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Article

Preparation and Characterization of New Ruthenium and Osmium Containing Polyoxometalates, $[M(DMSO)_3Mo_7O_{24}]^{4-}$ (M = Ru(II), Os(II)), and Their Use as Catalysts for the Aerobic Oxidation of Alcohols

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A new heptamolybdate polyoxometalate structure containing ruthenium(II) or osmium(II) metal centers, $[M(II)(DMSO)_3Mo_7O_{24}]^{4-}$ (M = Ru, Os), was synthesized by reaction between $(NH_4)_6Mo_7O_{24}$ and *cis*-$M(DMSO)_4Cl_2$. X-ray structure analysis revealed the complexes to contain a ruthenium/osmium center in a trigonal antiprismatic coordination mode bound to three DMSO moieties via the sulfur atom of DMSO and three oxygen atoms of the new heptamolybdate species. The heptamolybdate consists of seven condensed edge-sharing MoO_6 octahedra with C_{2v} symmetry. Three Mo atoms are in classic type II octahedra with a *cis* dioxo configuration. Two Mo atoms are also type-II-like, but one of the short Mo–O bonds is associated with bridging oxygen atoms rather than terminal oxygen atoms. Two molybdenum atoms are unique in that they are in a trigonally distorted octahedral configuration with three short Mo–O bonds and two intermediate-long M–O bonds and one long Mo–O bond. The $[M(II)(DMSO)_3Mo_7O_{24}]^{4-}$ polyoxometalates were effective and in some cases highly selective catalysts for the aerobic oxidation of alcohols to ketones/aldehydes. The integrity of the polyoxometalate was apparently retained at high turnover numbers and throughout the reaction, and a variation of an oxometal type mechanism was proposed to explain the results.

Introduction

Polyoxometalates as an important class of inorganic compounds exhibit a diverse compositional range and significant structural versatility. These qualities are especially important in the area of catalysis whereby the structure and composition of a polyoxometalate can be logically varied to determine the catalytic activity. During the past 15 years, important advances have been in the use of polyoxomolybdates and transition metal substituted polyoxometalates as catalysts for oxidative transformations.[1] In this context, the possibility of combining noble metals and polyoxometalates for catalytic applications would appear to be especially attractive. Thus, various noble metal substituted polyoxometalates based on the Keggin,[2] Wells–Dawson,[3] and "sandwich"[4] structure types have been prepared and used in oxidative catalytic transformations with molecular oxygen,[2e,4b–d] hydrogen peroxide,[4e–g] *t*-butylperoxide,[2b,c,4g] and others.[2b,c] Several types of polyoxometalates such as the

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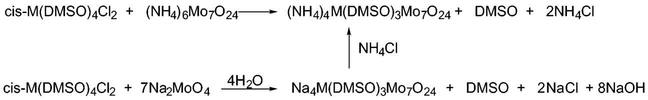
Lindqvist,[5] Keggin,[6] Wells−Dawson,[7] and smaller di- to pentametalate[8] structures have also been used to support noble metal complexes, although generally these compounds have not been investigated for oxidation catalysis. Organometallic cation salts of Keggin type anions are also known, and in one case, for $[(PPh_3)_2Rh(CO)]_x[XW_{12}O_{40}]$, combined hydroformylation−oxidation has been carried out.[9]

In this paper, we present the synthesis and characterization of a new type of polyoxometalate-supported organometallic complex (organometallic oxides),[10] analogous ruthenium(II) and osmium(II) DMSO complexes supported on a heptamolybdate, $[M(DMSO)_3Mo_7O_{24}]^{4-}$ (M = Ru(II), Os(II)). There are several novel features as per these compounds presented in this manuscript: (a) they are the first DMSO complexes supported on polyoxometalates although DMSO has been reported to be a ligand for ruthenium incorporated into polyoxometalates,[2a,e] (b) this is the first example of an osmium complex supported on a polyoxometalate, and (c) the heptamolybdate moiety is of a structure significantly different from that of the well-known paramolybdate anion, $[Mo_7O_{24}]^{6-}$. In addition, the $[M(DMSO)_3Mo_7O_{24}]^{4-}$ compounds are active and stable catalysts for the aerobic oxidation of alcohols. The selective oxidation of alcohols to carbonyl compounds is a very important transformation in organic synthesis. Over the past several years, an intense effort has been made to find environmentally benign methods to carry out these reactions with much emphasis on molecular oxygen as oxidant. Sheldon and Arends have summarized this subject with references up to the year 2000.[11] Since then, there has been additional substantial activity in this area with reports on the use of both heterogeneous and homogeneous catalytic systems. Homogeneous catalytic systems include those based on nitroxyl radicals (TEMPO) and various metal cocatalysts,[12] *N*-hydroxyphthalimide,[13] iron and ruthenium phthalocyanines,[14] and palladium[15] and ruthenium complexes.[16] In the domain of heterogeneous catalysis manganese,[17] nickel,[18] palladium,[19] platinum,[20] and ruthenium[21] based catalysts have been reported.

Scheme 1. Synthesis of $[Ru(II)(DMSO)_3Mo_7O_{24}]^{4}-$ and $[Os(II)(DMSO)_3Mo_7O_{24}]^{4}-$



Results and Discussion

Synthesis and Characterization. The $[Ru(II)(DMSO)_3Mo_7O_{24}]^{4-}$ and $[Os(II)(DMSO)_3Mo_7O_{24}]^{4-}$ polyanions are easily accessible as brown crystalline ammonium salts, NH_4-**1** and NH_4-**2**, respectively, by reaction of the known *cis*-Ru$(DMSO)_4Cl_2$ or *cis*-Os$(DMSO)_4Cl_2$ compounds with ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}$, Scheme 1. Alternatively, NH_4-**1** and NH_4-**2** were obtained by reaction of *cis*-Ru$(DMSO)_4Cl_2$ or *cis*-Os$(DMSO)_4Cl_2$ with sodium molybdate,

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Table 1. Crystal and Structure Refinement Data for $[M(DMSO)_3Mo_7O_{24}]^{4-}$ (M = Ru(II), Os(II))

	$[Ru(DMSO)_3Mo_7O_{24}]^{4-}$	$[Os(DMSO)_3Mo_7O_{24}]^{4-}$
empirical formula	$C_6H_{18}Mo_7O_{27}RuS_3 \cdot 6.5H_2O$, $4NH_4$	$C_6H_{18}Mo_7O_{27}OsS_3 \cdot 4.5H_2O$, $4NH_4$
fw	1551.07	1622.06
space group	$C2/c$	$C2/c$
T, K	120(2)	120(2)
λ	0.71073 Å	0.71073 Å
a, Å	36.310(7)	36.387(7)
b, Å	12.239(2)	12.248(2)
c, Å	22.379(5)	22.342(5)
β, deg	124.23(3)	124.23(3)
V, Å^3	8223(3)	8232(3)
Z	8	8
d_{calcd}, mg/cm^3	2.506	2.618
μ, mm^{-1}	2.674	5.387
final R indices[a] $[I > 2\sigma(I)]$	$R = 0.0572$, $R_w = 0.1429$	$R = 0.0554$, $R_w = 0.1655$
final R indices (all data)	$R = 0.0633$, $R_w = 0.1461$	$R = 0.0584$, $R_w = 0.1695$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = \sum[|F_o - F_c|]w^{1/2}]/\sum[F_o w^{1/2}]$.

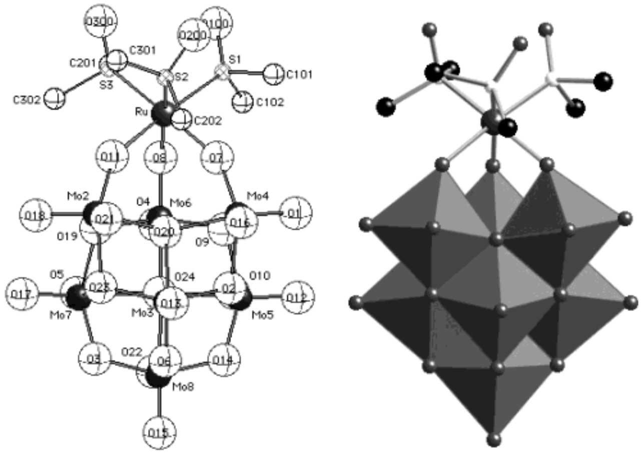

Figure 1. Structural representations of $[Ru(II)(DMSO)_3Mo_7O_{24}]^{4-}$ obtained from Crystal Maker.

Table 2. Selected Bond Distances and Angles for $[Ru(II)(DMSO)_3Mo_7O_{24}]^{4-}$

bond distances, Å		bond angles, deg	
Ru−S1	2.259(3) [2.253(3)][a]	O8−Ru−O7	84.9(3)
Ru−S2	2.250(3) [2.254(3)][a]	O8−Ru−O11	83.8(3)
Ru−S3	2.553(3) [2.242(3)][a]	O7−Ru−O11	93.1(3)
Ru−O11	2.080(8) [2.077(9)][a]	O9−Ru−S2	169.3 (2)
Ru−O8	2.059(8) [2.065(9)][a]	O7−Ru−S2	90.0(2)
Ru−O7	2.078(8) [2.077(9)][a]	O11−Ru−S2	87.1(2)
Mo2−O18	1.744(8)	O8−Ru−S3	90.6(2)
Mo2−O21	1.732(8)	O7−Ru−S3	174.9(2)
Mo2−O11	1.778(8)	O11−Ru−S3	88.8(2)
Mo2−O23	2.121(7)	S2−Ru−S3	94.86(11)
Mo2−O20	2.153(7)	O8−Ru−S1	92.4(2)
Mo2−O19	2.384(7)	O7−Ru−S1	84.0(2)
Mo3−O13	1.712(8)	O11−Ru−S1	175.4(2)
Mo3−O6	1.722(7)	S2−Ru−S1	96.49(11)
Mo3−O23	1.930(7)	S3−Ru−S1	93.79(11)
Mo3−O2	1.942(8)	Mo3−O20−Mo4	99.9(3)
Mo3−O20	2.070(7)	Mo3−O20−Mo2	99.6(3)
Mo3−O24	2.411(8)	Mo4−O20−Mo2	144.7(4)
Mo4−O16	1.729(8)	Mo3−O20−Mo6	110.4(3)
Mo4−O1	1.746(8)	Mo4−O20−Mo6	100.3(3)
Mo4−O7	1.783(8)	Mo2−O20−Mo6	100.1(3)
Mo4−O2	2.125(8)	Mo6−O24−Mo7	90.7(3)
Mo4−O20	2.135(7)	Mo6−O24−Mo5	90.1(3)
Mo4−O9	2.373(7)	Mo7−O24−Mo5	169.6(4)
Mo5−O12	1.708(8)	Mo6−O24−Mo8	163.1(4)
Mo5−O10	1.711(8)	Mo7−O24−Mo8	88.1(3)
Mo5−O14	1.909(8)	Mo5−O24−Mo8	88.1(2)
Mo5−O9	1.999(7)	Mo6−O24−Mo3	105.3(3)
Mo5−O2	2.311(8)	Mo7−O24−Mo3	94.6(3)
Mo5−O24	2.326(8)	Mo5−O24−Mo3	95.2(3)
Mo6−O4	1.691(7)	Mo8−O24−Mo3	91.5(3)
Mo6−O8	1.766(7)		
Mo6−O9	1.925(7)		
Mo6−O19	1.936(7)		
Mo6−O24	2.175(7)		
Mo6−O20	2.367(7)		
Mo7−O17	1.713(8)		
Mo7−O5	1.716(8)		
Mo7−O3	1.910(8)		
Mo7−O19	1.995(8)		
Mo7−O23	2.307(7)		
Mo7−O24	2.319(8)		
Mo8−O15	1.709(8)		
Mo8−O22	1.712(8)		
Mo8−O14	1.938(8)		
Mo8−O3	1.944(8)		
Mo8−O6	2.231(8)		
Mo8−O24	2.362(8)		

[a] Values for $[Os(II)(DMSO)_3Mo_7O_{24}]^{4-}$; complete data is included in the Supporting Information.

Na_2MoO_4, followed by recrystallization from aqueous NH_4Cl, Scheme 1.

Single-crystal X-ray structure analysis (crystallographic data in Table 1) of NH_4-**1** and NH_4-**2** revealed the complexes to contain a ruthenium/osmium center in a trigonal antiprismatic coordination mode bound to three DMSO moieties via the sulfur atom and three oxygen atoms of the new heptamolybdate species, Figure 1. The M−S and M−O bond distances, Table 2, are ∼2.25 and 2.06−2.08 Å, respectively. (Complete data for both $[Ru(II)(DMSO)_3Mo_7O_{24}]^{4-}$ and $[Os(II)(DMSO)_3Mo_7O_{24}]^{4-}$ are given as Supporting Information.) The well-known heptamolybdate (paramolybdate) $[Mo_7O_{24}]^{6-}$ is a type II polyoxometalate with a *cis* dioxo configuration at all molybdenum atoms and has seven condensed edge-sharing MoO_6 octahedra with C_{2v} symmetry and two tetra-coordinating bridging oxygens.[22] The heptamolybdate structure observed in this case is considerably different. It also has seven condensed edge-sharing MoO_6 octahedra with C_{2v} symmetry; however, it has one approximately tetrahedral coordinated oxygen atom, O20, and one pentacoordinated oxygen atom, O24, in a nearly pyramidal configuration. The molybdenum atoms, Mo5, Mo7, and Mo8, are classic type II centers with a *cis* dioxo configuration (two short, ∼1.7 Å, Mo−terminal oxygen bonds, two long, ∼2.3 Å, Mo−O bonds *trans* to the terminal oxygen atoms and two bridging Mo−O bonds of intermediate bond length, ∼1.9 Å). The molybdenum atoms, Mo6 and Mo3, are also type-II-like (two short Mo−O bonds), but the oxygen atoms O8 and O6 are bridging oxygen atoms to Ru and Mo8, respectively, rather than terminal oxygen atoms. The molybdenum−oxygen bonds, Mo6−O24 and Mo3−O20, opposite the terminal oxygen atoms, O13 and O4, are shorter than in the classical type II situation, 2.175 and 2.070 Å. The molybdenum atoms, Mo2 and Mo4, are unique in that they are in a considerably trigonally distorted octahedral configuration with three short Mo−O bonds (∼1.75 Å), two

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(22) Evans, H. T.; Gatehouse, B.; Leverett, P. *J. Chem. Soc., Dalton Trans.* **1975**, 505.

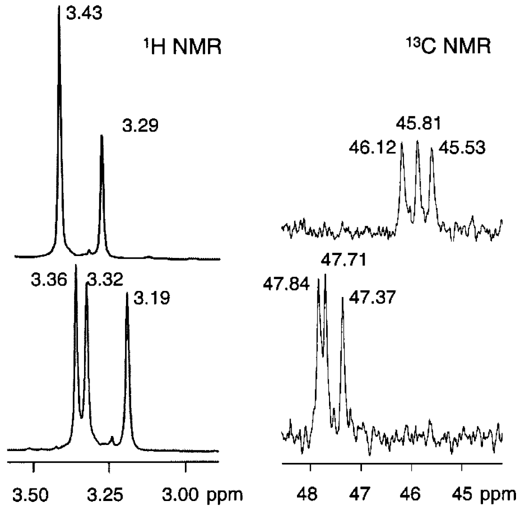

Figure 2. ^{1}H NMR and ^{13}C NMR spectra of $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ (bottom) and $(NH_4)_4[Os(II)(DMSO)_3Mo_7O_{24}]$ (top) taken in D_2O.

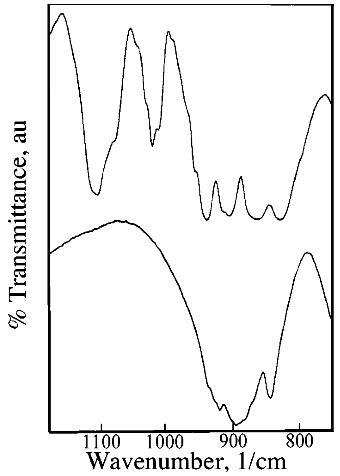

Figure 3. IR spectra of $[Ru(II)(DMSO)_3Mo_7O_{24}]^{4-}$ (top) and paramolybdate, $[Mo_7O_{24}]^{6-}$ (bottom).

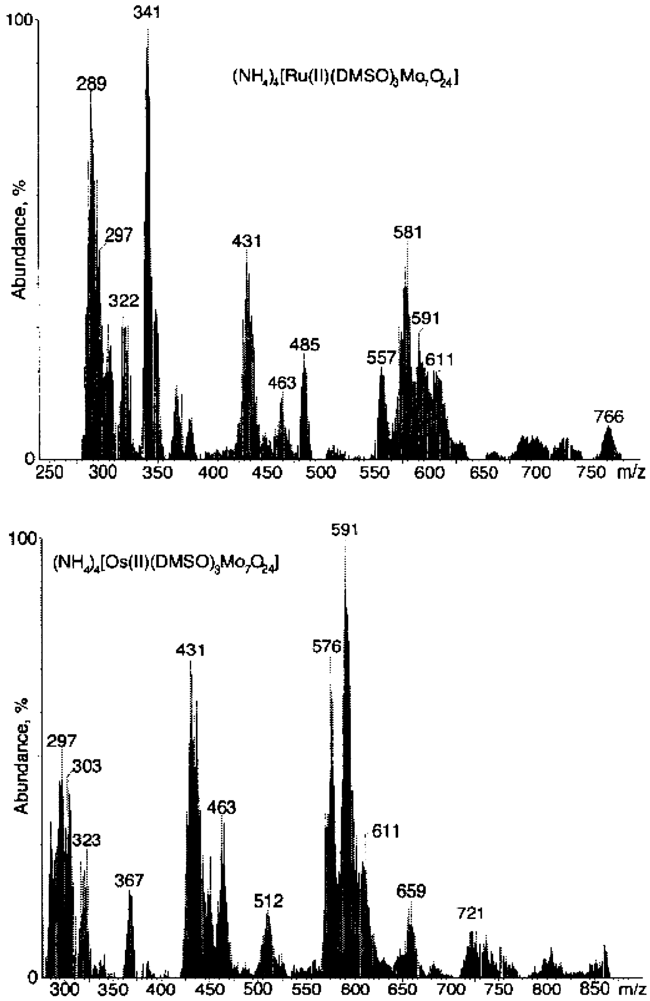

Figure 4. Negative ion electrospray ionization mass spectra of $(NH_4)_4$-$[M(II)(DMSO)_3Mo_7O_{24}]$.

intermediate-long M−O bonds (~2.13 Å), and one long Mo−O bond (~2.37 Å). Two of the short M−O bonds are associated with terminal oxygen atoms while one short Mo−O bond is associated with a bridging atom to the Ru/Os atom. Also notable is the observation that the DMSO ligands bound to Ru/Os via S1 and S3 are similar whereas the DMSO bound via S2 is different (see Figure 1).

The ^{1}H NMR spectra, Figure 2, of $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ in D_2O showed three singlets of equal intensity at $\delta = 3.36$, 3.32, and 3.19 ppm. Similarly, three peaks at $\delta = 47.84$, 47.71 and 47.37 ppm of similar intensity are observed in the ^{13}C NMR spectrum. The chemical shifts are typical for Ru(II)-DMSO complexes with coordination at the sulfur atom.[23] From the crystal structure, Figure 1, it is not immediately clear why one observes three distinct peaks rather than two peaks in a 2:1 ratio in both the ^{1}H and ^{13}C NMR spectra. The dissociation of DMSO from the Ru(II) center can be discounted as free DMSO in D_2O, since it has ^{1}H and ^{13}C NMR peaks considerably upfield at 2.6 ppm (^{1}H NMR) and 41.2 ppm (^{13}C NMR). More likely is the possibility that the rotation around the Ru−S1 and Ru−S3 bonds is hindered (sterically or by coordination by the solvent or countercation) leading to geometric differentiation of the C102 and C301 atoms from the C101 and C302 atoms in solution. Similar ^{1}H and ^{13}C NMR spectra, Figure 2, were observed for $(NH_4)_4[Os(II)(DMSO)_3Mo_7O_{24}]$ except that in the ^{1}H NMR peaks were less resolved with a double intensity singlet at 3.43 ppm along with another singlet at 3.29 ppm. The integrated ratio was 2:1. For $(NH_4)_4[Os(II)(DMSO)_3Mo_7O_{24}]$, the peaks in the ^{13}C NMR were shifted upfield relative to the peaks for $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]$. The IR spectrum, taken as KBr pellets, of NH$_4$-**1** and NH$_4$-**2**, Figure 3, shows the expected S−O stretching vibrations of coordinated DMSO at ~1105, ~1022, and ~1010 cm^{-1}.[23] Important are the peaks (stretching vibrations) attributable to the various Mo−O bonds at 956 (sh), 938, 914 (sh), 905, 858, and 826 cm^{-1}. The "fingerprint" region for the Mo−O stretching vibrations is significantly different than that of $(NH_4)_6Mo_7O_{24}$. The $(NH_4)_4[M(II)(DMSO)_3Mo_7O_{24}]$ compounds were also analyzed by electrospray ionization mass spectrometry, ESI-MS, in the negative ion mode, Figure 4. It should be noted that, to our knowledge, there is no literature precedent for analysis of polyoxometalate compounds by ESI-MS and no knowledge or "rules" about

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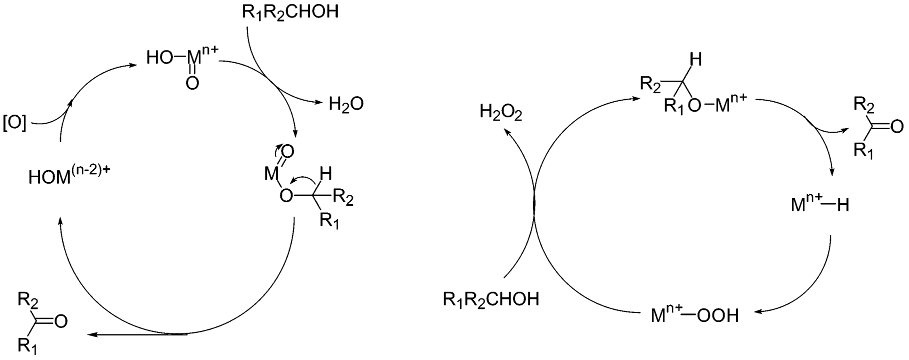
[23] Alessio, E.; Mestroni, G.; Nardin, G.; Attia, W. M.; Calligaris, M.; Sava, G.; Zorzet, S. *Inorg. Chem.* **1988**, *27*, 4099.

Scheme 2. Generalized Oxometal (left) and Hydridometal (right) Mechanisms



expected fragmentation patterns.[24] Indeed, the analysis of the spectra and assignment of peaks is not trivial, but the differences between $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ and $(NH_4)_4[Os(II)(DMSO)_3Mo_7O_{24}]$ both in relative peak intensities and some of peak positions in the mass spectra are obvious.[25] Only partial analysis and peak assignment of the spectra was possible. First, as a tool to provide analytical evidence for the elemental composition of the compounds, one should note the clusters centered at $m/z = 485$ and 512 attributable to $(M - NH_4)/3$ for the ruthenium and osmium compounds, respectively. The ESI-MS of $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ shows prominent clusters centered at $m/z = 289$ and 341 attributable to $RuMo_7O_{24}/4$ and $(NH_4)_3Ru(DMSO)_2Mo_7O_{24}/4$ fragments, respectively. The analogous clusters for $(NH_4)_4[Os(II)(DMSO)_3Mo_7O_{24}]$ are apparently absent, although a cluster of weak peak intensity at $m/z = 367$ could possibly be attributed to a $(NH_4)_3Os(DMSO)_2Mo_7O_{24}/4$ fragment that, however, appears also in the spectrum of the ruthenium compound. Finally, for $(NH_4)_4[Os(II)(DMSO)_3Mo_7O_{24}]$, peaks centered at $m/z = 659$ and attributable to $(NH_4)_4OsMo_7O_{24}/2$ were observed. Analogous peaks for the ruthenium compound could not be unequivocally discerned.

Since DMSO ligands are often considered weakly coordinating, the possibility of exchanging the DMSO ligands with pyridine or phosphine ligands was investigated. Addition of 4 equiv of pyridine to $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ showed by ^1H NMR no change in the complex. On the other hand, addition of a larger excess of pyridine (20−60 equiv) showed by ^1H NMR the release of the DMSO ligand into solution which changed from a red-brown to yellow color. Crystallization of this solution under methanol vapor produced white tiny crystals. X-ray analysis showed the formation of the known octamolybdate with two coordinated pyridine groups, $(NH_4)_4[(py)_2Mo_8O_{26}]$.[26] Apparently, $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ is decomposed due to the basicity of pyridine. The addition of a large excess (50 equiv) of water soluble triphenylphosphine-3,3′,3″-trisulfonic acid as trisodium salt showed by ^1H NMR no exchange of the DMSO ligands.

Aerobic Oxidation of Alcohols. As already noted, the liquid phase catalytic aerobic oxidation of alcohols is a transformation of significant practical importance, and to this end, both homogeneous and heterogeneous catalytic systems have been extensively studied.[11−21] Aerobic alcohol oxidation reactions may be differentiated by the mechanism of their reaction, and both oxometal and hydridometal type general mechanisms have been described, Scheme 2.[11]

It is valuable to note that oxometal type pathways are typically observed in catalysts based on high valent oxo species whereas hydridometal pathways are often observed with more reduced forms of catalysts such as Pd(II) and Ru(II). Also notable is that hydridometal type reactions are usually carried out under basic conditions, which facilitate alkoxide formation and then coordination to the metal center. For example, one of the most recent and best heterogeneous systems based on ruthenium[21e] requires loading the alumina support via a NaOH wash. Also, reactions using one of the best homogeneous palladium catalysts are carried out under basic conditions.[15d] We are interested in oxidation catalyzed by polyoxometalates. In this area, the catalysts showed significant activity only for benzylic alcohols[27] or required very long reaction times[21b] or the presence of a cocatalyst such as a nitroxyl radical,[12a] or quinones.[28] The similar heterobimetallic nature of the presently studied $[M(II)(DMSO)_3Mo_7O_{24}]^{4-}$ compounds to the heterobimetallic complexes of ruthenium or osmium with chromium that were shown to catalyze the oxidation of alcohols with molecular oxygen[29] suggested that the presently prepared compounds

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(24) Both FAB-MS (refs 24b−h) and MALDITOF-MS (ref 24a) have been occasionally used in polyoxometalate research; however, there has been no general study on the use of mass spectrometry in the polyoxometalate field. (a) Mayer, C. R.; Fournier, I.; Thouvenot, R. *Chem. Eur. J.* **2000**, *6*, 105. (b) Finke, R. G.; Droege, M. G.; Cook, J. C.; Suslick, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 5750. (c) Suslick, K. S.; Cook, J. C.; Rapko, B.; Droege, M. W.; Finke, R. G. *Inorg. Chem.* **1986**, *25*, 241. (d) Rapko, B. M.; Pohl, M.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 3625. (e) Liu, J.; Ortega, F.; Sethuraman, P.; Katsoulis, D. E.; Costello, C. E.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **1992**, 1901. (f) Judeinstein, P.; Deprun, C.; Nadjo, L. *J. Chem. Soc., Dalton Trans.* **1991**, 1991. (g) Boesing, M.; Noeh, A.; Loose, I.; Krebs, B. *J. Am. Chem. Soc.* **1998**, *120*, 7252. (h) Zhang, X.; Chen, Q.; Duncan, D. C.; Lachicotte, R. J.; Hill, C. L. *Inorg. Chem.* **1997**, *36*, 4381.

(25) The differences in ESI-mass spectra between similar compounds are often unexpected and not predictable. For example, in our unpublished research we have found that the negative ion ESI-MS of $H_3PW_{12}O_{40}$ gave an easily analyzable spectrum with major peaks at the molecular weight (MW/z for $z = 1$, 2, and 3). Amazingly, the isostructural $H_3PMo_{12}O_{40}$ gave *no* MW/z peaks but instead a much more complicated and difficult to analyze and understand fragmentation pattern.

(26) McCarron, E. M., III; Whitney, J. F.; Chase, D. B. *Inorg. Chem.* **1984**, *23*, 3275.

(27) Neumann, R.; Levin, M. *J. Org. Chem.* **1991**, *56*, 5707.

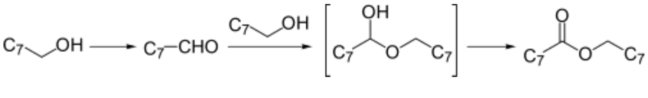
(28) Khenkin, A. M.; Vigdergauz, I.; Neumann, R. *Chem. Eur. J.* **2000**, *6*, 875.

Table 3. Aerobic Oxidation of Alcohols Catalyzed by $Q_4[M(dmso)_3Mo_7O_{24}]$ (M = Ru(II), Os(II))^{a}

substrate	product	conversion	TON	selectivity
benzyl alcohol	benzaldehyde	>99 (96)	500 (480)	>99 (>99)
4-methoxybenzyl alcohol	4-methoxybenzaldehdye	>99 (>99)	500 (500)	>99 (>99)
4-methylbenzyl alcohol	4-methylbenzaldehdye	>99 (>99)	500 (500)	>99 (>99)
4-bromobenzyl alcohol	4-bromobenzaldehdye	>99 (>99)	500 (500)	>99 (>99)
4-trifluoromethylbenzyl alcohol	4-trifluoromethyl-benzaldehyde	>99 (>99)	500 (500)	>99 (>99)
4-nitrobenzyl alcohol	4-nitrobenzaldehyde	>99 (>99)	500 (500)	>99 (>99)
cinnamyl alcohol	cinnamylaldehyde	>99	500	>99
2-cyclohexen-1-ol	2-cyclohexen-1-one	>99	500	>99
1-octen-3-ol	1-octene-3-one	89 (87)	445 (435)	90 (91)
cis−2-hexen-1-ol	2-hexenal	45 (49)	225 (245)	53 (52)^{b}
trans−2-hexen-1-ol	2-hexenal	56	280	48^{b}
cyclooctanol^{c}	cyclooctanone	80	400	>99
2-octanol^{c}	2-octanone	21	105	>99
1-octanol^{c}	octanal	15 (14)	75 (70)	32 (87)^{d}

^{a} Reaction conditions: 5 mmol substrate, 10 μmol of $Q_4[M(DMSO)_3Mo_7O_{24}]$, O_2 2 atm, 120 °C, 12 h. Conversion is mol % substrate reacted. Selectivity is mol % named product out of all products. Values given are those for Ru catalysts with those in parentheses for the Os catalyst. ^{b} 15−20% 2-hexenoic acid. ^{c} 170 °C. ^{d} The other product was 68 (23)% octyloctanoate.

Scheme 3. Formation of Esters



may also show activity for similar aerobic alcohol oxidation and raises the question of what type of mechanism is operating in this case since the polyoxometalate has properties that a priori could lead in general terms to either an oxometal or hydridometal type mechanism.

Indeed, benzylic alcohols are efficiently and selectively oxidized to the corresponding benzaldehyde derivatives at 120 °C with 0.2 mol % catalyst ($Q_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ or $Q_4[Os(II)(DMSO)_3Mo_7O_{24}]$) where $Q = (C_8H_{17})_3CH_3N^+$) in the absence of solvent, Table 3. Toluene as a solvent or diluent was also acceptable, although reactions were about 1.2−1.5 times slower using 1 M solutions of alcohol in toluene; rates were roughly estimated by conversion after 3 h reaction. Secondary allylic alcohols were also oxidized effectively to the corresponding β-unsaturated ketones with generally high, >90%, chemoselectivity. On the other hand, primary aliphatic allylic alcohols were less reactive, and the formation of β-unsaturated aldehydes as products proceeded only with ~50% chemoselectivity. Some over oxidation to the carboxylic acid, 10−20 mol %, was observed along with carbon−carbon bond cleavage products. Simple secondary alcohols reacted more slowly, but selectively, >99.5%, to yield ketones. The cyclic cyclooctanol was more reactive than the acyclic 2-octanol. 1-Octanol reacted slowly to yield octanal. However, octyloctanoate was the main product presumably formed via the oxidation of an intermediate hemiacetal, Scheme 3.

Control reactions (5 mmol of benzyl alcohol, 10 μmol of catalyst, O_2 2 atm, 120 °C, 12 h) with $Ru(DMSO)_4Cl_2$, $Os(DMSO)_4Cl_2$, $Q_3PMo_{12}O_{40}$ (Keggin phosphomolybdate), $Q_2Mo_6O_{19}$ (hexamolybdate), and Q_2MoO_4 as catalysts showed no oxidation while the use of the heptamolybdate, $Q_6Mo_7O_{24}$, showed some diminished activity for benzyl alcohol and considerable over oxidation to benzoic acid (~$^1/_{10}$ the rate), but no activity for allylic or aliphatic alcohols. It should also be noted that ^{1}H NMR spectra taken at specified reaction conditions (2 mmol of benzyl alcohol-d_7, 0.3 mL of toluene-d_8, 5 μmol of $Q_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ or $Q_4[Os(II)(DMSO)_3Mo_7O_{24}]$, O_2 2 atm, 120 °C) showed no evidence of dissociation of DMSO (different chemical shift for free DMSO) even after ~700 turnovers. The DMSO ligand was not disassociated from the polyanions. Furthermore, the IR spectrum of recovered catalyst at the completion of reaction showed no differences in the Mo−O "fingerprint" region. Also, there was no evidence for colloid formation by TEM. It would appear that the $Q_4[M(DMSO)_3Mo_7O_{24}]$ compound is stable and unchanged under reaction conditions.

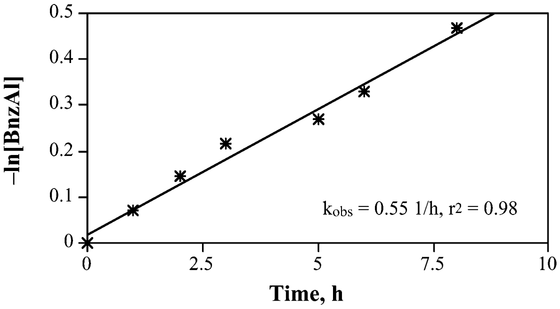


Figure 5. Reaction profile as a function of benzyl alcohol concentration. Reaction conditions: 5 mmol of benzyl alcohol, 10 μmol of $Q_4[Ru(DMSO)_3Mo_7O_{24}]$, 5 mL of toluene, O_2 2 atm, 120 °C.

A closer look at the oxidation of benzylic alcohols was carried out through a kinetic study using $Q_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ as catalyst. Reactions were shown to be cleanly first order in benzyl alcohol, Figure 5, and $Q_4[Ru(II)(DMSO)_3Mo_7O_{24}]$, Figure 6, and zero order in molecular oxygen at pressures above 1 atm. Almost identical results were obtained for $Q_4[Os(II)(DMSO)_3Mo_7O_{24}]$. There was a kinetic isotope effect, $k_H/k_D = 2.4 \pm 0.3$, for the oxidation of benzyl alcohol (2.5 mmol of benzyl alcohol, 2.5 mmol of benzyl alcohol-d_7, 10 μmol of $Q_4[Ru(DMSO)_3Mo_7O_{24}]$, 5 mL of toluene, O_2 2 atm, 120 °C). From these results, one may conclude, as is usually the case in aerobic alcohol oxidation in most mechanistic schemes, that the rate determining step is associated with C−H bond cleavage. In this context, it is important to note that autoxidation can also be ruled out as

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(29) Shapley, P. A.; Zhang, N.; Allen, J. L.; Pol, D. H.; Liang, H.-C. *J. Am. Chem. Soc.* **2000**, *122*, 1079.

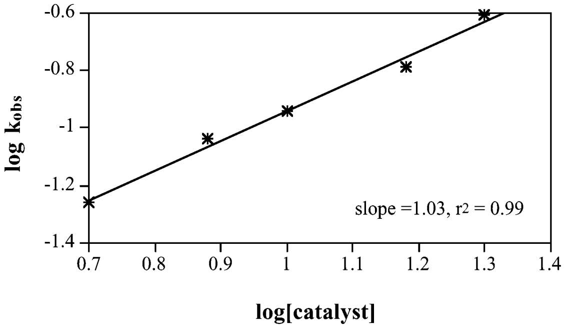

Figure 6. A log−log plot for the determination of the reaction order in $Q_4[Ru(DMSO)_3Mo_7O_{24}]$. Reaction conditions: 5 mmol of benzyl alcohol, 10−30 μmol of $Q_4[Ru(DMSO)_3Mo_7O_{24}]$, 5 mL of toluene, O_2 2 atm, 120 °C.

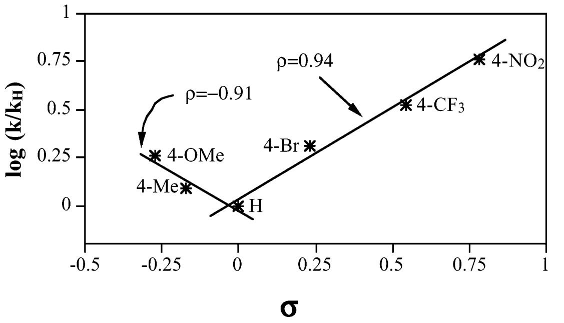

Figure 7. Hammett plot for the oxidation of benzylic alcohols catalyzed by $[Ru(II)(DMSO)_3Mo_7O_{24}]^{4-}$. Reaction conditions: 5 mmol of substrate, 10 μmol of $Q_4[Ru(DMSO)_3Mo_7O_{24}]$, 5 mL of toluene, O_2 2 atm, 120 °C.

a potential mechanism, since the product aldehydes are much more likely to undergo such autoxidation but are not reactive in these systems.[30] Most interestingly, however, a Hammett plot, Figure 7, indicated two mechanistic regimes, one with a ρ value of −0.91 for electron donating substituents, 4-OCH_3 and 4-CH_3, relative to H and another with a ρ value of 0.94 for electron withdrawing substituents, 4-NO_2, 4-CF_3, and 4-Br, relative to H. Thus, electron donating substituents stabilize a positively charged transition state, and electron withdrawing substituents stabilize a negatively charged transition state. One should note here that this type of Hammett plot clearly points against a hydridometal type mechanism in this reaction. Since an integral part of the hydridometal type mechanism is the hydride elimination step through heterolytic cleavage of the benzylic C−H bond, the formation of a positively charged transition state is necessarily implied, which would lead to a negative ρ value for the entire range of substituents. In fact, this behavior has just been recently observed.[21e] Also, one should note that the heterobimetallic complexes of ruthenium or osmium with chromium described by Shapley and co-workers were also concluded to catalyze aerobic alcohol oxidation via a hydridometal type mechanism at the noble metal site.[29] Those compounds are different from the presently used $Q_4[M(II)(DMSO)_3Mo_7O_{24}]$ in that they are coordinatively unsaturated and have a +6 valence state.

The fact that both the $Q_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ and $Q_4[Os(II)(DMSO)_3Mo_7O_{24}]$ compounds (a) showed very similar catalytic activity, (b) were stable under reaction conditions (no changes in NMR or IR and no colloids formed), and (c) appeared to remain coordinatively saturated (no noncoordinated or free DMSO formed) during the oxidation reactions leads us to conclude that the catalytically relevant species is connected to the new $[Mo_7O_{24}]^{6-}$ moiety or isomer obtained via coordination to Ru(II) or Os(II)-$(DMSO)_3$. Apparently, this unique $[Mo_7O_{24}]^{6-}$ isomer has improved catalytic properties toward aerobic alcohol oxidation relative to other molybdenum polyoxometalates.[31,32] From these observations, we propose a variation of an oxometal type mechanism for alcohol oxidation. In general terms and based also on previous research on oxidation catalyzed by polyoxomolybdates,[33] the oxidation of benzylic alcohols may possibly occur in two different ways as presented in Scheme 4.

For reactions accelerated by electron donating moieties, an oxygen atom of the polyoxometalate reacts by nucleophilic attack at the benzylic carbon leading to formation of a new carbon−oxygen bond with the hydroxide anion as leaving group. The identity of the relevant oxygen atom is unknown, but those adjacent to the noble metal are reasonable candidates. Subsequently, a proton and the reduced polyoxometalate are eliminated as shown with formation of the benzylic aldehyde. For reactions accelerated by electron withdrawing moieties, the significantly higher acidity (many orders of magnitude)[34] of the benzylic hydrogen leads to a partial negative charge at the benzylic carbon. We put forth the possibility of proton abstraction from benzylic alcohol by the polyoxometalate. The protonated polyoxometalate then may recombine with a carbanionic species leading to formation of the new carbon−oxygen bond. We believe that this reaction is possible vis-à-vis (re)protonation because the polyoxomolybdates are powerful electron acceptors or oxidants leading to formation of an electrophilic oxygen. As in the previous case, similar subsequent elimination of a proton, hydroxide, and polyoxometalate leads to formation of the benzylic aldehyde. The reduced, oxygen deficient polyoxometalate is quickly reoxidized by molecular oxygen by a yet unknown mechanism.[33b] From the reaction order observed and the kinetic isotope effect value for deuterated benzyl alcohol, it is clear that the carbon−hydrogen bond is being broken in the rate determining step in both postulated pathways, although at different stages of the reaction. Considering the p*K* values of nonbenzylic alcohols, one may

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(30) Sheldon, R. A.; Kocki, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

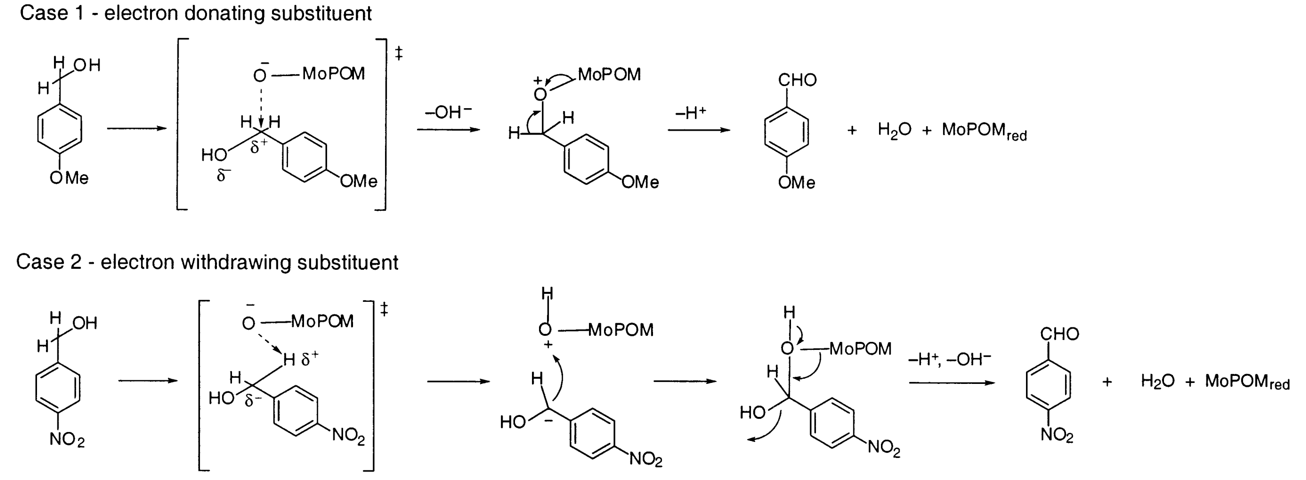
(31) An alternative explanation as suggested by a referee could be that a small amout of the catalyst is oxidized to a ruthenium or osmium(III) species that is in fact the active catalyst. While this possibility remains, we have observed that the original brown compounds and solutions are in fact (partially) reduced during the catalytic cycle to yield a green solution typical of molybdenum(V) containing polyoxometalates. At the completion of the reaction, the original brown solutions are recovered.

(32) The Hammett relationship observed also points against the possibility of a reaction initiated by electron transfer since in such a case a negative ρ value would also be expected for all substituents considering the much higher oxidation potential of, for example, nitro substituted substrates.

(33) (a) Khenkin, A. M.; Neumann, R. *J. Org. Chem.* **2002**, *67*, 7075. (b) Khenkin, A. M.; Weiner, L.; Wang, Y.; Neumann, R. *J. Am. Chem. Soc.* **2001**, *123*, 8531

(34) Bordwell, F. G. *Pure Appl. Chem.* **1977**, *49*, 963.

Scheme 4. Mechanistic Proposal for Oxidation of Benzylic Alcohols by $[M(II)(DMSO)_3Mo_7O_{24}]^{4-}$



postulate that such alcohols are more likely to react in a way proposed for 4-methoxy benzyl alcohol (Scheme 4, case 1).

Conclusion

We have prepared a new type of heterobimetallic polyoxometalate leading to the finding of a new heptamolybdate structure. These compounds are selective aerobic oxidation catalysts. A variation of an oxometal type mechanism has been proposed to explain the results.

Experimental Section

Ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, was recrystallized from hot water prior to use. Sodium molybdate $Na_2MoO_4\cdot 2H_2O$ was from Aldrich. Alcohol substrates and solvents were all from commercial sources (Aldrich, Fluka) of highest purity available and were used without further purification. Deionized water was used. *cis*-Ru(DMSO)$_4$Cl$_2$ or *cis*-Os(DMSO)$_4$Cl$_2$ was synthesized according to a literature method.[35] ^{1}H and ^{13}C NMR were measured on a Brucker Avance 400 instrument with TMS as standard. IR spectra were measured on a Nicolet 460 FTIR spectrophotometer. ESI-MS were measured using Micromass Platform LCZ 4000 with an aqueous sample infused at 5 μL/min. Electronic absorption spectra were recorded on an HP 8452A diode array UV−vis spectrophotometer. Thermogravimetric measurements for determination of water of hydration were taken on a Mettler 50M instrument. Elemental analysis for Mo, Ru, and Os was by ICP-MS. Reactions were quantified by GLC-FID (HP 6890) using a 30 m 5% phenylmethyl silicone capillary column with an i.d. of 0.32 mm and 0.25 μm coating (Restek 5MS), and products were identified by use of reference standards and by GC-MS (HP 5973) using the same column.

Synthesis of $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]\cdot 6.5H_2O$. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (1 g, 0.84 mmol) of was dissolved in 5 mL of boiled water, followed by addition of *cis*-Ru(DMSO)$_4$Cl$_2$ (0.39 mg, 0.84 mmol). The reaction mixture was refluxed with stirring for 30 min. The solution was allowed to cool to room temperature affording red-brown crystals. Yield: 0.85 g, 0.55 mmol (65%). Elemental analysis calcd (exptl): Mo 43.30 (42.9); Ru 6.51 (6.5); H_2O 7.55 (7.5). ^{1}H NMR (D_2O): $\delta = 3.36$ (s, 6H), 3.32 (s, 6H), 3.19 (s, 6H). ^{13}C NMR (D_2O): $\delta = 47.84$ (s), 47.71 (s), 47.37 (s). IR (KBr): $\nu = 1107$ (s), 1022 (m), 938 (s), 903 (s), 859 (s), 824 (s), 684 (w), 668 (s) cm^{-1}. UV−vis (H_2O): $\lambda_{max} = 204$ nm; $\epsilon = 32\,000$ mol^{-1} L cm^{-1}.

Alternative Synthesis of $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]\cdot 6.5H_2O$. A solution of $Na_2MoO_4\cdot 2H_2O$ (1.69 g, 7 mmol) in 3 mL of H_2O (pH was adjusted to 4.5 with HNO_3) and *cis*-Ru(DMSO)$_4$Cl$_2$ (486 mg, 1 mmol) was heated at 80 °C for 20 min. After cooling, the precipitate formed was collected and recrystallized from a 1 M solution of NH_4Cl, which afforded red-brown crystals of $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]\cdot 4H_2O$ that were also used for X-ray structure determination. Yield 1.2 g, 78 mmol (78%).

Synthesis of $(NH_4)_4[Os(II)(DMSO)_3Mo_7O_{24}]\cdot 6.5H_2O$. $(NH_4)_6Mo_7O_{24}\cdot H_2O$ (1 g, 0.84 mmol) of was dissolved in 5 mL of boiled water, followed by addition of *cis*-Os(DMSO)$_4$Cl$_2$ (0.48 mg, 0.84 mmol). The reaction mixture was refluxed with stirring for 30 min. The solution was allowed to cool to room temperature affording rhombic shaped brown crystals. Yield: 0.85 g, 0.39 mmol (46%). Elemental analysis calcd (exptl): Mo 40.22 (40.0); Os 11.39 (11.08); H_2O 7.01 (7.1). ^{1}H NMR (D_2O): $\delta = 3.43$ (s, 12H), 3.29 (s, 6H). ^{13}C NMR (D_2O): $\delta = 46.12$ (s), 45.81 (s), 45.53 (s). IR (KBr): $\nu = 1104$ (s), 1020 (m), 939 (s), 905 (s), 858 (s), 827 (s), 685 (w), 667 (s) cm^{-1}. UV−vis (H_2O): $\lambda_{max} = 208$ nm; $\epsilon = 58\,000$ mol^{-1} L cm^{-1}.

Synthesis of $Q_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ and $Q_4[Os(II)(DMSO)_3Mo_7O_{24}]$. The methyltricaprylammonium salts of $[Ru(II)(DMSO)_3Mo_7O_{24}]^{4-}$ and $[Os(II)(DMSO)_3Mo_7O_{24}]^{4-}$ were prepared by mixing a 10 mL aqueous solution of NH$_4$-**1** or NH$_4$-**2** (0.3 mmol) with a 10 mL dichloromethane solution of methyltricaprylammonium chloride (Aliquat 336) (1.2 mmol) in dichloromethane. The $Q_4[Ru(II)(DMSO)_3Mo_7O_{24}]$ and $Q_4[Os(II)(DMSO)_3Mo_7O_{24}]$ compounds are extracted into the organic phase, which was then separated and dried over sodium sulfate. The solvent was removed by evaporation, and the products were collected as brown oils. Analysis of the oil by ^{1}H NMR and IR showed the oil to contain the $[Ru(II)(DMSO)_3Mo_7O_{24}]^{4-}$ and $[Os(II)(DMSO)_3Mo_7O_{24}]^{4-}$ polyanions. Elemental analysis (CHN) calcd (exptl): for $Q_4[Ru(II)(DMSO)_3Mo_7O_{24}]$, C 44.42 (43.87); H 8.23 (8.41); 1.95 (1.74); for $Q_4[Os(II)(DMSO)_3Mo_7O_{24}]$, C 43.08 (44.34); H 7.98 (8.21); N 1.90 (2.00).

Crystallographic Data Collection and Structure Determination. The data were collected on brown monoclinic needles, cut to size 0.1 × 0.1 × 0.1 mm^3, using a Nonius-Kappa CCD diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. For $(NH_4)_4[Ru(II)(DMSO)_3Mo_7O_{24}]\cdot 4H_2O$, 11426 (6208 unique, R(int) = 0.0399) reflections were collected over a θ range

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[35] Antonov, P. G.; Kukushkin, Y. N.; Konnov, V. I.; Kostokov, Y. P. *Koord. Khim.* **1980**, *6*, 1585.

3.12−23.82 with limiting indices of $-41 \leq h \leq 41$, $-13 \leq k \leq 0$, $-25 \leq l \leq 25$. For $(NH_4)_4[Os(II)(DMSO)_3Mo_7O_{24}]\cdot 4H_2O$, 7022 (7022 unique, R(int) = 0.000) reflections were collected over a θ range 2.34−24.71 with limiting indices of $0 \leq h \leq 42$, $0 \leq k \leq 14$, $-26 \leq l \leq 21$. The data were processed with Denzo-Scalepack.[36] The structures were solved by direct methods with SHELXS-97. Full-matrix least-squares refinement was based on F^2 with SHELX-97. Idealized hydrogen atoms were placed and refined in a riding model. The crystallographic data are presented in Table 1. Additional electron density peaks, ∼5 e/Å^3, are seen. They are possibly additional disordered solvent, H_2O, but have not been modeled.

General Procedure for Oxidation of Alcohols. Reactions were carried out in 20 mL glass pressure tubes. Typically, the tubes or flasks were loaded with the polyoxometalate catalyst and the substrate, degassed by three successive “freeze−pump−thaw” cycles, and loaded with O_2 to 2 atm. The solution was brought to the appropriate temperature in a thermostated oil bath. After the reaction was completed and the mixture cooled, GLC and GC-MS analyses were performed on aliquots directly withdrawn from the reaction mixture after dilution with dichloromethane and addition of an external standard.

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Supporting Information Available: Complete crystallographic data in CIF format and ORTEP drawings of $[Ru(II)(DMSO)_3Mo_7O_{24}]^{4-}$ and $[Os(II)(DMSO)_3Mo_7O_{24}]^{4-}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Otwinowski, Z.; Minor, W. *Method Enzymol*. **1997**, *276*, 307.