



Amphiphilic organoruthenium oxomolybdenum and oxovanadium clusters†

Georg Süss-Fink,^{a*} Laurent Plasseraud,^a Vincent Ferrand,^a
Sandrine Stanislas,^a Antonia Neels,^a Helen Stoeckli-Evans,^a Marc Henry,^b
Gabor Laurenczy^c and Raymond Roulet^c

^a Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

^b Laboratoire de Chimie Moléculaire de l'Etat Solide, Université Louis Pasteur, Institut Le Bel, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex, France

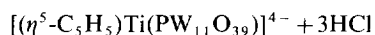
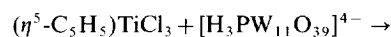
^c Institut de Chimie Minérale et Analytique, Université de Lausanne-BCH, CH-1015 Lausanne, Switzerland

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Abstract—*Para*-cymene ruthenium dichloride dimer reacts in aqueous solution with sodium molybdate or sodium vanadate to give the amphiphilic clusters $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{Ru}_4\text{Mo}_4\text{O}_{16}]$ (**1**) and $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{Ru}_4\text{V}_6\text{O}_{19}]$ (**4**) respectively. The analogous reaction of hexamethylbenzene ruthenium dichloride dimer with sodium vanadate gives $[(\eta^6\text{-C}_6\text{Me}_6)_4\text{Ru}_4\text{V}_6\text{O}_{19}]$ (**5**). The mixed-metal clusters $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)_3\text{Rh}_3\text{Mo}_4\text{O}_{16}]$ (**2**) and $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_3\text{Rh}_2\text{Mo}_4\text{O}_{16}]$ (**3**) are accessible from a mixture of *para*-cymene ruthenium dichloride dimer and pentamethylcyclopentadienyl rhodium dichloride dimer with sodium molybdate in aqueous solution. The crystal structure analyses of **1** and **4** reveal different framework geometries of the metal oxygen skeletons. ¹⁷O NMR spectroscopy and partial charge calculations confirm the presence of three different types of oxygen atoms in **1**. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: arene; ruthenium; molybdenum; vanadium; oxo clusters; X-ray structure.

The past two decades have witnessed a steadily growing interest in molecules containing both, organometallic groups and oxometallic entities [1]. Such clusters are accessible by metathesis reaction between an organometallic halide and an oxometallic anion.



Since the discovery of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{PW}_{11}\text{O}_{39})]^{4-}$ in 1978 by W. G. Klemperer and co-workers [2], a large number of organometallic oxide complexes have been prepared, in particular by W. G. Klemperer [3], K.

Isobe [4] and R. G. Finke [5]. This type of compound contains soft as well as hard metal centers and hydrophobic as well as hydrophilic ligands. The combination of low- and high-valent transition metals and the amphiphilic character predispose these molecules also as homogeneous catalysts for oxidation reactions; the catalytic potential of these compounds has been reviewed recently [6]. Furthermore organometallic oxo clusters provide molecular models for heterogeneous catalysts derived from organometallic complexes adsorbed at metal oxide surfaces [7].

Recently, in a preliminary communication, we reported the neutral amphiphilic cluster $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{Ru}_4\text{Mo}_4\text{O}_{16}]$ (**1**) which was found to present a unique framework geometry [8]. In this paper we extend our study to hexamethylbenzene ruthenium and pentamethylcyclopentadienyl rhodium units as well as to vanadate. Thus, the synthesis and characterisation of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)_3$

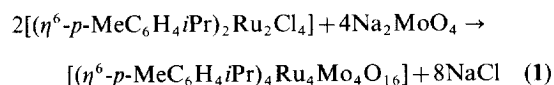
† Dedicated to The Lord Lewis of Newnham—mentor, inspirer and friend.

* Author to whom correspondence should be addressed.

$\text{Rh}_3\text{Mo}_4\text{O}_{16}$] (2) $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2\text{Mo}_4\text{O}_{16}]$ (3), $[(p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{Ru}_4\text{V}_6\text{O}_{19}]$ (4) and $[(\eta^6\text{-C}_6\text{Me}_6)_4\text{Ru}_4\text{V}_6\text{O}_{19}]$ (5) are reported; in addition we describe the characterisation of the three different types of oxygen atoms in **1** by ^{17}O NMR spectroscopy and by electron-density calculations.

RESULTS AND DISCUSSION

The *para*-cymene complex $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2\text{Ru}_2\text{Cl}_4]$ reacts with Na_2MoO_4 in aqueous solution at room temperature to give the neutral organoruthenium oxomolybdenum cluster $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{Ru}_4\text{Mo}_4\text{O}_{16}]$ (**1**) only. Complex **1** is sparingly soluble in water and aromatic hydrocarbons, and well soluble in polar organic solvents such as dichloromethane or methanol.



Single-crystal X-ray structure analysis of $1 \cdot 2 \text{C}_6\text{H}_5\text{Me}$ (orange, rod-like crystals) revealed the molecule to contain a unique $\text{Ru}_4\text{Mo}_4\text{O}_{12}$ framework which can be described as a central Mo_4O_4 cube with four folded ORuO flaps resembling the sails of a windmill. The molecular structure of **1** is depicted in Fig. 2. Important bond lengths and angles are presented in Table 1. The distortion $[\text{Mo}(2)\text{—O}(2)\text{—Mo}(1) 106.04(12)^\circ, \text{O}(12)\text{—Mo}(1)\text{—O}(2) 71.37(10)^\circ]$ with respect to the idealized cubic representation is due to the geometry of the oxygen atoms of the central cube which is more tetrahedral than octahedral. Eight of the twelve framework oxygen atoms are doubly bridging, while four are quadruply bridging. Each ruthenium atom is coordinated to an $\eta^6\text{-}p\text{-cymene}$ ligand $[\text{Ru}(1)\text{—C6 ring centroid } 1.627 \text{ \AA}]$, and each

molybdenum atom carries a terminal oxo ligand $[\text{Mo}(1)\text{—O}(7) 1.706(3) \text{ \AA}]$.

A calculation of the charge distribution in **1**, based on the application of the partial charge model [9], to the structural data of **1** gave the following results: The partial charge on the four ruthenium atoms is +1.093, and on the four molybdenum atoms +1.737, reflecting the electronegativity difference between ruthenium and molybdenum. The four *p*-cymene ligands have a partial charge of -0.412 , whereas there is a clear differentiation of the different oxo ligands: The terminal oxo ligands ($\text{O}_4, \text{O}_7, \text{O}_8$ and O_{14}) have a partial charge of -0.492 , the doubly bridging oxo ligands ($\text{O}_1, \text{O}_3, \text{O}_5, \text{O}_6, \text{O}_{10}, \text{O}_{11}, \text{O}_{13}$ and O_{16}) -0.578 , and the quadruply bridging oxo ligands ($\text{O}_2, \text{O}_9, \text{O}_{12}$ and O_{15}) -0.769 . Thus, the electronic density driven from the metal atoms has flown mainly onto oxo atoms, but also onto the aromatic ligands. It is interesting to note the strong discrimination among the oxygen atoms due to their relative structural environment, with the lowest electronic structural density found on the terminal oxygen atoms.

The three different types of oxygen atoms in **1** are also confirmed by ^{17}O NMR spectroscopy: A sample of **1**, enriched in ^{17}O , prepared from enriched Na_2MoO_4 , gives rise to three completely resolved signals, in addition to the signal of the MoO_4^{2-} anion at $\delta 748$ ppm. These signals can be easily assigned on the basis of a qualitative correlation between the shift of ^{17}O signal and the decreasing number of metal centres bound to the oxygen atom [10]. Thus, the signal at $\delta 783$ ppm corresponds to the four terminal (μ_1) oxygen atoms in **1**, while the eight doubly bridging (μ_2) and the four quadruply bridging (μ_4) oxygen atoms give rise to a resonance at $\delta 21$ and -7 ppm, respectively.

Sodium molybdate reacts with a 1:1 mixture of *para*-cymene ruthenium dichloride dimer and pentamethylcyclopentadienyl rhodium dichloride dimer

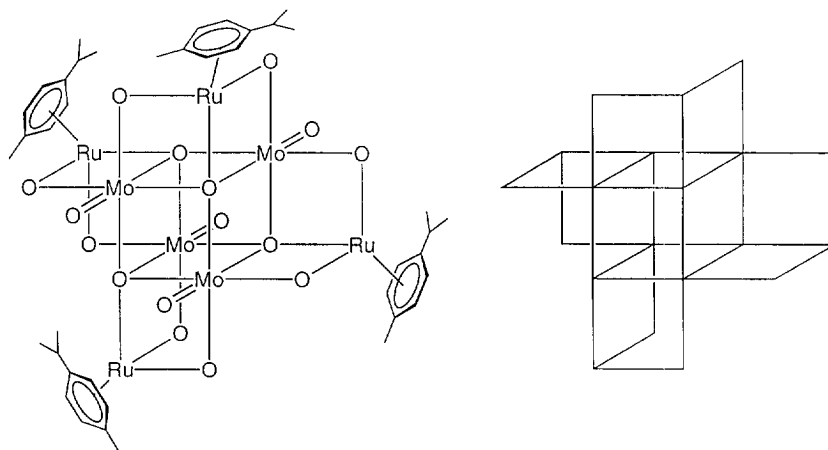


Fig. 1. Molecular representation of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{Ru}_4\text{Mo}_4\text{O}_{16}]$ (**1**).

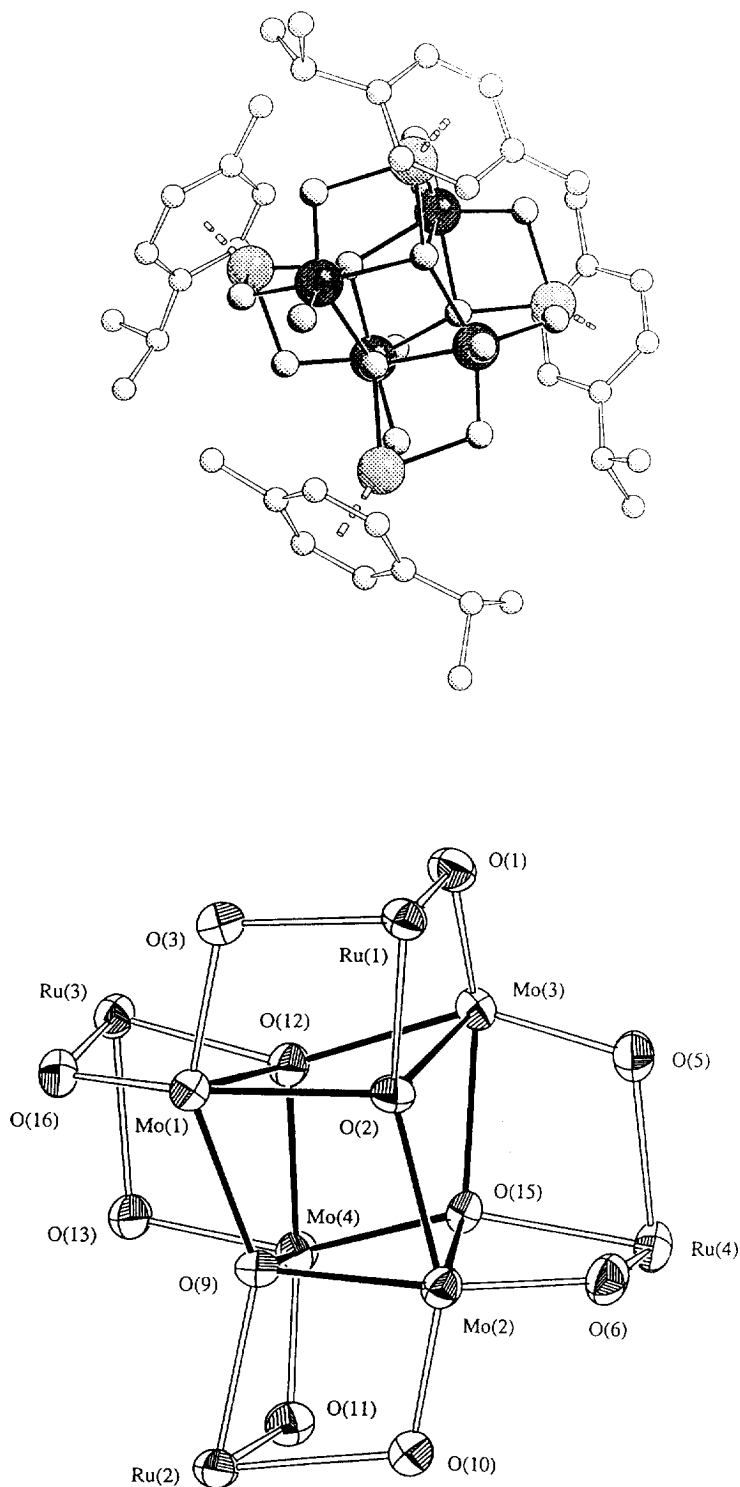
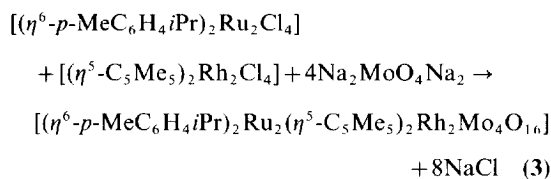
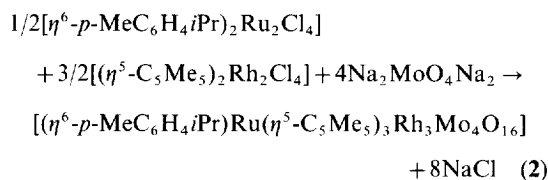


Fig. 2. Molecular structure of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{Ru}_4\text{Mo}_4\text{O}_{16}]$ (1). (a) Hydrogen atoms and two toluene molecules have been omitted for clarity. (b) $\text{Ru}_4\text{Mo}_4\text{O}_{12}$ framework with labelling scheme.

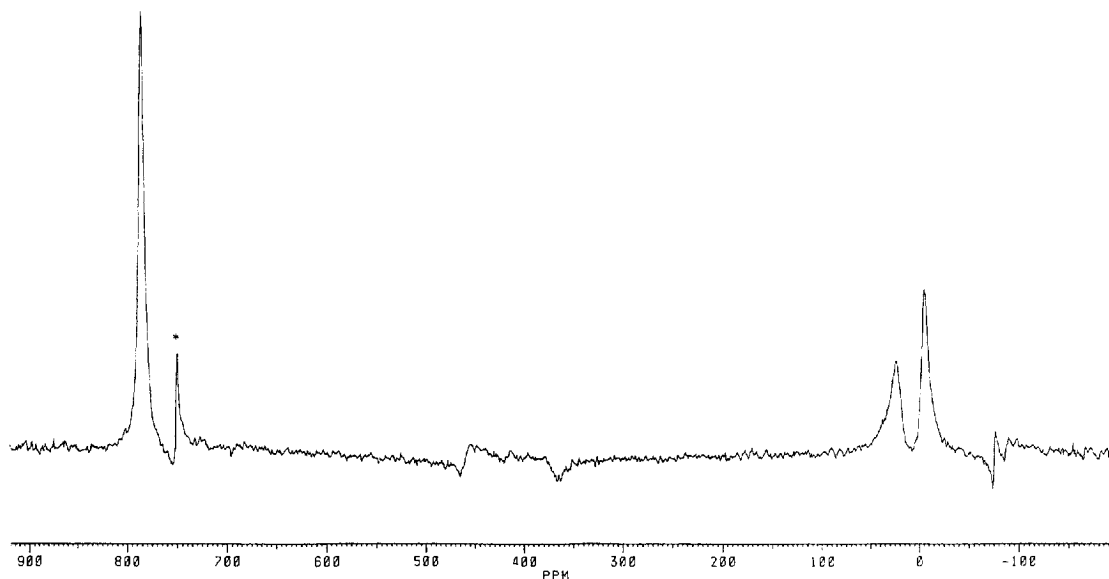
Table 1. Selected bond lengths (Å) and angles (°) for $[(\eta^6-p\text{-MeC}_6\text{H}_4i\text{Pr})_4\text{Ru}_4\text{Mo}_4\text{O}_{16}]$ (**1**)

Ru(1)—O(1)	2.088(3)
Ru(1)—O(2)	2.089(3)
Mo(1)—O(2)	2.122(3)
Mo(1)—O(3)	1.804(3)
Ru(1)—O(3)	2.094(3)
Mo(1)—O(7)	1.706(3)
Mo(1)—O(9)	2.073(3)
Mo(1)—O(12)	2.365(3)
Mo(1)—O(16)	1.798(3)
Mo(2)—O(2)—Mo(1)	106.04(12)
Mo(1)—O(9)—Ru(2)	145.40(14)
Mo(3)—O(12)—Mo(1)	105.31(11)
O(10)—Ru(2)—O(11)	80.53(12)
O(7)—Mo(1)—O(16)	103.93(14)
O(9)—Mo(1)—O(12)	72.20(10)
O(2)—Mo(1)—O(12)	71.37(10)

in aqueous solution to yield a mixture of mixed ruthenium-rhodium complexes, from which $[(\eta^6-p\text{-MeC}_6\text{H}_4i\text{Pr})\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)_3\text{Rh}_3\text{Mo}_4\text{O}_{16}]$ (**2**) and $[(\eta^6-p\text{-MeC}_6\text{H}_4i\text{Pr})_2\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2\text{Mo}_4\text{O}_{16}]$ (**3**) can be isolated by thin-layer chromatography.



The two mixed ruthenium-rhodium clusters **2** and **3** have a very similar infrared spectrum which, however, differs significantly from that of **1** but resembles the Mo—O absorption pattern of the known [4a] rhodium cluster $[(\eta^5\text{-C}_5\text{Me}_5)_4\text{Rh}_4\text{Mo}_4\text{O}_{16}]$. Both **2** and **3** show two strong bands at 925, 898 cm^{-1} and 927, 901 cm^{-1} respectively, which can be assigned to the vibrations of the terminal Mo=O bonds. Characteristic absorptions at 689, 642, 584, 538 cm^{-1} (**2**) and 692, 641, 587, 538 cm^{-1} (**3**) are attributed to the Mo—O vibrations of the internal oxygen atoms, in line with the assignment proposed by K. Isobe *et al.* for $[(\eta^5\text{-C}_5\text{Me}_5)_4\text{Rh}_4\text{Mo}_4\text{O}_{16}]$ [4a]. On the basis of the infrared spectra, it can be concluded that the mixed ruthenium-rhodium clusters **2** and **3** do not adopt the structure of the windmill-like ruthenium cluster **1**, but the triple cube-like structure of the rhodium cluster $[(\eta^5\text{-C}_5\text{Me}_5)_4\text{Rh}_4\text{Mo}_4\text{O}_{16}]$. Accordingly, the ^1H NMR spectrum of **2** shows a 1 : 3 ratio of the *p*-cymene and pentamethylcyclopentadienyl signals. However, there are three possibilities of replacing two $(\text{C}_5\text{Me}_5)\text{Rh}$ units in $[(\eta^5\text{-C}_5\text{Me}_5)_4\text{Rh}_4\text{Mo}_4\text{O}_{16}]$ by two $(\eta^6-p\text{-MeC}_6\text{H}_4i\text{Pr})\text{Ru}$ fragments, so that three isomers can be expected for **3**. Indeed, the ^1H NMR spectrum reveals **3** to be a mixture of at least two isomers, because, instead of one CH_3 doublet of the isopropyl substituent of the *p*-cymene ligand, two doublet signals centered at $\delta = 1.38$ and 1.37 ppm are observed.

Fig. 3. ^{17}O NMR spectrum of $[(\eta^6-p\text{-MeC}_6\text{H}_4i\text{Pr})_4\text{Ru}_4\text{Mo}_4\text{O}_{16}]$ (**1**) in CDCl_3 (*excess of MoO_4^{2-}).

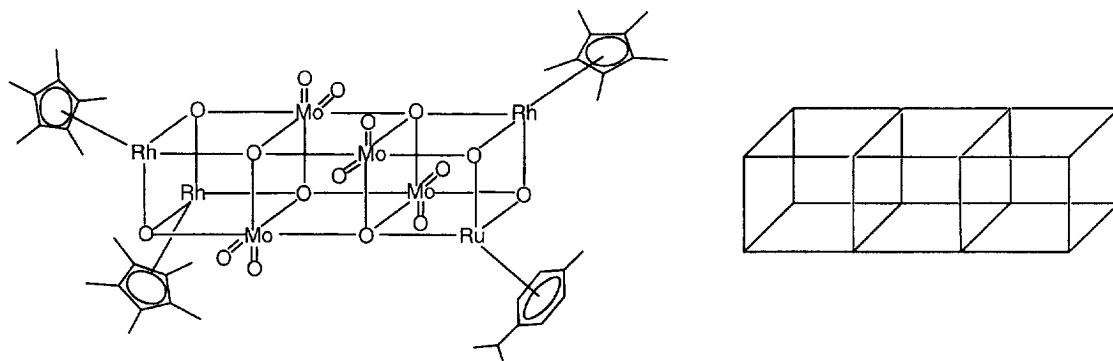
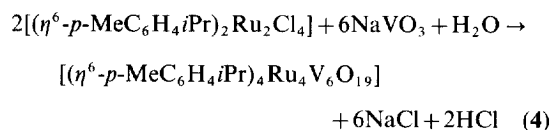


Fig. 4. Proposed molecular representation of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{Ru}(\eta^6\text{-C}_5\text{Me}_5)_3\text{Rh}_3\text{Mo}_4\text{O}_{16}]$ (**2**) with the triple-cube geometry of the $\text{RuRh}_3\text{Mo}_4\text{O}_8$ framework.

With sodium vanadate, *p*-cymene ruthenium dichloride dimer reacts in aqueous solution to give organoruthenium oxovanadium cluster $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})_4\text{Ru}_4\text{V}_6\text{O}_{19}]$ (**4**). Complex **4** is also soluble in both, dichloromethane and water.



The ^1H NMR spectrum of **4** shows the four *p*-cymene ligands to be equivalent, since there is only one set of signals for the methyl, isopropyl and aromatic protons with correct integral ratio. In the IR spectrum of **4**, the absorptions at 1089, 1037, and 944 cm^{-1} correspond to the stretching vibration of the terminal $\text{V}=\text{O}$ bonds. Bands at 677 and 568 cm^{-1} can be assigned to the vibrations of bridging (μ_3) oxygen atoms, while an absorption at 493 cm^{-1} is attributed to the vibration of a central (μ_6) oxygen atom.

The structure analysis of a single crystal of **4** reveals a $\text{Ru}_4\text{V}_6\text{O}_{13}$ framework which can be described as a quadruple-cube with a μ_6 -oxygen atom at the centre. This structure can be derived from that of the hypothetical $\text{V}_6\text{O}_{19}^{8-}$ anion, isostructural with the well-known $\text{Nb}_6\text{O}_{19}^{8-}$ [11], $\text{Ta}_6\text{O}_{19}^{8-}$ [12], $\text{Mo}_6\text{O}_{19}^{2-}$ [13] and $\text{W}_6\text{O}_{19}^{2-}$ [14] anions. It is also found in the known clusters $[(\text{C}_5\text{Me}_5)_4\text{Rh}_4\text{V}_6\text{O}_{19}]$ and $[(\text{C}_5\text{Me}_5)_4\text{Ir}_4\text{V}_6\text{O}_{19}]$ reported by K. Isobe *et al.* [4c,15]. The structure of **4** is shown in Fig. 5. Selected bond distances and angles are listed in Table 4. The cluster presents a quadruple-cube framework that contains four RuV_3O_4 cubic units alternatively fitted through $\text{V}-\text{O}$ bonds at the three edges of the cube. The central oxygen atom of the V_6O_{19} group is common to all four RuV_3O_4 units, thus all oxygen atoms of the V_6O_{19} group, except for the terminal oxygen atom, participate in the quadruple-cube cluster. Each vanadium atom carries a terminal oxygen atom [$\text{O}(6)-\text{V}(4)$ 1.607(4) Å], and each ruthenium atom is coordinated to a η^6 -*p*-cymene ligand. In an alternative view, **4** can be considered as

comprising one $\text{V}_6\text{O}_{19}^{8-}$ unit and four $(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{Ru}^{2+}$ groups, sitting on alternating faces of the octahedron formed by the hexavanadate unit through oxygen bridges. The vanadium atoms can be described as octahedrally coordinated. The ruthenium atom in the $(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{Ru}^{2+}$ group is bound to three adjacent bridging O atoms [$\text{Ru}(4)-\text{O}(8)$ 2.103(4) Å].

Whereas sodium molybdate does not react with the hexamethylbenzene analogue $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2\text{Cl}_4]$ to give a complex analogous to **1**, sodium vanadate reacts to give $[(\eta^6\text{-C}_6\text{Me}_6)_4\text{Ru}_4\text{V}_6\text{O}_{19}]$ (**5**), analogous to **4**. Like **4**, complex **5** is soluble in both water and organic solvents, but it forms blue crystals, while **4** has a violet colour. The IR, MS and ^1H NMR data of **5** suggest the compound to have the same structure as the *p*-cymene analogue **4**.

EXPERIMENTAL

The following chemicals were purchased from commercial sources and used without further purification: $\text{RuCl}_3 \cdot n \text{H}_2\text{O}$ (Johnson Matthey); $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Métaux Précieux); (R)-(-)-5-Isopropyl-2-methyl-1,3-cyclo-hexadiene (Merck); hexamethylde-warbenzene (Aldrich); hexamethylbenzene (Lancaster), $\text{Na}_2\text{MoO}_4 \cdot 2 \text{H}_2\text{O}$ (Fluka); NaVO_3 (Fluka). The organic solvents were refluxed over appropriate desiccants, distilled, and saturated with nitrogen. The bidistilled water degassed and saturated with N_2 prior to use. The ^1H NMR spectra were recorded on a Varian Gemini 200 BB instrument. ^{17}O NMR spectra were measured on a Bruker AM 360 spectrometer working at 48.82 MHz and using 10 mm o.d. sample tubes, the solvent was CD_2Cl_2 . Total spectral width of 55.6 kHz with 8 K data points for the FIDs (10^4 – 10^5 transients added) were used. ^{17}O chemical shift were measured with respect to bulk water (external reference, 0 ppm). To flatten the baseline larger pre-scan-delay values (DE) were used causing some first order phase errors. The IR spectra were recorded on a Perkin-Elmer FTIR 1720 X spectrophotometer (4000–400 cm^{-1}) as KBr pellets. The mass spectra (FAB)

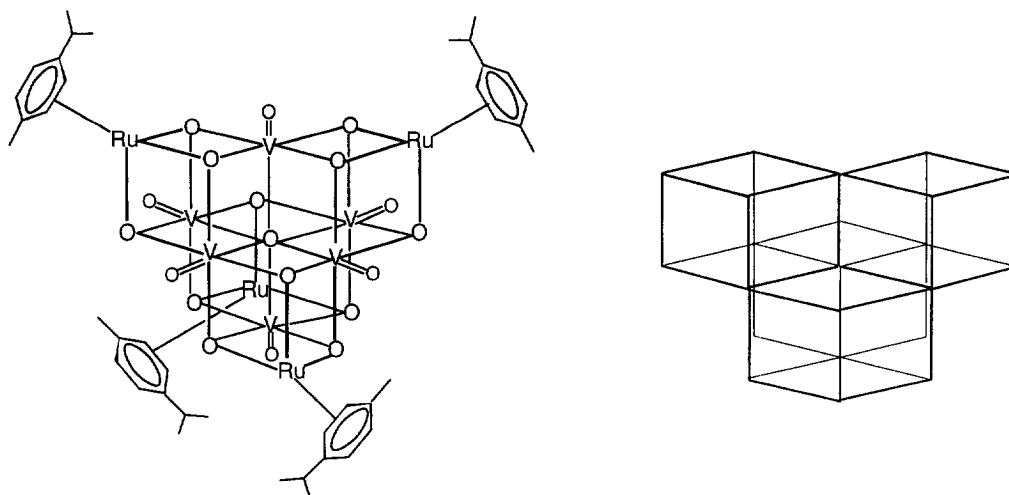


Fig. 5. Molecular representation of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{Ru}_4\text{V}_6\text{O}_{19}]$ (**4**).

were performed by Prof. Titus A. Jenny, University of Fribourg. Microanalytical data were obtained from the Mikroelementaranalytisches Laboratorium ETH Zürich. The starting materials $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2\text{Ru}_2\text{Cl}_4]$ [16], $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2\text{Cl}_4]$ [16] and $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2\text{Cl}_4]$ [17] were synthesised according to the literature procedures.

Preparation of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{Ru}_4\text{Mo}_4\text{O}_{16}]$ (**1**)

A suspension of $[(p\text{-MeC}_6\text{H}_4\text{iPr})_2\text{Ru}_2\text{Cl}_4]$ (200 mg, $3.27 \cdot 10^{-4}$ mol) in 20 cm^3 of water was added dropwise to an aqueous solution (10 cm^3) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (790 mg, $3.3 \cdot 10^{-3}$ mol). The mixture was stirred for 4 h at 25°C . After evaporation of the water, the product was extracted with CH_2Cl_2 (20 cm^3) and dried over MgSO_4 . (**1**) was recrystallised from a mixture of dichloromethane and toluene (1:1) to give analytically pure orange crystals (155 mg, 60% yield). IR (KBr): $\nu[\text{cm}^{-1}] = 921, 874$ (terminal oxygen atom); 785, 739, 642 and 602 (bridging oxygen atom). MS (FAB+): m/z : 1581 (^{101}Ru , ^{96}Mo). ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 1.39$ (d, 6H, $\text{CH}(\text{CH}_3)_2$), 2.27 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.97 (sp, ^1H , $\text{CH}(\text{CH}_3)_2$), 5.30 (d, 2H, C_6H_4), 5.37 (d, 2H, C_6H_4). Found: C, 30.33; H 3.51. Calc. for $\text{C}_{40}\text{H}_{56}\text{Mo}_4\text{O}_{16}\text{Ru}_4$: C, 30.39; H, 3.57%.

Preparation of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)_3\text{Rh}_3\text{Mo}_4\text{O}_{16}]$ (**2**) and $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2\text{Mo}_4\text{O}_{16}]$ (**3**)

$[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2\text{Cl}_4]$ (200 mg, $3.24 \cdot 10^{-4}$ mol) and $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2\text{Ru}_2\text{Cl}_4]$ (200 mg, $3.27 \cdot 10^{-4}$ mol) were suspended in 50 cm^3 of water and treated with an aqueous solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (1.57 g, $6.5 \cdot 10^{-3}$ mol) in 20 cm^3 of water. The mixture was stirred for 12 h. The resulting red-orange solution was extracted with 30 cm^3 of dichloromethane, then the

organic layer was collected and dried with MgSO_4 , giving a crude red-orange powder product on evaporation of the solvent. The crude product was dissolved in a minimum of dichloromethane and separated by thin-layer chromatography on silica ($\text{CH}_2\text{Cl}_2/\text{acetone}/\text{methanol}$, 5:10:3). The products **2** and **3** were isolated from the two main bands by elution with $\text{CH}_2\text{Cl}_2/\text{acetone}/\text{methanol}$ (5:10:3) and evaporation to dryness after filtration of MgSO_4 . (a) $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)_3\text{Rh}_3\text{Mo}_4\text{O}_{16}]$ (**2**): IR (KBr): $\nu[\text{cm}^{-1}] = 925, 898$ (terminal oxygen atom); 689, 642, 584 and 538 (bridging oxygen atom). MS (FAB+): m/z : 1590 (^{101}Ru , ^{103}Rh , ^{96}Mo). ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 1.38$ (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.68 (s, 45H, $\text{C}_5(\text{CH}_3)_5$), 2.25 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.99 (sp, ^1H , $\text{CH}(\text{CH}_3)_2$), 5.31 (d, 2H, C_6H_4), 5.37 (d, 2H, C_6H_4). Found: C, 35.22; H 4.36. Calc. for $\text{C}_{40}\text{H}_{59}\text{Mo}_4\text{O}_{16}\text{RuRh}_3 \cdot 2\text{C}_6\text{H}_{12}$: C, 35.45; H, 4.97% (20% yield). (b) $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2\text{Ru}_2(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2\text{Mo}_4\text{O}_{16}]$ (**3**): IR (KBr): $\nu[\text{cm}^{-1}] = 927, 901$ (terminal oxygen atom); 692, 641, 587 and 538 (bridging oxygen atom). MS (ES): $[\text{M} + \text{H}]^+ = 1588$ (^{101}Ru , ^{103}Rh , ^{96}Mo). ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 1.38, 1.37$ (2 doublets, 12H, $\text{CH}(\text{CH}_3)_2$), 1.67 (s, 30H, $\text{C}_5(\text{CH}_3)_5$), 2.25 (s, 6H, $\text{C}_6\text{H}_4\text{CH}_3$), 2.99 (sp, 2H, $\text{CH}(\text{CH}_3)_2$), 5.35 (m, 8H, C_6H_4). Found: C, 32.57; H, 3.81. Calc. for $\text{C}_{40}\text{H}_{58}\text{Mo}_4\text{O}_{16}\text{Ru}_2\text{Rh}_2 \cdot \text{C}_6\text{H}_{12}$: C, 33.03; H, 4.34% (15% yield).

Preparation of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_4\text{Ru}_4\text{V}_6\text{O}_{19}]$ (**4**)

A suspension of $[(p\text{-C}_6\text{H}_4\text{iPrMe})_2\text{Ru}_2\text{Cl}_4]$ (200 mg, $3.27 \cdot 10^{-4}$ mol) in 20 cm^3 of water was added dropwise to an aqueous solution (35 cm^3) of NaVO_3 (398 mg, $3.27 \cdot 10^{-3}$ mol). The mixture was stirred for 4 h at 25°C . After evaporation of the water, the solid was extracted with CH_2Cl_2 (20 cm^3). The dichloromethane solution was dried over MgSO_4 , and evaporated to

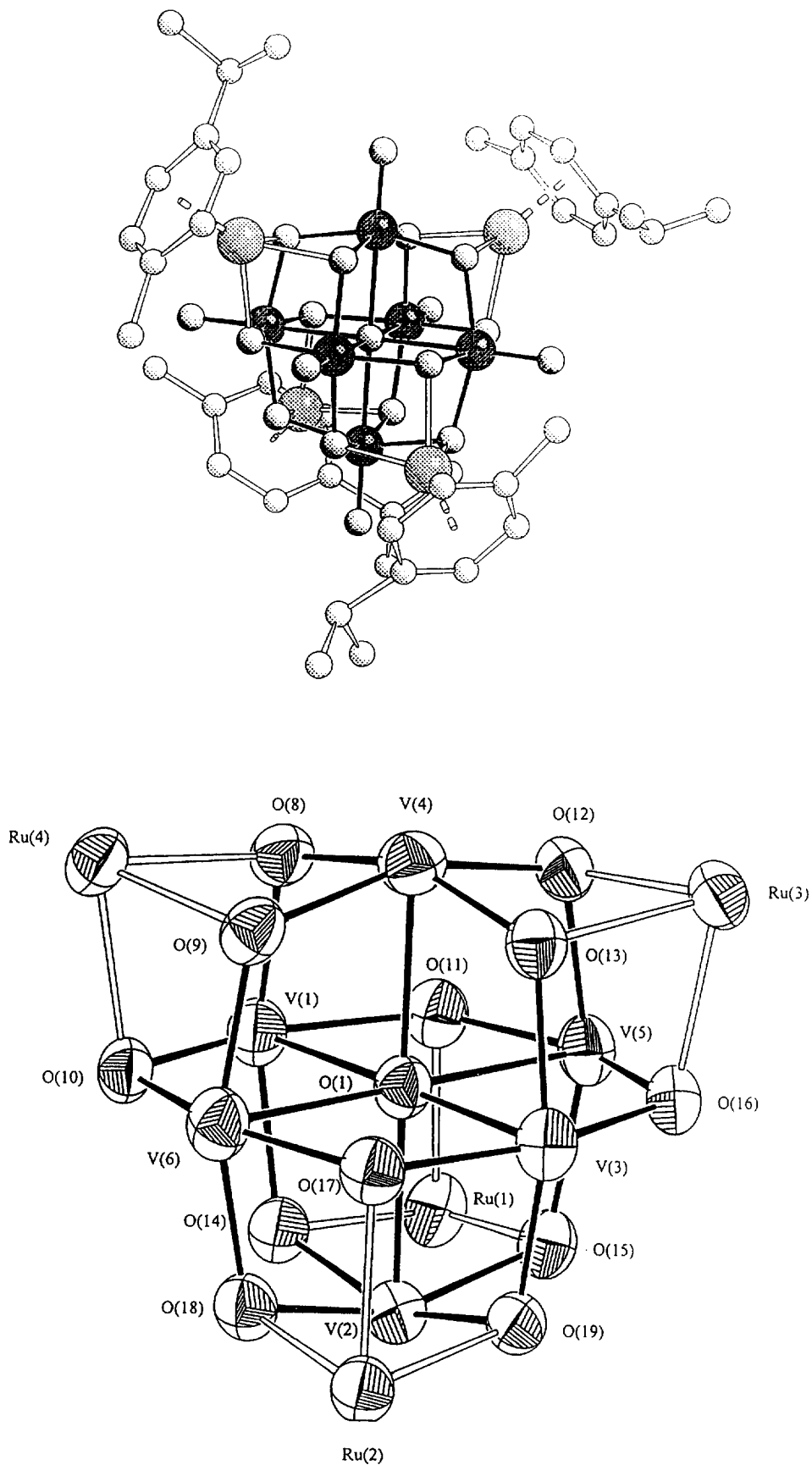


Fig. 6. Molecular structure of $[(\eta^6-p\text{-MeC}_6\text{H}_4i\text{Pr})_4\text{Ru}_4\text{V}_6\text{O}_{19}]$ (4). (a) Hydrogen atoms and two water molecules have been omitted for clarity. (b) $\text{Ru}_4\text{V}_6\text{O}_{13}$ framework with labelling scheme.

Table 2. Selected bond lengths (Å) and angles (°) for $[(\eta^6-p\text{-MeC}_6\text{H}_4\text{Pr})_2\text{Ru}_4\text{V}_6\text{O}_{19}]$ (**4**)

Ru(1)—O(11)	2.082(4)	V(1)—O(7)	1.607(4)	V(4)—O(1)	2.240(4)	V(6)—O(1)	2.235(4)
Ru(4)—O(8)	2.103(4)	V(1)—O(8)	1.905(4)	V(4)—O(6)	1.607(4)	V(6)—O(3)	1.610(4)
Ru(4)—O(9)	2.108(4)	V(1)—O(10)	1.922(4)	V(4)—O(8)	1.928(4)	V(6)—O(9)	1.890(4)
Ru(4)—O(10)	2.103(4)	V(1)—O(11)	1.912(4)	V(4)—O(9)	1.924(4)		
V(1)—O(1)	2.232(4)	V(2)—O(1)	2.239(4)	V(5)—O(11)	1.916(4)		
V(1)—O(1)—V(6)	90.27(13)	V(1)—O(1)—V(2)	89.86(14)	V(6)—O(1)—V(2)	90.24(14)	V(1)—O(1)—V(4)	90.40(14)
V(6)—O(1)—V(4)	90.34(13)	V(2)—O(1)—V(4)	179.4(2)	V(1)—O(1)—V(3)	179.8(2)	V(6)—O(1)—V(3)	89.81(14)
V(6)—O(1)—V(5)	179.5(2)	V(1)—O(8)—Ru(4)	96.6(2)	V(4)—O(8)—Ru(4)	97.0(2)	V(6)—O(9)—V(4)	112.6(2)
V(6)—O(9)—Ru(4)	95.5(2)	V(4)—O(9)—Ru(4)	96.9(2)	V(6)—O(10)—V(1)	111.3(2)	V(6)—O(10)—Ru(4)	95.0(2)
V(1)—O(10)—Ru(4)	96.1(2)	O(7)—V(1)—Ru(4)	93.7(2)	Ru(3)—V(4)—Ru(4)	174.08(4)	O(3)—V(6)—O(9)	101.7(2)
O(3)—V(6)—O(10)	101.3(2)	O(9)—V(6)—O(10)	86.9(2)	O(3)—V(6)—O(18)	101.0(2)	O(9)—V(6)—O(18)	157.3(2)
O(10)—V(6)—O(18)	89.4(2)	O(3)—V(6)—O(17)	100.5(2)	O(9)—V(6)—O(17)	90.3(2)	O(10)—V(6)—O(17)	158.2(2)
O(3)—V(6)—O(1)	179.2(2)	O(9)—V(6)—O(1)	78.9(2)	O(10)—V(6)—O(1)	79.3(2)	O(18)—V(6)—O(1)	78.4(2)
O(17)—V(6)—O(1)	79.0(2)	O(10)—Ru(4)—O(8)	76.49(14)	O(10)—Ru(4)—O(9)	76.8(2)	O(8)—Ru(4)—O(9)	76.0(2)

dryness to give the product as a dark purple powder (199 mg, 78% yield). **4** was recrystallised from a mixture of cyclohexane and toluene (1 : 1) to give purple crystals. IR (KBr): $\nu[\text{cm}^{-1}] = 1089, 1037, 944$ (terminal oxygen atom), 677, 568 (bridging oxygen atom), 493 (central oxygen atom). MS (FAB+): m/z : 1551 (^{101}Ru , ^{51}V). ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 1.43$ (d, 6H, $\text{CH}(\text{CH}_3)_2$), 2.40 (s, 3H, $\text{C}_6\text{H}_4\text{CH}_3$), 3.09 (sp, ^1H , $\text{CH}(\text{CH}_3)_2$), 5.75 (d, 2H, C_6H_4), 5.81 (d, 2H, C_6H_4). Found: C, 31.05; H, 3.60. Calc. for $\text{C}_{40}\text{H}_{56}\text{O}_{19}\text{Ru}_4\text{V}_6$: C, 30.98; H, 3.64%.

Preparation of $[(\eta^6\text{-C}_6\text{Me}_6)_4\text{Ru}_4\text{V}_6\text{O}_{19}]$ (**5**)

A suspension of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2\text{Cl}_4]$ (100 mg, $1.49 \cdot 10^{-4}$ mol) in 25 cm^3 of water was added dropwise to an aqueous solution (20 cm^3) of NaVO_3 (181 mg, $1.49 \cdot 10^{-3}$ mol). The mixture was stirred for 4 h at 25 °C. After evaporation of the water, the solid was extracted with CH_2Cl_2 (20 cm^3). The dichloromethane solution was dried over MgSO_4 , and evaporated to dryness to give the product as a dark blue powder (95 mg, 68% yield). IR (KBr): $\nu[\text{cm}^{-1}] = 1075, 1024, 939$ (terminal oxygen atom), 675, 567 (bridging oxygen atom), 492 (central oxygen atom). ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 2.29$ (s, 18H, $\text{C}_6(\text{CH}_3)_6$), MS (FAB+): m/z : 1663 (^{101}Ru , ^{51}V). Found: C, 31.11; H, 3.97. Calc. for $\text{C}_{48}\text{H}_{72}\text{O}_{19}\text{Ru}_4\text{V}_6 \cdot 4\text{CH}_2\text{Cl}_2$: C, 31.19; H, 4.03%.

^{17}O -enrichment procedure

A solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (395 mg, $1.63 \cdot 10^{-3}$ mol) in 1 cm^3 of 10% enriched H_2^{17}O (Yeda, Israel) was heated to 90 °C for 3 h with stirring and cooled to 25 °C. To the resulting solution, containing ^{17}O -enriched MoO_4^{2-} , 200 mg ($3.27 \cdot 10^{-4}$ mol) of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr})_2\text{Ru}_2\text{Cl}_4]$ were added, then the mixture was heated to 95 °C with vigorous stirring during 3 h. Then the solvent was removed, the residual orange solid was extracted with dichloromethane (25 cm^3) and crystallised from a mixture of dichloromethane and toluene (1 : 1).

X-ray structure determination of **1** and **4**

Suitable crystals of **1** and **4** were obtained as indicated in the synthetic section. Selected experimental crystallographic details of the structure determination of **1** and **4** are given in Tables 3 and 4. For **1**, single-crystal X-ray diffraction data were collected at -50 °C on a Stoe-Siemens AED2 4-circle diffractometer using Mo-K_α graphite monochromated radiation ($\lambda = 0.71073$ Å; $\omega/2\theta$ scans), whereas for **4**, the X-ray diffraction data were collected at room temperature on a Stoe Imaging Plate Diffractometer System (Stoe and Cie 1995) equipped with a one-circle goniometer and a graphite Mo-K_α monochromated

Table 3. Crystallographic and refinement data for $\mathbf{1} \cdot 2(\text{CH}_3\text{C}_6\text{H}_5)$

Compound	1
Crystal habit	Red-orange rod
Crystal size (mm)	0.57 × 0.27 × 0.17
Empirical Formula	$\text{C}_{40}\text{H}_{36}\text{Mo}_4\text{O}_{16}\text{Ru}_4 \cdot 2\text{CH}_3\text{C}_6\text{H}_5$
Formula Weight (g mol ⁻¹)	1765.30
Temperature (K)	223
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	13.846(2)
<i>b</i> (Å)	15.210(2)
<i>c</i> (Å)	16.104(1)
α (°)	88.12(1)
β (°)	78.94(1)
γ (°)	65.47(1)
<i>U</i> (Å ³)	3023.7(6)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	1.939
Diffractometer	Stoe-Siemens AED2 4-circle
Radiation	Mo- <i>K</i> _α graphite monochromated
λ (Å)	0.71073
Scan type	ω -2 θ
Absorption coefficient (Mo- <i>K</i> _α , mm ⁻¹)	1.659
<i>F</i> (000)	1736
θ Scan range(°)	2.01 ≤ θ ≤ 25.50
<i>h</i> , <i>k</i> , <i>l</i> ranges	-16 ≤ <i>h</i> ≤ 16, -18 ≤ <i>k</i> ≤ 18, 0 ≤ <i>l</i> ≤ 19
Reflections collected	11234
Independent reflections	11234
Reflections observed [<i>I</i> > 2 σ (<i>I</i>)]	9940
Data/restraints/parameters	11234/0/717
R_1 [<i>I</i> > 2 σ (<i>I</i>)]/ <i>R</i> ₁ (all data) ^a	0.0324/0.0404
wR_2 [<i>I</i> > 2 σ (<i>I</i>)]/ <i>wR</i> ₂ (all data) ^b	0.0701/0.0736
Goodness of fit on <i>F</i> ^{2c}	1.118
Largest diff. Peak and hole (e Å ⁻³)	0.749 and -0.580
Empirical Absorption correction	Empirical [DIFABS]
Transmission factors: min/max	0.667/1.248

$$^a R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}}$$

$$^c S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2} \quad (n = \text{number of reflections, } p = \text{number of parameters}).$$

radiation ($\lambda = 0.71073$ Å, φ oscillation). Data were collected in one stage: 120 exposures (3 min per exposure) were obtained at 80 mm with $0 \leq \varphi \leq 120^\circ$ and with the crystal oscillated through 1° in φ . The structure of **1** was solved by Patterson methods and that of **4** by direct methods using the program SHELXS 86 [18]. For both compounds, **1** and **4**, the structure refinement, using weighted full-matrix least-square on *F*², was carried out using the program SHELXL 93 [19]. During the refinement of **1**, two molecules of toluene were located. Two partially occupied H₂O positions were found for **4** (occupancies 0.33 and 0.5). For compound **1**, an empirical absorption correction was applied using DIFABS (PLATON) [20]. Non-H atoms were refined anisotropically, and hydrogen atoms were included in calculated positions and refined as riding atoms using the SHELXL 93 default parameters. The figures were drawn using the programs ZORTEP [21] (thermal ellipsoids, 50%

probability level) and SCHAKAL [22]. Complete tables of bond lengths and angles and lists of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ (U.K.).

Application of the partial charge model

The partial charge model [9] was applied to the crystallographic data of **1**, using the following parametrization: Electronegativities (Mulliken scale, values in eV): $\chi(\text{H}) = 7.176$; $\chi(\text{C}, \text{sp}^2) = 8.876$; $\chi(\text{C}, \text{sp}^3) = 8.148$; $\chi(\text{O}) = 9.630$; $\chi(\text{Ru}) = 4.11$ and $\chi(\text{Mo}) = 8.876$. Atomic sizes (covalent radii in Å): $r(\text{H}) = 0.37$; $r(\text{C}) = 0.77$; $r(\text{O}) = 0.73$; $r(\text{Ru}) = 1.25$; $r(\text{Mo}) = 1.30$. Total electrical charge = 0.0 (neutral complex). The program calculated the minimum interatomic distance to be 0.94

Table 4. Crystallographic and refinement data for $4 \cdot 0.83 \text{ H}_2\text{O}$

Compound	4
Crystal habit	dark-brown block
Crystal size (mm)	$0.38 \times 0.34 \times 0.23$
Empirical Formula	$\text{C}_{40}\text{H}_{56}\text{O}_{19}\text{Ru}_4\text{V}_6 \cdot 0.83\text{H}_2\text{O}$
Formula Weight (g mol^{-1})	1565.78
Temperature (K)	293(2)
Crystal system	Cubic
Space group	$Pa\bar{3}$
a (Å)	31.753(2)
b (Å)	31.753(2)
c (Å)	31.753(2)
α (°)	90
β (°)	90
γ (°)	90
U (Å ³)	32016(3)
Z	24
D_{calc} (g cm^{-3})	1.949
Diffraction	Stoe Imaging Plate Diffractometer System (IPDS)
Radiation	Mo- K_α
λ (Å)	0.71073
Scan type	φ oscillation scans
Absorption coefficient (Mo- K_α , mm^{-1})	2.166
$F(000)$	18488
θ Scan range(°)	$1.81 \leq \theta \leq 24.08$
h, k, l ranges	$-36 \leq h \leq 36, -36 \leq k \leq 23, -36 \leq l \leq 31$
Reflections collected	119211
Independent reflections	8432
Reflections observed [$I > 2\sigma(I)$]	5677
Data/restraints/parameters	8428/0/646
$R_1 [I > 2\sigma(I)]/R_1$ (all data) ^a	0.0366/0.0602
$wR_2 [I > 2[\text{gkS1}](I)]/wR_2$ (all data) ^b	0.0964/0.1076
Goodness of fit on F^2 ^c	0.906
Largest diff. Peak and hole (e Å^{-3})	1.033 and -0.534

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)} \right]^{1/2}$$

$$^c S = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{(n-p)} \right]^{1/2} \quad (n = \text{number of reflections}, p = \text{number of parameters}).$$

Å, the mean electronegativity to be 8.03 eV, the dipolar moment to be 0.07 D and the electrostatic balance to be -127.7 eV.

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REFERENCES

- Day, V. W. and Klemperer, W. G., *Science*, 1985, **228**, 533.
- Ho, R. K. C. and Klemperer, W. G., *J. Am. Chem. Soc.*, 1978, **100**, 6772.
- (a) Chae, H. K., Klemperer, W. G. and Day V. W., *Inorg. Chem.*, 1989, **28**, 1424; (b) Chae, H. K., Klemperer, W. G., Paez Loyo, D. E., Day, V. W. and Ebersbacher T. A., *Inorg. Chem.*, 1991, **31**, 3187; (c) Klemperer, W. G. and Marquart, T. A., *Coord. Chem. Rev.*, 1993, **128**, 209.
- (a) Hayashi, Y., Toriumi, K. and Isobe, K., *J. Am. Chem. Soc.*, 1988, **110**, 3666; (b) Do, Y., You, X.-Z., Zhang, C., Ozawa, Y. and Isobe, K., *J. Am. Chem. Soc.*, 1991, **113**, 5892; (c) Hayashi, Y., Ozawa, Y. and Isobe, K., *Inorg. Chem.*, 1991, **30**, 1025; (d) Park, T. J., Nishioka, T., Suzuki, T. and Isobe, K., *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1968.
- (a) Lin, Y., Nomiya, K. and Finke R. G., *Inorg. Chem.*, 1993, **32**, 6040; (b) Trovarelli, A. and Finke, R. G., *Inorg. Chem.*, 1993, **32**, 6034; (c) Pohl, M. and Finke R. G., *Organometallics*, 1993, **12**, 1453; (d) Rapko, B. M., Pohl, M. and Finke, R. G., *Inorg. Chem.*, 1994, **33**, 3625; (e) Pohl, M., Lyon, D. K., Mizuno, N., Nomiya, K. and Finke, R. G., *Inorg. Chem.*, 1995, **34**, 1413; (f) Nomiya, K., Nozaki, Ch., Kaneko, M., Finke, R. G. and Pohl, M., *J. Organomet. Chem.*, 1995, **505**, 23; (g) Pohl, M., Lin, Y., Weakley, T. J. R., Nomiya, K., Kaneko, M., Weiner, H. and Finke, R. G., *Inorg. Chem.*, 1995, **34**, 767.
- Hill, C. L. and Prosser-McCartha, C. M., *Coord. Chem. Rev.*, 1995, **143**, 407.

7. Ichikawa, M., Pan, W., Imada, Y., Yamaguchi, M., Isobe, K. and Shido, T., *J. Mol. Catal.*, 1996, **107**, 23.
8. Süss-Fink, G., Plasseraud, L., Ferrand, V. and Stoeckli-Evans, H., *J. Chem. Soc., Chem. Commun.* 1997, in press.
9. Henry, M., *Top. Mol. Organ. Eng.*, 1997, **15**, 273.
10. Filowitz, M., Klemperer, W. G., Messerle, L. and Shum, W., *J. Am. Chem. Soc.*, 1976, **98**, 2345.
11. Lindqvist, I., *Arkiv. Kemi.*, 1952, **5**, 247.
12. Lindqvist, I. and Aronsson, B., *Arkiv. Kemi.*, 1954, **7**, 49.
13. Nagano, O. and Sasaki, Y., *Acta. Cryst.*, 1979, **B35**, 2387.
14. Fuchs, J., Freiwald, W. and Hartl, H., *Acta. Cryst.*, 1978.
15. Hayashi, Y., Ozawa, Y. and Isobe, K., *Chem. Lett.*, 1989, 425.
16. Bennett, M. A., Huang, T.-N., Matheson, T. W. and Smith, A. K., *Inorg. Synth.*, 1982, **21**, 74.
17. Booth, B. L., Haszeldine, R. N. and Hill, M., *J. Chem. Soc. (A)*, 1969, 1299.
18. Sheldrick, G. M., SHELXL 86. *Acta Crystallogr., Sect. A.*, 1990, **46**, 467.
19. Sheldrick, G. M., SHELXL 93, A Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1993.
20. Spek, A. I., *Acta Crystallogr., Sect. A.*, 1990, **46**, C 34.
21. Zsolnai, L., Pritzkow, H., ZORTEP: University of Heidelberg, Heidelberg, Germany, 1994 (a modified version of ORTEP (for PC) by Johnson, C. K., Oak Ridge National Laboratory, Oak Ridge, TN).
22. Keller, E., SCHAKAL 92/V256, A Fortran Program for The Graphical Representation of Molecular and Crystallographic Models, University of Freiburg, Freiburg, Germany, 1992.