and 2), was analogous to that of the chosen structural prototype,  $\text{I}_2\text{Zn}_2\text{Ta}_4\text{O}_4(\text{O}^i\text{Pr})_{14}$  [12]. It is composed of centrosymmetric hexanuclear molecules, with the Ta–O distances (see Table 2) divided into two large groups, the first of which includes the bonds with the bridging alkoxoligands (Ta(1)–O(2) 2.125(7), Ta(2)–O(2) 2.128(7), Ta(1)–O(6) 2.125(7), Ta(2)–O(4) 2.043(7) Å) and the triply-bridging oxoatom (Ta(1)–O(3) 2.044(7), Ta(2)–O(3) 2.026(7) Å), and the second includes the bonds to the terminal alkoxide ligands (Ta(1)–O(5) 1.859(8), Ta(1)–O(9) 1.859(8), Ta(2)–O(7) 1.852(8),

Ta(2)–O(8) 1.865(8) Å) and the doubly-bridging oxoatom (Ta(1)–O(1) 1.890(7) and Ta(2)–O(1) # 1.931(7) Å). The Ta(1)–Ta(2) distance of 3.155(9) Å is quite short (compared with 3.31 Å in the Zn–Ta complex). The coordination of the doubly-bridging oxogroups is also almost linear, Ta(1)–O(1)–Ta(2) # 172.0(4)°. The coordination of the Mo atom is rather distorted in comparison with that usually observed [14]. The Mo–O distances themselves fall into the common ranges: 1.686–1.700(9) for the double bonds, 1.883(8) for the terminal alkoxide one and 2.134–2.279(8) for the alkoxide and oxo-bridging groups. However, the sum of the bond lengths in the *trans*-position differ noticeably (3.873(15), 3.979(17) and 4.017(16) Å) and the bond angles deviate strongly from 180° (O(10)–Mo(1)–O(6) 161.3(3), O(11)–Mo(1)–O(4) 164.1(4) and O(12)–Mo(1)–O(3) 151.7(4)°).

The IR spectrum of **I** is in good agreement with its molecular structure: there is a strong doublet present at 935 and 912 cm<sup>-1</sup>, corresponding to vibrations in the *cis*-MoO<sub>2</sub> fragment [14], a very strong and broad band at 837 cm<sup>-1</sup>, that can be attributed to vibrations with participation of oxobridging ligands, and a number of strong and well-defined bands in the area correspond-

ing to the M–OR vibrations (616 s br, 578 m, 547 s, 540 s, 527 s, 502 s, 494 s, 449 m br). It should be mentioned that **I** supposedly does not exist in solution: it is almost insoluble in toluene at r.t. and when dissolved under reflux does not crystallize on cooling for several weeks. The <sup>1</sup>H NMR spectra of **I** (see Fig. 1) are strikingly complex: at least 20 sharp and well defined signals are observed between 4.40 and 5.20 ppm indicating presumably the destruction of the molecules on dissolution and the coexistence in solution of different molecular aggregates. The dissolution in MeOH in contrast occurs easily at r.t. and a very high solubility can in fact be observed on dissolution, but after several hours precipitation of an insoluble sediment characterized as MoO<sub>2</sub>(OMe)<sub>2</sub> takes place (see above). Compound **I** is almost insoluble in hexane even on heating.

Analogous experiments to those used in the preparation of **I** were carried out with the isopropoxides of the title elements but did not lead to isolation of any crystalline product. At the same time it was found that oxidation of the bimetallic alkoxides of molybdenum(V) and tantalum, such as Mo<sub>4</sub>Ta<sub>2</sub>O<sub>8</sub>(O<sup>i</sup>Pr)<sub>14</sub> or Mo<sub>3</sub>Ta<sub>2</sub>O<sub>8</sub>(O<sup>i</sup>Pr)<sub>10</sub>, with dry air led to the formation of a colorless crystalline product containing Mo and Ta in

Table 1  
Crystal data and structure refinement parameters for compounds **I–III**

	C <sub>8</sub> H <sub>24</sub> MoO <sub>12</sub> Ta <sub>2</sub>	C <sub>36</sub> H <sub>84</sub> Mo <sub>4</sub> O <sub>28</sub> Ta <sub>4</sub>	C <sub>36</sub> H <sub>84</sub> LiMo <sub>4</sub> O <sub>29</sub> Ta <sub>3</sub>
Empirical formula	C <sub>8</sub> H <sub>24</sub> MoO <sub>12</sub> Ta <sub>2</sub>	C <sub>36</sub> H <sub>84</sub> Mo <sub>4</sub> O <sub>28</sub> Ta <sub>4</sub>	C <sub>36</sub> H <sub>84</sub> LiMo <sub>4</sub> O <sub>29</sub> Ta <sub>3</sub>
Formula weight	770.11	2072.59	1914.58
Temperature (K)	295(2)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	tetragonal	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>I</i> 4	<i>P</i> 1
Unit cell dimensions			
<i>a</i> (Å)	9.3422(18)	14.998(6)	14.628(4)
<i>b</i> (Å)	9.455(2)	14.998(6)	14.721(4)
<i>c</i> (Å)	22.621(6)	14.974(8)	17.238(6)
<i>α</i> (°)	90	90	90.620(17)
<i>β</i> (°)	99.94(3)	90	95.908(18)
<i>γ</i> (°)	90	90	118.354(9)
Volume (Å <sup>3</sup> )	1968.3(8)	3368(3)	3241.6(16)
<i>Z</i>	4	2	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.599	2.044	1.962
Absorption coefficient (mm <sup>-1</sup> )	11.766	7.255	5.862
<i>F</i> (000)	1424	1968	1844
Crystal size (mm)	0.50 × 0.15 × 0.10	0.5 × 0.2 × 0.15	1.1 × 0.4 × 0.3
<i>θ</i> Range for data collection (°)	1.83–28.29	1.92–20.79	1.59–22.50
Index ranges (°)	–11 ≤ <i>h</i> ≤ 12, –12 ≤ <i>k</i> ≤ 12, –25 ≤ <i>l</i> ≤ 29	–10 ≤ <i>h</i> ≤ 14, –10 ≤ <i>k</i> ≤ 14, –14 ≤ <i>l</i> ≤ 14	–15 ≤ <i>h</i> ≤ 15, 15 ≤ <i>k</i> ≤ 15, 15 ≤ <i>l</i> ≤ 18
Reflections collected	11 104	785	12 866
Independent reflections	4414 [ <i>R</i> <sub>int</sub> = 0.1053]	785 [ <i>R</i> <sub>int</sub> = 0.0000]	8399 [ <i>R</i> <sub>int</sub> = 0.0534]
Completeness to <i>θ</i> = 28.29° (%)	90.1	84.9	99.1
Refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>	full-matrix least-squares on <i>F</i> <sup>2</sup>	full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	4414/0/208	785/33/88	8399/0/473
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.867	1.039	0.838
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0501, <i>wR</i> <sub>2</sub> = 0.0711	<i>R</i> <sub>1</sub> = 0.0766, <i>wR</i> <sub>2</sub> = 0.1933	<i>R</i> <sub>1</sub> = 0.0636, <i>wR</i> <sub>2</sub> = 0.1516
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1342, <i>wR</i> <sub>2</sub> = 0.0865	<i>R</i> <sub>1</sub> = 0.0867, <i>wR</i> <sub>2</sub> = 0.2081	<i>R</i> <sub>1</sub> = 0.1080, <i>wR</i> <sub>2</sub> = 0.1612
Largest difference peak and hole (e Å <sup>-3</sup> )	1.224 and –1.299	0.800 and –1.201	1.848 and –3.048
Absolute structure parameter		0.14(11)	

Table 2  
Selected bond distances (Å) and angles (°) of compound I<sup>a</sup>

Ta(1)–O(5)	1.859(8)	Ta(2)–O(4)	2.043(7)
Ta(1)–O(9)	1.859(8)	Ta(2)–O(2)	2.128(7)
Ta(1)–O(1)	1.890(7)	O(1)–Ta(2) # 1	1.931(7)
Ta(1)–O(3)	2.044(7)	Ta(1)–Ta(2)	3.3155(9)
Ta(1)–O(2)	2.125(7)	Mo(1)–O(12)	1.686(8)
Ta(1)–O(6)	2.125(7)	Mo(1)–O(11)	1.700(9)
Ta(2)–O(7)	1.852(8)	Mo(1)–O(10)	1.883(8)
Ta(2)–O(8)	1.865(8)	Mo(1)–O(6)	2.134(8)
Ta(2)–O(1) # 1	1.931(7)	Mo(1)–O(3)	2.187(7)
Ta(2)–O(3)	2.026(7)	Mo(1)–O(4)	2.279(8)
O(5)–Ta(1)–O(9)	100.2(3)	O(7)–Ta(2)–O(8)	101.3(3)
O(5)–Ta(1)–O(1)	99.5(3)	O(7)–Ta(2)–O(1) # 1	97.9(3)
O(9)–Ta(1)–O(1)	94.7(3)	O(8)–Ta(2)–O(1) # 1	92.0(3)
O(5)–Ta(1)–O(3)	154.7(3)	O(7)–Ta(2)–O(3)	159.4(3)
O(9)–Ta(1)–O(3)	97.1(3)	O(8)–Ta(2)–O(3)	93.9(3)
O(1)–Ta(1)–O(3)	97.3(3)	O(1) # 1–Ta(2)–O(3)	95.3(3)
O(5)–Ta(1)–O(2)	88.9(3)	O(7)–Ta(2)–O(4)	89.2(3)
O(9)–Ta(1)–O(2)	170.4(3)	O(8)–Ta(2)–O(4)	94.4(3)
O(1)–Ta(1)–O(2)	86.7(3)	O(1) # 1–Ta(2)–O(4)	169.3(3)
O(3)–Ta(1)–O(2)	73.4(3)	O(3)–Ta(2)–O(4)	75.8(3)
O(5)–Ta(1)–O(6)	87.7(3)	O(7)–Ta(2)–O(2)	91.8(3)
O(9)–Ta(1)–O(6)	90.5(3)	O(8)–Ta(2)–O(2)	166.8(3)
O(1)–Ta(1)–O(6)	170.2(3)	O(1) # 1–Ta(2)–O(2)	85.0(3)
O(3)–Ta(1)–O(6)	73.8(3)	O(3)–Ta(2)–O(2)	73.6(3)
O(2)–Ta(1)–O(6)	86.9(3)	O(4)–Ta(2)–O(2)	86.9(3)
O(12)–Mo(1)–O(11)	105.6(5)	O(10)–Mo(1)–O(3)	92.3(3)
O(12)–Mo(1)–O(10)	100.9(4)	O(6)–Mo(1)–O(3)	70.8(3)
O(11)–Mo(1)–O(10)	99.8(4)	O(12)–Mo(1)–O(4)	88.0(4)
O(12)–Mo(1)–O(6)	91.4(4)	O(11)–Mo(1)–O(4)	164.1(4)
O(11)–Mo(1)–O(6)	90.3(4)	O(10)–Mo(1)–O(4)	85.2(3)
O(10)–Mo(1)–O(6)	161.3(3)	O(6)–Mo(1)–O(4)	81.1(3)
O(12)–Mo(1)–O(3)	151.7(4)	O(3)–Mo(1)–O(4)	68.0(3)
O(11)–Mo(1)–O(3)	96.6(4)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: # 1  $-x, -y+1, -z$ .

1:1 composition (according to EDS analysis) in minor yields [9]. The solution containing  $\text{MoO}(\text{O}^i\text{Pr})_4$  and  $\text{Ta}(\text{O}^i\text{Pr})_5$  in a 1:1 molar ratio in toluene was then prepared and subjected to thermal treatment in an analogous manner to that used for the complete reduction of Mo(VI) to Mo(V). It was then left at r.t. in a flask covered by a serup cup that provides good protection against moisture but not against oxygen in air. Complete oxidation, accompanied by the appropriate color change, occurred in 2 weeks and the bimetallic complex  $\text{Mo}_4\text{Ta}_4\text{O}_{16}(\text{O}^i\text{Pr})_{12}$  (**II**) was obtained on crystallization from hexane in rather low yields. One of the major difficulties in the isolation of **II** appears to be its very high solubility in hydrocarbon solvents (achieving at least 50 wt% in both toluene and hexane).

The molecular structure of **II** (see Figs. 3 and 4 and Tables 1 and 3) is composed of non-centrosymmetric octanuclear molecules, the arrangement of the metal atoms in which can be described best as a distorted cube. The vertexes of this cube contain the molybdenum and tantalum atoms in turn. The former are tetraordinated, building tetraoxomolybdate anions,

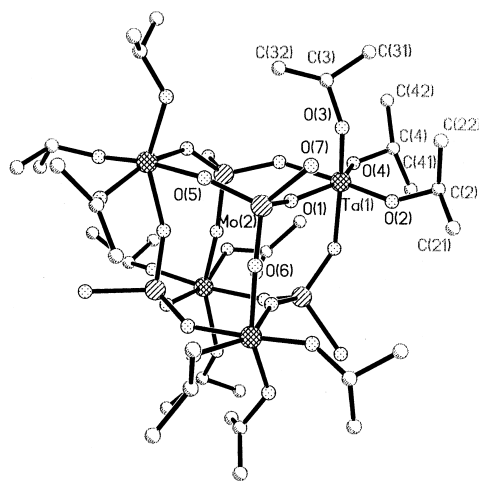


Fig. 3. The molecular structure of  $\text{Mo}_4\text{Ta}_4\text{O}_{16}(\text{O}^i\text{Pr})_{12}$  (**II**).

$\text{Mo}(\text{O})_4\{\mu\text{-O}(1)\}\{\mu\text{-O}(5)\}\{\mu\text{-O}(6)\}$ , the latter hexacoordinated, forming  $\text{Ta}(\text{O})_6\{\mu\text{-O}(1)\}\{\mu\text{-O}(5)\}\{\mu\text{-O}(6)\}\{\text{O}(2)\}\{\text{O}(3)\}\{\text{O}(4)\}$  octahedral units. The bonding parameters (Table 3) inside the tetraoxomolybdate unit are quite close to those usually observed for such fragments in polyoxometallate structures [15] (Mo–O 1.76(3)–1.77(3) for Mo–O–Ta bridging fragments and Mo(2)–O(7) 2.04(6) for the terminal Mo=O bond, the O–Mo–O angles being quite close to the tetrahedral ones, i.e. 110(4)–116(3)°). The bond lengths and angles inside the  $\text{Ta}(\mu\text{-O})_3(\text{OR})_3$  octahedron (see Table 3) are within the ranges usually observed for tantalum oxoalkoxides [7]. The metal–oxygen core in structure **II** can be considered as the first representative of an unusual oxometallate core composed by four tetrahedra

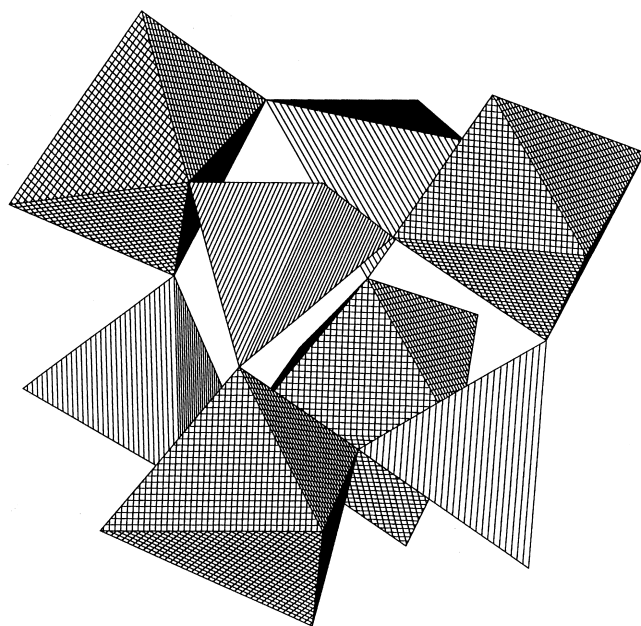


Fig. 4. A polyhedral presentation of the metal–oxygen core in the structure of **II**.

Table 3  
Selected bond distances (Å) and angles (°) of compound **II**<sup>a</sup>

O(1)–Ta(1)	2.09(3)	O(5)–Ta(1) # 3	2.09(3)
Ta(1)–O(2)	1.83(6)	O(6)–Ta(1) # 1	2.08(3)
Ta(1)–O(3)	1.97(11)	Mo(2)–O(1)	1.77(3)
Ta(1)–O(6) # 1	2.08(3)	Mo(2)–O(6)	1.76(3)
Ta(1)–O(5) # 2	2.09(3)	Mo(2)–O(5)	1.77(3)
Ta(1)–O(4)	2.08(7)	Mo(2)–O(7)	2.04(6)
Mo(2)–O(1)–Ta(1)	158(4)	O(6)–Mo(2)–O(5)	110(4)
O(2)–Ta(1)–O(3)	85(4)	O(6)–Mo(2)–O(1)	116(3)
O(2)–Ta(1)–O(6) # 1	84(3)	O(5)–Mo(2)–O(1)	110(4)
O(3)–Ta(1)–O(6) # 1	156(4)	O(6)–Mo(2)–O(7)	111(3)
O(2)–Ta(1)–O(5) # 2	172(3)	O(5)–Mo(2)–O(7)	113(4)
O(3)–Ta(1)–O(5) # 2	93(4)	O(1)–Mo(2)–O(7)	97(3)
O(6) # 1–Ta(1)–O(5) # 2	95(3)	Mo(2)–O(5)–Ta(1) # 3	149(3)
O(2)–Ta(1)–O(1)	97(3)	Mo(2)–O(6)–Ta(1) # 1	142(2)
O(3)–Ta(1)–O(1)	78(3)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: # 1  $-x+2, -y+1, z$ ; # 2  $-y+3/2, x-1/2, -z+3/2$ ; # 3  $y+1/2, -x+3/2, -z+3/2$ .

and four octahedra, sharing vertexes with each other (see Fig. 4).

The IR spectrum of **II** appears to be in good agreement with its molecular structure described above: it displays three broad and intensive lines that correspond to the vibration of the tetraoxomolybdate core at 877, 840 and 840  $\text{cm}^{-1}$  and two strong lines at 583 and 455  $\text{cm}^{-1}$  typical of Ta–OR bond vibration. Structure of **II** is preserved in hydrocarbon solution because the NMR spectra obtained in toluene display only one kind of well-defined signal for both methyne and methyl protons (all the isopropoxide groups in the solid state structure of **II** are terminal and have analogous bonding parameters), while the dissociation in solution would supposedly lead to the appearance of several different signals.

An attempt to prepare a trimetallic alkoxide complex using  $\text{LiMo}_2\text{O}_4(\text{O}^i\text{Pr})_4(\text{OC}_2\text{H}_4\text{OMe})$  instead of  $\text{MoO}(\text{O}^i\text{Pr})_4$  yielded trimetallic  $\text{LiMo}_4\text{Ta}_3\text{O}_{14}(\text{O}^i\text{Pr})_9(\text{OC}_2\text{H}_4\text{OMe})_3$  (**III**) in minor yields (only a small crop of single crystals could be isolated from the viscous liquid media on complete removal of the solvent). Compound **III**, in analogy with **II**, possesses very high solubility in hydrocarbon solvents. The molecular structure of **III** (see Figs. 5 and 6 and Tables 1 and 4) is closely related to that of **II** and can be obtained from the latter by replacement of one of the  $[(^i\text{PrO})_3\text{Ta}(\mu\text{-O})_3]$  octahedra with a  $[\text{Li}(\mu_3\eta^2\text{-OC}_2\text{H}_4\text{OMe})_3]$  trigonal prism and demonstrates a distorted trigonal symmetry. The three  $[\text{MoO}(\mu\text{-O})_3]$  tetrahedra that were in contact with the  $[(^i\text{PrO})_3\text{Ta}(\mu\text{-O})_3]$  octahedron that is removed get their  $\mu\text{-O}$  groups, which became 'free', fused to one  $\mu_3\text{-O}$  ligand. The molybdenum atoms complete their coordination number to six by coordinating two additional  $\mu\text{-OR}$  2-methoxyethoxide groups each. The coor-

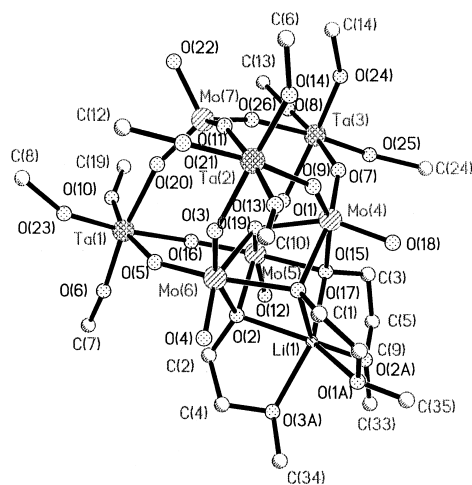


Fig. 5. The molecular structure of  $\text{LiMo}_4\text{Ta}_3\text{O}_{14}(\text{O}^i\text{Pr})_9(\text{OC}_2\text{H}_4\text{OMe})_3$  (**III**): the  $\beta$ -carbon atoms of the isopropoxide groups are omitted for clarity.

dination of the tantalum atoms is very close to that observed in **II** (the distances to the oxygen atoms of the terminal  $\text{O}^i\text{Pr}$ -groups are essentially the same 1.832(14)–1.865(11) Å, while the lengths of the oxo-bridges vary a little more 1.988(10)–2.114(10) Å, with no obvious difference observed between the bridges to the tetrahedrally coordinated Mo(7) and 'pseudo-octahedrally'- $4+2$  coordinated Mo(4), Mo(5) and Mo(6) atoms). The bonding parameters for Mo(7) indicate a rather regular tetrahedral coordination (Mo(7)–O 1.697(13)–1.772(13) Å, the O–Mo(7)–O angles usual for a tetrahedron 105.8(6)–113.6(6)°). The bonding

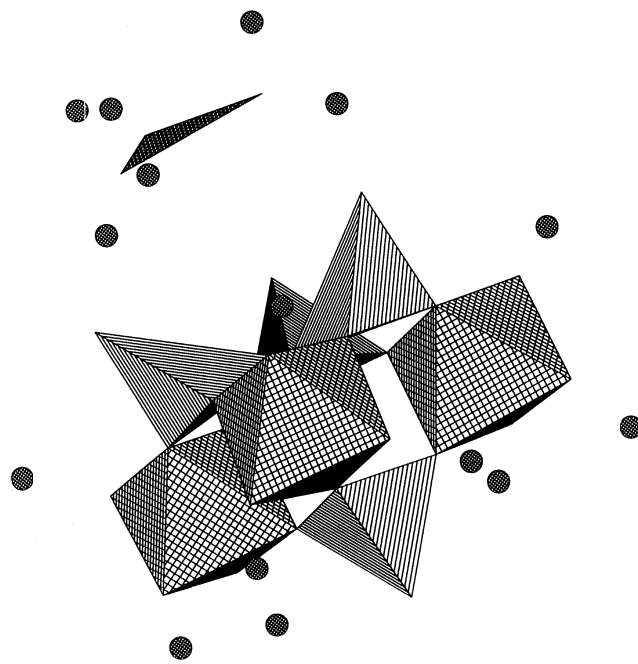


Fig. 6. A polyhedral presentation of the metal–oxygen core in the structure of **III**.

Table 4  
Selected bond distances (Å) and angles (°) of compound **III**

Ta(1)–O(10)	1.832(13)	Mo(5)–Li(1)	3.30(4)
Ta(1)–O(23)	1.846(13)	Mo(6)–Li(1)	3.35(3)
Ta(1)–O(6)	1.861(11)	Mo(4)–O(18)	1.739(10)
Ta(1)–O(5)	1.988(10)	Mo(4)–O(7)	1.771(11)
Ta(1)–O(16)	2.065(11)	Mo(4)–O(9)	1.823(11)
Ta(1)–O(20)	2.124(11)	Mo(4)–O(19)	2.065(10)
Ta(2)–O(13)	1.850(13)	Mo(4)–O(17)	2.155(12)
Ta(2)–O(14)	1.857(13)	Mo(4)–O(15)	2.184(9)
Ta(2)–O(21)	1.856(13)	Mo(5)–O(12)	1.690(11)
Ta(2)–O(9)	2.020(11)	Mo(5)–O(16)	1.815(10)
Ta(2)–O(11)	2.091(12)	Mo(5)–O(1)	1.831(11)
Ta(2)–O(3)	2.114(10)	Mo(5)–O(19)	2.075(10)
Ta(3)–O(25)	1.814(14)	Mo(5)–O(15)	2.170(10)
Ta(3)–O(8)	1.849(12)	Mo(5)–O(2)	2.168(11)
Ta(3)–O(24)	1.868(13)	Mo(6)–O(4)	1.721(12)
Ta(3)–O(1)	2.026(10)	Mo(6)–O(3)	1.781(10)
Ta(3)–O(26)	2.089(13)	Mo(6)–O(5)	1.840(10)
Ta(3)–O(7)	2.100(11)	Mo(6)–O(19)	2.045(11)
O(2)–Li(1)	2.16(3)	Mo(6)–O(17)	2.164(10)
O(15)–Li(1)	2.08(3)	Mo(6)–O(2)	2.168(11)
O(17)–Li(1)	2.17(3)	Mo(7)–O(22)	1.697(13)
O(1A)–Li(1)	2.17(4)	Mo(7)–O(20)	1.748(11)
O(2A)–Li(1)	2.09(3)	Mo(7)–O(11)	1.771(12)
O(3A)–Li(1)	2.16(3)	Mo(7)–O(26)	1.772(13)
Mo(4)–Li(1)	3.33(3)		
O(10)–Ta(1)–O(23)	96.1(6)	O(18)–Mo(4)–O(19)	152.5(5)
O(10)–Ta(1)–O(6)	95.6(6)	O(7)–Mo(4)–O(19)	91.5(4)
O(23)–Ta(1)–O(6)	98.1(5)	O(9)–Mo(4)–O(19)	93.4(4)
O(10)–Ta(1)–O(5)	165.2(5)	O(18)–Mo(4)–O(17)	89.7(5)
O(13)–Ta(2)–O(14)	96.4(6)	O(7)–Mo(4)–O(17)	158.8(4)
O(13)–Ta(2)–O(21)	94.4(6)	O(9)–Mo(4)–O(17)	86.7(5)
O(14)–Ta(2)–O(21)	97.8(5)	O(19)–Mo(4)–O(17)	69.8(4)
O(13)–Ta(2)–O(9)	93.6(5)	O(18)–Mo(4)–O(15)	86.8(5)
O(14)–Ta(2)–O(9)	93.1(5)	O(7)–Mo(4)–O(15)	89.0(4)
O(21)–Ta(2)–O(9)	165.7(5)	O(9)–Mo(4)–O(15)	159.5(4)
O(13)–Ta(2)–O(11)	171.1(5)	O(19)–Mo(4)–O(15)	70.8(4)
O(22)–Mo(7)–O(20)	105.8(6)	O(17)–Mo(4)–O(15)	75.8(4)
O(22)–Mo(7)–O(11)	106.7(6)	O(15)–Li(1)–O(2A)	80.4(12)
O(20)–Mo(7)–O(11)	113.6(6)	O(15)–Li(1)–O(2)	79.1(13)
O(22)–Mo(7)–O(26)	106.5(6)	O(2A)–Li(1)–O(2)	127.8(17)
O(20)–Mo(7)–O(26)	111.2(5)	O(15)–Li(1)–O(17)	77.8(12)
O(11)–Mo(7)–O(26)	112.5(6)	O(2A)–Li(1)–O(17)	142.2(16)
O(18)–Mo(4)–O(7)	104.3(5)	O(2)–Li(1)–O(17)	77.4(12)
O(18)–Mo(4)–O(9)	103.8(5)	O(15)–Li(1)–O(3A)	144.1(17)
O(7)–Mo(4)–O(9)	104.8(5)	O(2A)–Li(1)–O(3A)	91.7(13)

parameters for Mo(4), Mo(5) and Mo(6) are very similar and indicate the same kind of distortion for the octahedra: the shortest bonds are those to the terminal oxygen atoms (1.690(11)–1.739(10) Å), the oxobridges to the tantalum atoms are also rather short (1.771(11)–1.840(10) Å), the triply bridging oxoatom has a longer Mo–O(19) distance, essentially same for all the three Mo atoms (2.045(10)–2.075(10) Å) and the longest distances are those to the alkoxobridges (2.155(12)–2.168(11) Å). It is very interesting to note that the lithium atoms definitely do not have an octahedral coordination but, indeed, have a trigonal prismatic

coordination analogous to that observed for one of the symmetrically independent Li atoms in the structure of  $\{[\text{LiWO}_2(\text{OC}_2\text{H}_4\text{OCH}_3)_3]_2 \cdot 2\text{Li}(\text{HOC}_2\text{H}_4\text{OCH}_3)_2\}^{2+}$  cations [6]. In both cases, this coordination appears to be forced by the parallel arrangement of the three 2-methoxyethoxide groups providing a pair of donor atoms each.

The molecule of **III** also represents a new type of a polyoxometallate core with a combination of octahedral and tetrahedral elements via sharing the common vertexes.

#### 4. Supplementary material

Supplementary data are available from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>) on request, quoting the deposition numbers CCDC-139287 (**I**), CCDC-142959 (**II**), and CCDC-142960 (**III**).

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