[(*p*-Pr^{i}C$_6$H$_4$Me)$_4$Ru$_4$Mo$_4$O$_{16}$]: an amphiphilic organoruthenium oxomolybdenum cluster presenting a unique framework geometry

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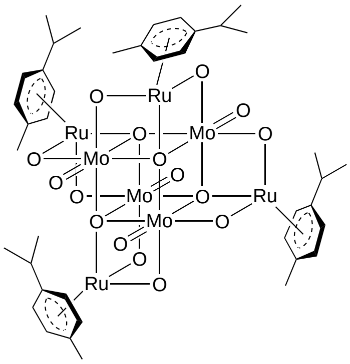
The amphiphilic title compound, easily accessible from (*p*-cymene)ruthenium dichloride dimer and sodium molybdate in aqueous solution, presents an unprecedented $Ru_4Mo_4O_{12}$ framework comprising a central Mo_4O_4 cube with four folded ORuO flaps resembling the sails of a windmill.

The past two decades have witnessed a steadily growing interest in molecules containing both organometallic groups and oxometallic entities,[1] particularly since they provide molecular models for heterogeneous catalysts derived from organometallic complexes adsorbed at metal oxide surfaces.[2] Organometallic metaloxo clusters contain soft as well as hard metal centers, and hydrophobic as well as hydrophilic ligands. Since the discovery of the first species of this type, $[(C_5H_5)TiPW_{11}O_{39}]^{4-}$ in 1978,[3] this field has been pioneered mainly by the groups of Klemperer,[4] Isobe,[5] and Finke.[6] 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.[7]



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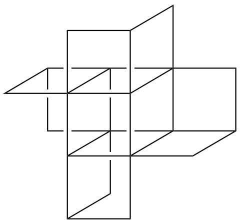


Here, we report the synthesis and structure of [(*p*-Pr^{i}C$_6$H$_4$-Me)$_4$Ru$_4$Mo$_4$O$_{16}$] **1**, a neutral organoruthenium oxomolybdenum cluster which presents an unprecedented geometry of the $Ru_4Mo_4O_{12}$ framework. Compound **1** is easily accessible from (*p*-cymene)ruthenium dichloride dimer and sodium molybdate in aqueous solution (Scheme 1).† Orange crystals of correct elemental composition are obtained by crystallization from dichloromethane–toluene. Compound **1** is amphiphilic, that is to say sparingly soluble in both water and aromatic hydrocarbons, and well soluble in polar organic solvents such as dichloromethane or methanol.

$$2\,[(p\text{-Pr}^iC_6H_4Me)_2Ru_2Cl_4] + 4\,Na_2MoO_4$$
$$\downarrow$$
$$[(p\text{-Pr}^iC_6H_4Me)_4Ru_4Mo_4O_{16}] + 8\,NaCl$$

Scheme 1

The FAB mass spectrum of **1** shows the molecular ion at *m/z* 1581 presenting the expected Ru_4Mo_4 isotope pattern. In the ^1H NMR spectrum (CD_2Cl_2) of **1**, the four *p*-cymene ligands give rise to only one set of signals at δ 1.39 (d, 6, *J* 7 Hz), 2.27 (s, 3), 2.97 (spt, 1, *J* 7 Hz), 5.30 (d, 2, *J* 6 Hz) and 5.37 (d, 2, *J* 6 Hz), showing all ruthenium positions to be equivalent. In the IR spectrum (KBr) of **1**, the Mo=O stretching vibrations are observed at 921s and 874m cm^{-1}, while the Mo–O–Ru stretches are assigned to the absorptions at 785s, 739s, 642m and 602s cm^{-1}.

Single-crystal X-ray structure analysis§ of **1**·$2C_6H_5Me$ (orange, rod-like crystals) revealed the molecule to contain a unique $Ru_4Mo_4O_{12}$ framework which can be described as a central Mo_4O_4 cube with four folded ORuO flaps resembling the sails of a windmill. The distortion [Mo(2)–O(2)–Mo(1) 106.04(12)°, O(12)–Mo(1)–O(2) 71.37(10)°] with respect to

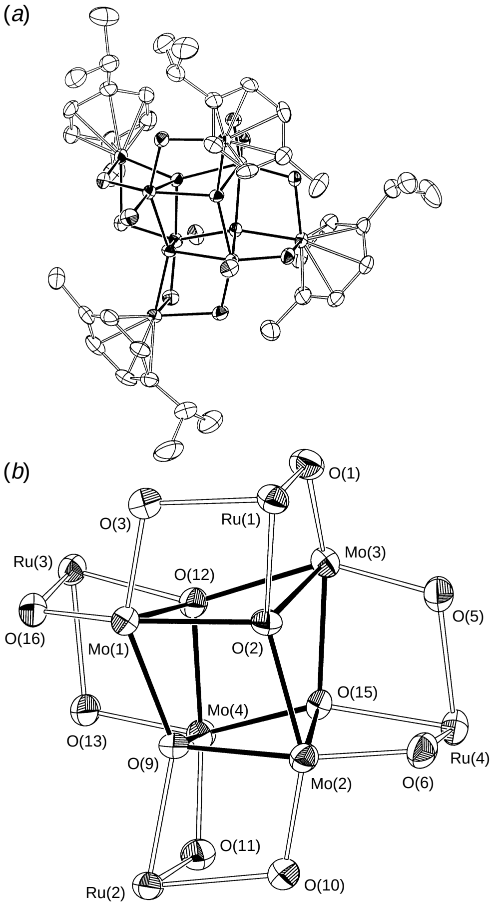
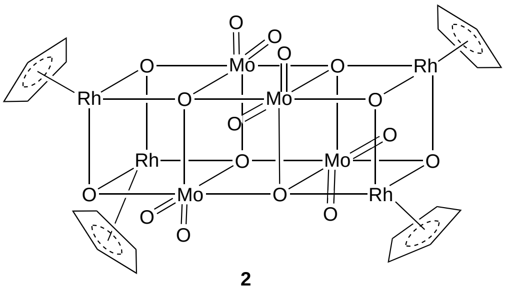


Fig. 1 ORTEP[11] representation of the molecular structure of **1**. (*a*) Complete molecule, hydrogen atoms and two toluene molecules (in the crystal) omitted for clarity. (*b*) $Ru_4Mo_4O_{12}$ framework with labelling scheme. Selected bond distances and angles (°): Mo(1)–O(2) 2.122(3), Mo(1)–O(3) 1.804(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). Ru(1)–O(1) 2.088(3), Ru(1)–O(2) 2.089(3), Ru(1)–O(3) 2.094(3); O(12)–Mo(1)–O(9) 72.20(11), Mo(3)–O(12)–Mo(1) 105.31(11), O(7)–Mo(1)–O(16) 103.93(2). Ru(2)–O(9)–Mo(1) 145.40(2), O(10)–Ru(2)–O(11) 80.53(12).

the idealized cubic representation is due to the geometry of the oxygen atoms of the central cube which is more tetrahedral than octahedral (Fig. 1). Eight of the twelve framework oxygen atoms are doubly bridging, while four are quadruply bridging. Each ruthenium atom is coordinated to an η^6-*p*-cymene ligand [Ru(1)–C_6 ring centroid 1.627 Å], and each molybdenum atom carries a terminal oxo ligand [Mo(1)–O(7) 1.706(3) Å].

The cluster [$(C_5Me_5)_4Rh_4Mo_4O_{16}$] **2**, reported by Isobe and coworkers,[5a] which is isoelectronic to **1**, has a completely different structure: the $Rh_4Mo_4O_{12}$ framework forms a triple cube which is more closed than the open windmill-like structure of **1**. As a consequence, each molybdenum atom carries two terminal oxo ligands, and four of the eight framework oxygen atoms are triply bridging, while the other four are quadruply bridging.



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Another Mo_4O_{16} unit, found in the solid phase $Cs_3Mo_4P_3O_{16}$, also contains a central Mo_4O_{16} cube; however, the framework geometry is completely different: the Mo_4O_{16} core must be considered as four MoO_6 octahedra each sharing three edges with three MoO_6 units giving an array with tetrahedral symmetry.[7]

Interestingly, with ruthenium the reaction seems to work only for the *p*-cymene derivative. Up to now it has not been possible to isolate the benzene and hexamethylbenzene analogues of **1**.

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Footnotes and References

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† *Synthesis* of **1**: A suspension of [$(p\text{-Pr}^iC_6H_4Me)_2Ru_2Cl_4$] (200 mg, 3.27×10^{-4} mol) in 20 cm^3 of water was added dropwise to an aqueous solution (10 cm^3) of $Na_2MoO_4\cdot 2H_2O$ (790 mg, 3.3×10^{-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 crystallized from dichloromethane–toluene (1 : 1) to give, after drying *in vacuo*, analytically pure orange crystals (155 mg, 60%).

§ *Crystal structure data* for **1**: $C_{40}H_{56}Mo_4O_{16}Ru_4\cdot 2C_7H_8$ (including two molecules of toluene per cluster), triclinic, space group, $P\bar{1}$, a = 13.846(2), b = 15.210(2), c = 16.1038(14) Å, α = 88.124(11), β = 78.938(10), γ = 65.471(11)°, U = 3023.7(6) Å^3, Z = 2, D_c = 1.939 g cm^{-3}, T = 223 K, μ(Mo-Kα) = 1.66 mm^{-1}. The data were measured using a Stoe-Siemens AED2 four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). 11234 independent reflexions were measured by ω–2θ scans in the range $2.0 < \theta < 25.5°$; 9939 were considered observed [$I > 2\,\sigma(I)$]. The structure was solved by Patterson and Fourier techniques using the program SHELXS-86[8] and refined by full-matrix least squares on F^2, using SHELXL-93.[9] Hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-93 default parameters. An empirical absorption correction was applied using DIFABS[10] (transmission factors min., max. 0.722, 1.174). Refinement converged at R_1 = 0.0337 and wR_2 = 0.0757 (observed data). CCDC 182/532.

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