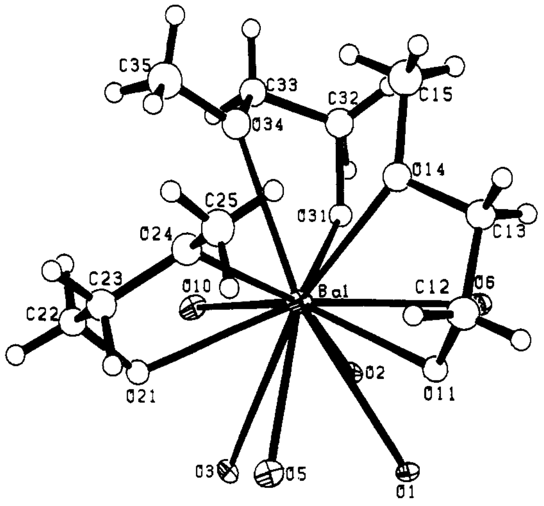

Figure 2. ORTEP plot (35% probability ellipsoids) of the barium coordination sphere showing the atom-labeling scheme. Barium and oxo oxygen atoms are represented by boundary ellipsoids, oxygen atoms of methoxyethoxide ligands are represented by large spheres, and carbon atoms are represented by small spheres. Selected average bond lengths (Å) and bond angles (deg): Ba–O(ether), 2.908 (9); Ba–OR, 2.693 (9); RO–Ba–O(ether), 60.9 (3).

$Ti_{13}O_{42}$ core is coordinated to six, not four, oxygen atoms. Each barium atom interacts with twelve oxygen atoms, six from three chelating alkoxide ether ligands and six from oxo ligands (see Figure 2). The unique central titanium atom is octahedrally coordinated to six trigonal-bipyramidal oxo ligands. Each of these internal oxo ligands is axially coordinated to two barium atoms and equatorially coordinated to the central and two external titanium atoms. External titanium atoms are coordinated to one internal (μ_5) and two bridging (μ_3) oxo ligands in addition to one terminal (μ_1-η^1) and two bridging (μ_1,μ_3-η^2) alkoxide oxygen atoms. The distorted octahedral coordination geometry of each external titanium atom is on average trigonally compressed in the direction of its three alkoxide ligands and expanded in the direction of its three oxo ligands. The chelating nature of the twelve bridging alkoxide ligands entraps the barium atoms within the cluster, in sharp contrast with the structure reported for lead(II) methoxyethoxide, which shows that methoxyethoxide ligands do not chelate through alkoxide ether oxygen atoms.[11]

$Ba_4Ti_{13}O_{18}(OCH_2CH_2OCH_3)_{24}$ was characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy in CD_2Cl_2 at 293 K. The ^{17}O NMR spectrum was recorded on material synthesized by hydrolysis with 10 wt % ^{17}O-enriched water. Six resonances of ^1H and $^{13}C\{^1H\}$ NMR spectra of this compound can be assigned to two types of methoxyethoxide ligands: terminal and bridging. The ^{17}O NMR spectrum of $Ba_4Ti_{13}O_{18}(OCH_2CH_2OCH_3)_{24}$ shows resonances at δ 651 and 487, which can be assigned, by analogy to other titanium oxide alkoxide systems,[12] to OTi_2Ba and OTi_3Ba_2 oxygens, respectively.

Thermal and X-ray powder diffraction analyses of the decomposition of $Ba_4Ti_{13}O_{18}(C_3O_2H_7)_{24}$ in air indicate the decomposition of alkoxide ligands between 255 and 355 °C. Crysallization of the $Ba_4Ti_{13}O_{30}$ phase occurred at 670 °C.[13a]

Preliminary results of experiments involving the partial hydrolysis of $BaTi(OCH_2CH_2OCH_3)_6$ suggest changes in powder stoichiometry at early stages of sol–gel processing. Heat treatment of gels formed by the addition of excess water to solutions of $BaTi(OCH_2CH_2OCH_3)_6$ results in the eventual formation of the perovskite structure, $BaTiO_3$, at temperatures as low as 400 °C.[13a] Both compounds, $Ba_4Ti_{13}O_{30}$ and $BaTiO_3$, have significant applications in electrical ceramics and now can be synthesized at greatly reduced temperatures compared with those for conventional mixed oxide processing (e.g. 1100 °C).[13b] The implications with respect to integration with semiconductors are profound.[14]

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Supplementary Material Available: An ORTEP diagram including all alkoxide ligands and the labeling scheme and tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles (12 pages); a listing of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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Department of Materials Science and Engineering
Materials Research Laboratory
Beckman Institute
School of Chemical Sciences
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

Jean-Florent Campion
David A. Payne*
Hee K. Chae
Jan K. Maurin
Scott R. Wilson

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The Bis(methylcyclopentadienyl)titanium(IV) Molybdate Dimer: A Titanium(IV)–Molybdenum(VI) Eight-Membered Metal–Oxo Ring

Complexation of organometallic cations by polyoxoanions was elegantly pioneered by Klemperer.[1] We found, however, a single report on simple anions like MoO_4^{2-} or similar ones acting as ligands toward organometallic cations[2] in complexes $[(\eta^5\text{-}RC_5H_4)_2M_2O_4]$ (R = H, Me; M = Mo, W).[3] Compounds derived from such reactions may be suitable precursors of metal–oxo aggregates via the oxidation of the organic ligand under reductive coupling[4] or acid–base condensation reactions.[1] We are concerned in this paper with the high-yield synthesis of the bis(methylcyclopentadienyl)titanium(IV) molybdate dimer and its structural characterization.

An aqueous solution of $[(\eta^5\text{-}MeC_5H_4)_2TiCl_2]$ was reacted with an aqueous solution of $Na_2MoO_4\cdot 2H_2O$[5] (eq 1). The resulting

$$\underset{\mathbf{1}}{(\eta^5\text{-}MeC_5H_4)_2TiCl_2} + Na_2MoO_4\cdot 2H_2O \xrightarrow{H_2O} \underset{\mathbf{2}}{[(\eta^5\text{-}MeC_5H_4)_2Ti(\mu_2\text{-}MoO_4)]_2} \quad (1)$$

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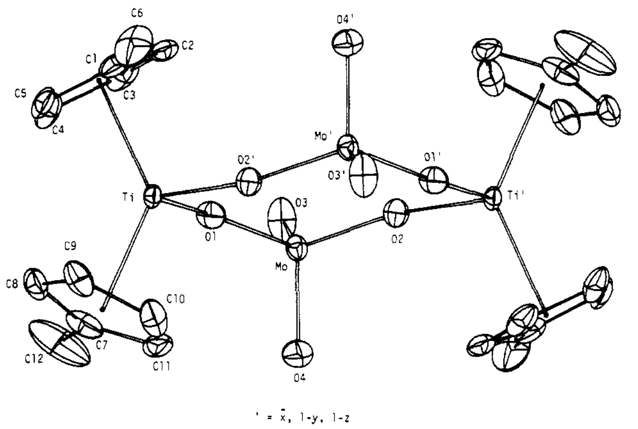
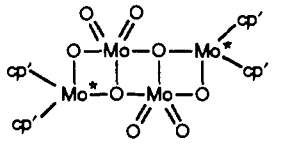


Figure 1. ORTEP view of $[(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Ti}(\mu_2\text{-MoO}_4)]_2$ (30% probability ellipsoids). Bond distances (Å) and angles (deg): Mo–O(1), 1.805 (3); Mo–O(2), 1.803 (3); Mo–O(3), 1.711 (3); Mo–O(4), 1.702 (3); Ti–O(1), 1.933 (3); Ti–O(2′), 1.936 (3); Ti–cp(1), 2.063 (5); Ti–cp(2), 2.069 (5); O(3)–Mo–O(4), 106.2 (2); O(2)–Mo–O(4), 107.1 (2); O(2)–Mo–O(3), 110.8 (2); O(1)–Mo–O(4), 107.1 (2); O(1)–Mo–O(3), 110.7 (1); O(1)–Mo–O(2), 114.5 (1); Mo–O(1)–Ti, 155.7 (2); O(1)–Ti–O(2′), 95.9 (1); cp(1)–Ti–cp(2), 130.6 (2); O(1)–Ti–cp(2), 106.4 (2); O(1)–Ti–cp(1), 106.2 (2); O(2′)–Ti–cp(2), 106.2 (2); O(2′)–Ti–cp(1), 106.3 (2); Mo–O(1)–Ti, 155.7 (2); Mo–O(2)–Ti′, 161.5 (2)′. Primed atoms have equivalent coordinates $-x$, $1-y$, $-z$.

solid extracted first with $CHCl_3$ and then with CH_2Cl_2 gave orange crystals of **2** (85%). Complex **2** shows a limited thermal stability depending on the nature of the solvent. Gentle heating of **2** in pyridine or dimethyl sulfoxide led to oxidation of the cyclopentadienyl ligand and formation of inorganic unsoluble materials. Attempts to form the corresponding chromate or tungstate derivative are so far unsuccessful. This is mainly due to the fact that an aqueous solution of $(cp)_2TiCl_2$ has a very acidic pH (i.e. pH = 1.72 for a solution of 1.76×10^{-2} M). The acidic conditions cause the condensation of the MO_4^{2-} anions,[1,6] so a mixture of different anions is expected to react with the aqueous solution of **1**. Furthermore, in the case of CrO_4^{2-} a significant oxidation of the organic part is observed. The use of η^5-MeC_5H_4 rather than other substituted cyclopentadienyl ligands was mainly dictated by the solubility of **2** in the solvent sequence used. Complex **2** has been analytically and spectroscopically characterized, including an X-ray analysis.[7]

Complex **2** has the cyclic tetranuclear eight-membered centrosymmetric structure shown in Figure 1. The four metal atoms are coplanar, with the oxygen atoms tilted up (O1, O2) and down (O1′, O2′; $\bar{x}$, $1-y$, $1-z$) by 0.229 (3) and 0.238 (3) Å, respectively. It resembles the structure of $[(\eta^5\text{-MeC}_5\text{H}_4\text{Ti})_4\text{O}_4\text{Cl}_4]$.[8] Structural parameters concerning the Mo–O–Ti fragment are in agreement with a significant Mo–O multiple bond[9] and a rather long Ti–O bond compared with the same bonds in other organotitanoxanes.[8,10] The structure of complex **2** is remarkably different from that of the stoichiometrically analogous molybdenum derivative $(cp')_2Mo_2O_4$ (**3**)[2b] (cp′ = η^5-MeC_5H_4), having the following skeleton:



3

The major difference is seen in the structural parameters related to the Ti–O–Mo and Mo*–O–Mo fragments. The equivalent Mo–O bond distances are much longer in **3**, ranging from 1.86 (1) to 2.11 (1) Å, than in **2** (see caption of Figure 1). The Ti–O–Mo bond angles are much wider than the corresponding Mo–O–Mo in **3**, ranging from 103.0 (5) to 113.5 (6)°. The presence of Mo(IV) in the $(\eta^5\text{-MeC}_5\text{H}_4)_2$Mo fragment does not allow the formation of an M–O multiple bond as much as in complex **2** and makes the bridging oxygen in **3** available for binding a further metal atom. The Mo–O(terminal) distances have double-bond character[2,9] (see caption of Figure 1). The molecules of **2** are held together in chains parallel to the [001] axis by centrosymmetric Mo···O3″ contacts [Mo···O3″ = 3.307 (3) Å] (Figure 2).

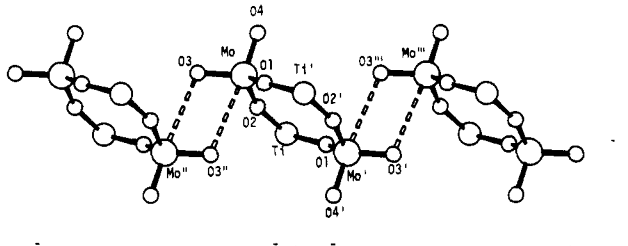


Figure 2. Packing of the molecules along [001].

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-28470.90) for financial support.

Supplementary Material Available: For complex **2**, complete listings of crystallographic data, fractional atomic coordinates for all atoms, anisotropic thermal parameters, and bond distances and angles (6 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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(5) Preparation of $[(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Ti}(\mu_2\text{-MoO}_4)]_2$ (**2**) is as follows. $[(\eta^5\text{-MeC}_5\text{H}_4)_2\text{TiCl}_2]$ (5.0 g, 18.05 mmol) was dissolved in water (250 mL) by refluxing for 15 min. By addition of an aqueous solution of $Na_2MoO_4 \cdot 2H_2O$ (4.37 g, 18.05 mmol) to the red solution of **1**, a salmon red solid suddenly formed. The solid was extracted with $CHCl_3$ and the resulting solution dried over $MgSO_4$ and evaporated to dryness. The microcrystalline solid, extracted with CH_2Cl_2 (150 mL), gave **2** as orange crystals (85%). Anal. Calcd for $C_{24}H_{28}Mo_2O_8Ti_2$: C, 39.33; H, 3.82. Found: C, 39.29; H, 3.81. ^1H NMR (200 MHz, $CDCl_3$, ppm, room temperature): δ 2.29 (s, 3 H, Me), 6.32 (m, 2 H, cp), 6.42 (m, 2 H, cp). ν(M–O) (Nujol): a very large envelope band in the 700–900-cm^{-1} region.

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(7) Crystal data for complex **2**: $C_{24}H_{28}Mo_2O_8Ti_2$, $M_n = 732.2$, monoclinic, space group $P2_1/n$, $a = 15.336$ (1) Å, $b = 12.466$ (1), $c = 6.756$ (1) Å, $\beta = 96.81$ (1)°; $V = 1282.5$ (2) Å^3, $Z = 2$, $D_c = 1.896$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.71069$ Å), crystal dimensions $0.25 \times 0.28 \times 0.30$ mm. The structure was solved by the heavy-atom method and anisotropically refined by block full-matrix least squares. For 1673 unique observed structure amplitudes $[I > 2\sigma(I)]$ collected at room temperature on a Philips PW 1100 diffractometer in the range $6° < 2\theta < 50°$ the R value is 0.026 ($R_w = 0.029$). All calculations were carried out by using SHELX76.

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Section de Chimie
Université de Lausanne
Place du Château 3
CH-1005 Lausanne, Switzerland

Tommaso Carofiglio
Carlo Floriani*

Dipartimento di Chimica
Università di Perugia
I-06100 Perugia, Italy

Marzio Rosi

Istituto di Strutturistica Chimica
Centro di Studio per la Strutturistica
Diffrattometrica del CNR
Università di Parma
I-43100 Parma, Italy

Angiola Chiesi-Villa
Corrado Rizzoli

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