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Synthesis and Structure of a High-Nuclearity Oxomolybdenum(V) Complex, $[(C_5Me_5Rh^{III})_8(Mo^V{}_{12}O_{36})(Mo^{VI}O_4)]^{2+}$

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Unlike oxomolybdenum(VI) complexes, which are known to contain as many as 36 Mo^{VI} centers,[1] polynuclear oxomolybdenum(V) complexes are restricted to dimers, several tetramers, a cyclic hexamer, and a cyclic octamer.[2] We report here the synthesis and structure of a larger, dodecanuclear oxomolybdenum(V) complex, $[(C_5Me_5Rh)_8(Mo^V{}_{12}O_{36})(Mo^{VI}O_4)]^{2+}$, prepared hydrothermally as a chloride salt from $[(C_5Me_5Rh)_2(OH)_3]Cl$ and $MoO_3{\cdot}2H_2O$ using the organometal hydroxide route previously employed in the synthesis of $[(C_5Me_5Rh)_4(V_6O_{19})]$.[3,4]

Mixtures of finely powdered $MoO_3{\cdot}2H_2O$[5] (83 mg, 0.46 mmol) and $[(C_5Me_5Rh)_2(OH)_3]Cl$[6] (0.10 g, 0.16 mmol) in 2 mL of water were heated at 190 °C for 2 days in several sealed, fused quartz tubes. Crystalline products from two such reactions (50 mg) were collected on a sintered glass frit and purified as follows. First, the crude product was extracted with 20 mL of acetone, the resulting dark red solution was filtered, and solvent was removed under vacuum to yield a brown powder. This material was then dissolved into 3 mL of acetonitrile, and the solution obtained was filtered. Addition of 15 mL of toluene followed by slow evaporation at 0 °C yielded 37 mg of crystalline product, **1**, that was collected by filtration and air-dried. Analytical data[7,8] were most consistent with the formulation $[(C_5Me_5Rh)_8(Mo_{13}O_{40})]Cl_2{\cdot}13H_2O$, implying a yield of 0.12 mmol or 13% based on Mo.

X-ray structural analysis[9] of crystals prepared as described above revealed the presence of discrete, ordered $[(C_5Me_5Rh)_8(Mo_{13}O_{40})]^{2+}$ cations (Figure 1a,b), disordered Cl^- and OH^- anions and disordered solvent molecules of crystallization. Each cation contains eight Rh^{III}, 12 Mo^V and one Mo^{VI} metal centers and although these metals, the 40 oxygen atoms (Figure 1c) and the eight cyclopentadienyl ring centers-of-gravity (designated as Cg) approximate rather closely full tetrahedral T_d symmetry, the cation possesses only rigorous C_s-*m* symmetry in crystals of **1**. Metal atoms Rh_1, Rh_2, Rh_4, Rh_5, Mo_1, Mo_2, and Mo_8 and oxygen atoms O_{1a}, O_{3a}, O_{6b}, O_{7b}, O_{3d}, O_{5d}, O_{1e}, and O_{2e} lie in the crystallographic mirror plane at $y = {}^1/_4$ in the unit cell; this mirror plane also bisects the $C_5(CH_3)_5{}^-$ ligands bonded to Rh_1, Rh_2, Rh_4, and Rh_5.

The 12 Mo^V centers, which are at the vertices of a truncated tetrahedron (Figure 1d), form six Mo_2O_{10} metal–metal-bonded dimers with the 2.661 (3, 5, 9, 4) Å[10] Mo^V–Mo^V bonds lying along the six tetrahedral edges. The cation of **1** is therefore a hexamer of Mo^V dimer a (structure a), just as lower nuclearity species are known to be tetramers,[2d] trimers,[2c] and dimers[2b] of the same, essentially isostructural, $Mo^V{}_2O_{10}$ unit. The eight Rh^{III} centers cap the eight faces of the $Mo^V{}_{12}$ truncated tetrahedron

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(7) Anal. Calcd for $C_{80}H_{120}Rh_8Mo_{13}O_{40}Cl_2{\cdot}13H_2O$:[8] C, 23.45; H, 3.59; Rh, 20.09; Mo, 30.44; Cl, 1.73. Found: C, 23.64; H, 3.53; Rh, 20.12; Mo, 30.18; Cl, 1.53. ^1H NMR (CD_3CN, TMS): δ 1.76 (CH_3, s), 1.89 (CH_3, s). ^{13}C NMR (CD_3CN, TMS): δ 9.44 (s, C_5Me_5), 9.89 (s, C_5Me_5), 93.27 (d, C_5Me_5, $J_{Rh-C} = 9$ Hz), 94.41 (d, C_5Me_5, $J_{Rh-C} = 10$ Hz). IR (Nujol mull, 400–1000 cm^{-1}): 968 (s), 954 (m), 851 (s), 756 (m), 736 (s), 624 (m), 612 (m), 549 (m), 502 (s), 468 (m) cm^{-1}.

(8) A typical analytical result is given in ref 7: chlorine and solvent contents varied significantly from sample to sample depending on the details of reaction, crystallization, and drying conditions.

(9) Single crystals of $[(C_5(CH_3)_5Rh)_8(Mo_{12}O_{36})(MoO_4)]Cl_{0.82}(OH)_{1.18}{\cdot}6.55H_2O{\cdot}2C_7H_8$ are, at 20 ± 1 °C, monoclinic, space group $P2_1/m\text{-}C^2_{2h}$ (No. 11) with $a = 16.884\ (4)$ Å, $b = 24.953\ (6)$ Å, $c = 19.868\ (5)$ Å, $\beta = 114.55\ (2)°$, $V = 7614\ (3)$ Å^3, and $Z = 2$ formula units ($d_{calcd} = 1.806$ g cm^{-3}; $\mu_a(Mo\ K\bar{\alpha}) = 1.95$ mm^{-1}). A total of 12454 independent absorption-corrected reflections having $2\theta(Mo\ K\bar{\alpha}) < 48.3°$ (the equivalent of 0.7 limiting Cu $K\bar{\alpha}$ spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (1.10° wide) ω scans and graphite-monochromated Mo $K\bar{\alpha}$ radiation. The structure was solved using the direct methods techniques with the Siemens SHELXTL-PLUS software package as modified at Crystalytics Co. The resulting structural parameters have been refined to convergence [R_1 (unweighted, based on F) = 0.054 for 7590 independent absorption-corrected reflections having $2\theta(Mo\ K\bar{\alpha}) < 48.3°$ and $I > 3\sigma(I)$] using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all but six full-occupancy and 10 partial-occupancy non-hydrogen atoms (which could not be satisfactorily refined as anisotropic atoms) and isotropic thermal parameters for the remaining non-hydrogen atoms and all hydrogen atoms of the cation. Methyl groups of the cation were included in the structural model as fixed idealized rigid rotors with sp^3-hybridized geometry and C–H bond lengths of 0.96 Å. The anion site is disordered, being occupied by Cl^- 41% of the time and OH^- 59% of the time. This site had the highest electron density in a difference Fourier phased on (anisotropic) metal atoms and isotropic oxygen and carbon atoms for the cation; the occupancy factor for an oxygen atom at this position refined to a value of 1.45. The crystal contains disordered solvent molecules of crystallization with the following atom types and occupancy factors: O_{1w} to O_{10w}, oxygen atoms with occupancies of 1.00, 0.40, 0.30, 0.30, 0.20, 0.15, 0.25, 0.40, 0.40, and 0.20, respectively; C_{1s} to C_{7s}, carbon atoms with occupancies of 1.00, 1.00, 0.50, 1.00, 0.60, 0.50, and 0.30, respectively. The compound was formulated as the water and toluene solvate principally because the disordered solvent sites $C_{1s} \rightarrow C_{6s}$ described a nearly planar six-membered ring with "interatomic" separations of 1.09–1.57 Å, even though the electron density at $C_{1s} \rightarrow C_{7s}$ could equally well be accounted for by disordered hydrogen-bonded water molecules. If water was the only solvent of crystallization present in the lattice and all sites with reasonable van der Waals and/or hydrogen bonding contacts were fully occupied, the formula for the crystal of **1** used in this study would be $[(C_5(CH_3)_5Rh)_8(Mo_{12}O_{36})(MoO_4)]Cl_{0.82}(OH)_{1.18}{\cdot}11H_2O$, in better agreement with the analytical data.[7,8] Presumably, this region of the lattice is occupied by a toluene molecule at least part of the time.

(10) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation in an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements included in the averaged value.

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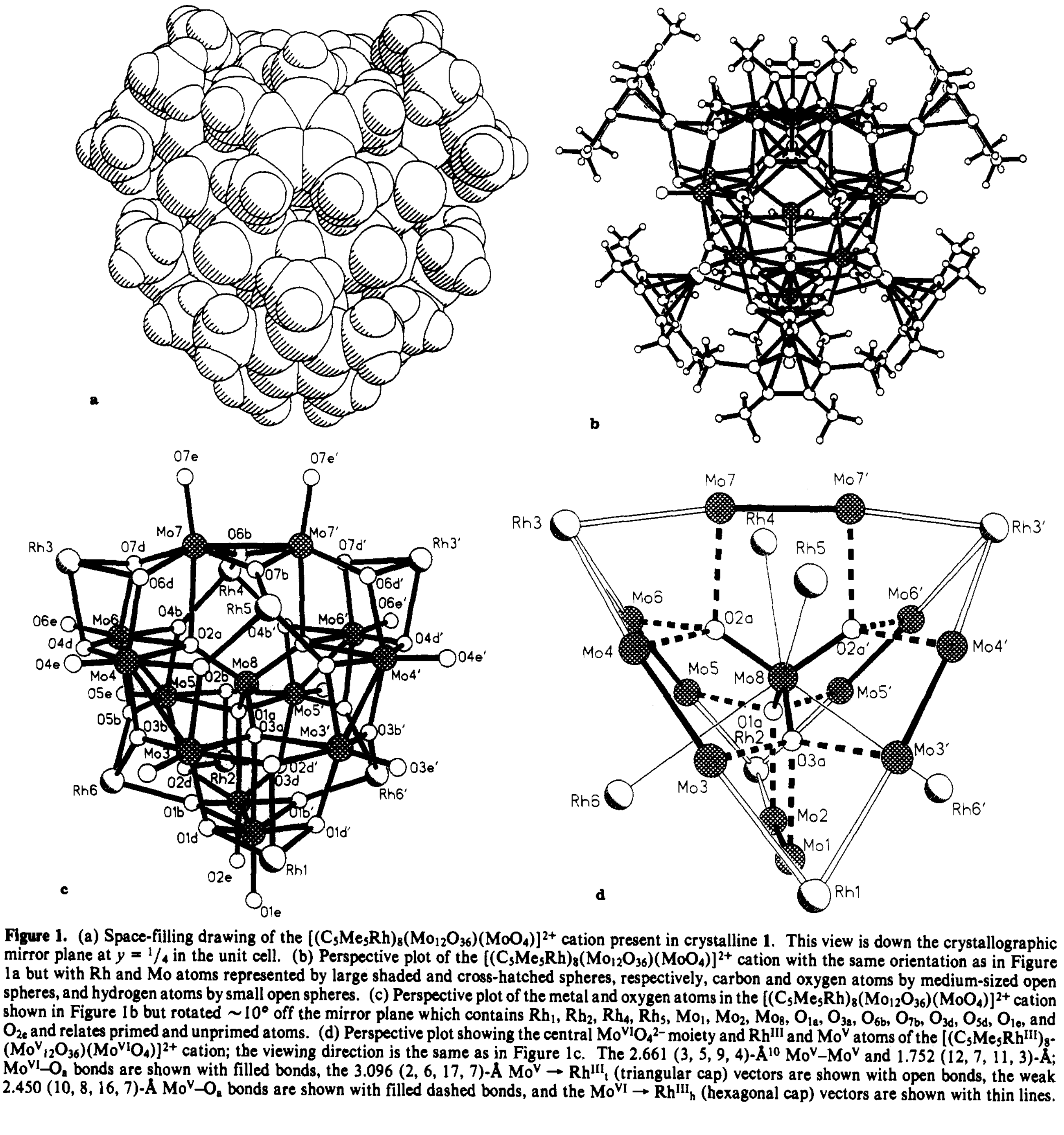
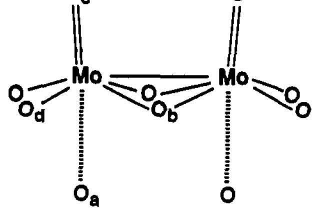


Figure 1. (a) Space-filling drawing of the $[(C_5Me_5Rh)_8(Mo_{12}O_{36})(MoO_4)]^{2+}$ cation present in crystalline 1. This view is down the crystallographic mirror plane at $y = {}^1/_4$ in the unit cell. (b) Perspective plot of the $[(C_5Me_5Rh)_8(Mo_{12}O_{36})(MoO_4)]^{2+}$ cation with the same orientation as in Figure 1a but with Rh and Mo atoms represented by large shaded and cross-hatched spheres, respectively, carbon and oxygen atoms by medium-sized open spheres, and hydrogen atoms by small open spheres. (c) Perspective plot of the metal and oxygen atoms in the $[(C_5Me_5Rh)_8(Mo_{12}O_{36})(MoO_4)]^{2+}$ cation shown in Figure 1b but rotated ~10° off the mirror plane which contains Rh_1, Rh_2, Rh_4, Rh_5, Mo_1, Mo_2, Mo_8, O_{1a}, O_{3a}, O_{6b}, O_{7b}, O_{3d}, O_{5d}, O_{1e}, and O_{2e} and relates primed and unprimed atoms. (d) Perspective plot showing the central $Mo^{VI}O_4{}^{2-}$ moiety and Rh^{III} and Mo^V atoms of the $[(C_5Me_5Rh^{III})_8(Mo^V{}_{12}O_{36})(Mo^{VI}O_4)]^{2+}$ cation; the viewing direction is the same as in Figure 1c. The 2.661 (3, 5, 9, 4)-Å[10] Mo^V–Mo^V and 1.752 (12, 7, 11, 3)-Å Mo^{VI}–O_a bonds are shown with filled bonds, the 3.096 (2, 6, 17, 7)-Å $Mo^V \rightarrow Rh^{III}{}_t$ (triangular cap) vectors are shown with open bonds, the weak 2.450 (10, 8, 16, 7)-Å Mo^V–O_a bonds are shown with filled dashed bonds, and the $Mo^{VI} \rightarrow Rh^{III}{}_h$ (hexagonal cap) vectors are shown with thin lines.



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and form two interpenetrating $Rh^{III}{}_4$ tetrahedra. Four Rh^{III} atoms (Rh_1, Rh_2, Rh_3, and Rh'_3, collectively designated as Rh_t) cap triangular faces, and the other four Rh^{III} atoms (Rh_4, Rh_5, Rh_6, and Rh'_6, collectively designated as Rh_h) cap hexagonal faces (Figure 1d). A tetrahedral $Mo^{VI}O_4{}^{2-}$ anion is "encapsulated" at the center of the cation and each of its O_a oxygens is weakly bonded to three Mo^V centers of the $(Mo^V{}_{12}O_{36})^{12-}$ "cage". The 40 oxygen atoms of the cation are distributed among four distinct structural types: four O_a oxygens, each of which is strongly bonded at 1.752 (12, 7, 11, 3) Å to the central tetrahedral Mo^{VI} atom and weakly bonded at 2.450 (10, 8, 16, 7) Å to three Mo^V atoms; 12 O_b oxygens, each of which bridges the Mo^V atoms of a single Mo_2O_{10} dimer (structure a) and a face-capping $Rh^{III}{}_h$ atom; 12 O_d oxygen atoms, each of which bridges Mo^V atoms of adjacent Mo_2O_{10} dimers and a $Rh^{III}{}_t$ atom; and 12 O_e oxygens, each of which is terminally bonded at 1.679 (12, 4, 10, 7) Å to a Mo^V atom. Each Rh^{III} atom achieves an $18e^-$ configuration by being η^5-bonded to a $C_5(CH_3)_5{}^-$ ligand and three μ_3-oxygen atoms (O_b for Rh_h and O_d for Rh_t). Each Mo^V atom is octahedrally coordinated to one μ_4-O_a, two μ_3-O_b, two μ_3-O_d, and one terminal O_e oxygens. Additional average bond lengths and angles of interest include the following: Mo^V–O_b, 1.967 (10, 8, 19, 12) Å; Mo^V–O_d, 2.022 (10, 9, 19, 12) Å; Rh_t–Mo^V, 3.096 (2, 6, 17, 7) Å; $O_aMo^VO_e$, 169.9 (5, 3, 10, 7)°; $O_bMo^VO_e$, 107.3 (5, 4, 10, 12)°; $O_dMo^VO_e$, 101.0 (5, 5, 11, 12)°; $O_aMo^{VI}O_a$, 109.6 (5, 5, 9, 4)°; $Mo^VO_aMo^{VI}$, 122.9 (5, 4, 11, 7)°; $Mo^VO_aMo^V$, 93.2 (4, 2, 5, 7)°; $Mo^VO_bMo^V$, 85.1 (5, 4, 8, 7)°; $Mo^VO_dMo^V$, 123.4 (6, 5, 12, 7)°; $Mo^VO_bRh_h$, 137.5 (5, 4, 11, 12)°; $Mo^VO_dRh_t$, 96.2 (4, 6, 14, 12)°.

The $Mo_{13}O_{40}^{14-}$ core of the title complex has a metal–oxygen framework structure observed previously only in the $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ [11] and $[Al_{13}O_4(OH)_{25}(H_2O)_{11}]^{8+}$ [12] cations. Isomeric configurations of 40 oxygen atoms, 12 octahedral centers, and one tetrahedral center have been observed in molybdate chemistry, namely, the α-Keggin structure in α-$PMo^{VI}_{12}O_{40}^{3-}$,[13] α-$SiMo^{VI}_{12}O_{40}^{4-}$,[14] and α-$GeMo^{VI}_{12}O_{40}^{4-}$ [15] and the β-Keggin structure in β-$SiMo^{VI}_{12}O_{40}^{4-}$,[16] β-$PMo^V_4Mo^{VI}_8O_{40}^{7-}$,[17] and β-$AsMo^V_2Mo^{VI}_{10}O_{40}^{5-}$.[18] The so-called ε-Keggin structure[19] is presumably adopted in the title complex since it brings the octahedral metal centers together pairwise into close proximity, facilitating the formation of localized Mo–Mo bonds.

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Supplementary Material Available: For **1**, crystal structure analysis report, tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and ORTEP plots (31 pages); structure factor tables (18 pages). Ordering information is given on any current masthead page.

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