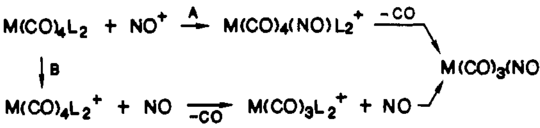
labilize the remaining carbonyl that it is not stable enough to be isolated when reactions are carried out at room temperature.

We are aware that the substitution of CO in nitrosyl complexes by phosphine or halide ligands can be associative but we believe that (1) probable reluctance of tungsten to allow the nitrosyl ligand to bend and (2) the steric crowding of the seven-coordinate intermediate might hinder this pathway. The fast rate of CO substitution by NO^+ has been noted and discussed in the above context. With our present information, however, we cannot rule out two other commonly cited substitution mechanisms,[8] acid–base adduct formation (pathway A) and electron transfer (pathway B) shown in eq 17.



(17)

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Ligating Properties of Monomeric *cis*-Trioxometal(VI) Complexes of Molybdenum(VI) and Tungsten(VI). Preparation and Spectroscopic Characterization of LMO_3 and $[(LMO_3)_4Co^{II}](ClO_4)_2$ (M = Mo, W; L = Cyclic Triamine)

Partha S. Roy and Karl Wieghardt*

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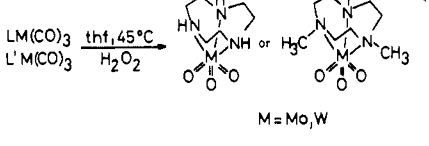
Oxidative decarbonylation of $LM(CO)_3$ and $L'M(CO)_3$, where L represents 1,4,7-triazacyclononane, L′ is *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane, and M = Mo, W, with 30% H_2O_2 in tetrahydrofuran afforded essentially quantitatively monomeric LMO_3 and $L'MO_3$ complexes containing a *fac*-trioxometal(VI) unit. The ligating properties of these complexes have been investigated, and the complexes $[(L'MoO_3)_4Co](ClO_4)_2$, $[(L'MoO_3)_2Fe](ClO_4)_2$, and $[(L'MoO_3)_4Fe](ClO_4)_3$ have been isolated. ^{95}Mo, ^{183}W, and ^{17}O, NMR spectra were recorded; magnetic properties and electronic as well as infrared spectra are reported.

Introduction

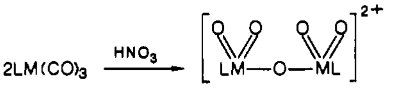
Recently we have reported that the low-valent carbonylnitrosylrhenium complex $[LRe(CO)_2NO]^{2+}$ is readily oxidatively decarbonylated with H_2O_2 in aqueous solution, yielding the *fac*-trioxorhenium(VII) complex $[LReO_3]^+$ in excellent yields[1] (L represents the cyclic triamine 1,4,7-triazacyclononane). This type of chemistry has attracted considerable interest, since Herrmann and co-workers have shown that the reaction of $Me_5CpRe(CO)_3$ with H_2O_2 yields the organometallic rhenium(VII) species Me_5CpReO_3.[2] The formal oxidation state of the metal center changes in both cases by six units without apparent loss of the coordinated cyclic triamine or Me_5Cp^-. We have now extended this scheme to complexes of molybdenum and tungsten. Thus the reaction of $LM(CO)_3$ or $L'M(CO)_3$ (M = Mo, W; L = 1,4,7-triazacyclononane; L′ = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane)[3–6] with H_2O_2 in tetrahydrofuran (thf) yields essentially quantitatively LMO_3 and $L'MO_3$ (M = Mo, W):



(1)

The complexes $LMoO_3$[7] and $L'MoO_3$[8] have been prepared previously from MoO_3 and the respective cyclic triamine in analogy to the preparation of $(dien)MoO_3$[9] (dien = diethylenetriamine) although in lower yields. Complexes containing a *fac*-WO_3 unit have not been extensively studied in the past[10] —the only reported examples appear to be $(dien)WO_3$[11] and $[WO_3(nta)]^{3-}$[12] (nta = nitrilotriacetate), where the former is labile in solution and the latter has not been isolated.

Since we have shown that $LMoO_3$ and $L'MoO_3$ are stable both in solution and in the solid state, it was interesting to study the chemistry of these LMO_3 species in more detail. The electrochemistry of $LMoO_3$ and $L'MoO_3$ has been described.[8] We report here on their ligating properties toward Co(II), Fe(II), and Fe(III). This was initiated by the observation that decarbonylation of $LM(CO)_3$ with 2 M nitric acid yielded dimers with a (*μ*-oxo)bis[dioxometal(VI)] moiety (eq 2).[6,13] Thus at least one terminal



(2)

oxo group in LMO_3 may bind to other centers, forming LO_2M–O–M′ units.

Experimental Section

The macrocyclic ligands 1,4,7-triazacyclononane (L) and *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (L′) have been prepared according to published procedures.[14,15]

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Preparation of Complexes. $LMoO_3$ and $L'MoO_3$. Preparation of these complexes from an ethanol/water mixture containing MoO_3 and the respective cyclic triamine has been described previously.[7,8] Higher yields were obtained by using an oxidative decarbonylation reaction of $LMo(CO)_3$[3] or $L'Mo(CO)_3$[4] with H_2O_2 as described below.

$LMoO_3$. To a suspension of $LMo(CO)_3$ (1 g) in tetrahydrofuran (thf) was added dropwise with stirring 30% H_2O_2 (50 mL) at room temperature. The reaction mixture was gently warmed to 50 °C and vigorously stirred for 2.5 h. Finally a colorless clear solution was obtained, the volume of which was reduced to ca. 5 mL in a rotary evaporator while the temperature was kept below 45 °C. Addition of thf (200 mL) to this solution afforded the compound $LMoO_3$ as a colorless microcrystalline solid, which was filtered off, washed with ethanol and ether, and dried over $CaCl_2$ (yield 0.8 g, 90%). Anal. Calcd for $(C_6H_{15}N_3)MoO_3$: C, 26.38; H, 5.53; N, 15.38. Found: C, 26.45; H, 5.30; N, 15.36.

$L'MoO_3$. This compound was prepared analogously with $L'Mo(CO)_3$ as starting material (yield 0.87 g, 97%). Anal. Calcd for $(C_9H_{21}N_3)MoO_3$: C, 34.29; H, 6.71; N, 13.32. Found: C, 34.1; H, 6.5; N, 13.4. It is noted that both $LMoO_3$ and $L'MoO_3$ precipitate with two molecules of water of crystallization, which are readily lost over $CaCl_2$ in vacuo.

$LWO_3 \cdot 2H_2O$ and $L'WO_3 \cdot 3H_2O$. Both complexes were prepared in excellent yields (90%) from $LW(CO)_3$[5] and $L'W(CO)_3$[13] via oxidative decarbonylation with use of H_2O_2 (30%) as oxidant in thf as described above. Colorless microcrystalline solids were obtained, which contained two and three molecules of water of crystallization, respectively. These could readily be removed in an exsiccator over P_2O_5 at room temperature. Anal. Calcd for $(C_6H_{15}N_3)WO_3 \cdot 2H_2O$: C, 18.15; H, 4.82; N, 10.55. Found: C, 18.3; H, 4.4; N, 10.6. Anal. Calcd for $(C_9H_{21}N_3)WO_3 \cdot 3H_2O$: C, 23.64; H, 5.90; N, 9.19. Found: C, 23.4; H, 5.5; N, 8.9.

$[(L'MoO_3)_4Co](ClO_4)_2$. $L'MoO_3$ (0.5 g) was dissolved in dry methanol (30 mL), and solid $Co(ClO_4)_2 \cdot 6H_2O$ (0.3 g) was added with stirring until a clear blue solution was obtained. Dark blue crystals of $[(L'MoO_3)_4Co](ClO_4)_2$ separated out within 12 h at room temperature (yield 0.2 g). Anal. Calcd for $[((C_9H_{21}N_3)MoO_3)_4Co](ClO_4)_2$: C, 28.46; H, 5.57; N, 11.06; Co, 3.88. Found: C, 28.7; H, 5.5; N, 11.0; Co, 4.2. A hexafluorophosphate salt, $[(L'MoO_3)_4Co](PF_6)_2$, was prepared analogously with $Co(PF_6)_2 \cdot 6H_2O$ as starting material.

$[(L'WO_3)_4Co](ClO_4)_2 \cdot 4H_2O$. Into a suspension of $L'WO_3 \cdot 3H_2O$ (0.5 g) in dry acetone (15 mL) was added solid $Co(ClO_4)_2 \cdot 6H_2O$ (0.1 g) with stirring for 30 min at room temperature, whereupon a solid blue mass was obtained. This was filtered off and washed with dry acetone and ether (yield 0.3 g). Anal. Calcd for $[((C_9H_{21}N_3)WO_3)_4Co](ClO_4)_2 \cdot 4H_2O$: C, 22.26; H, 4.77; N, 8.65. Found: C, 22.1; H, 4.9; N, 8.5.

$[(L'MoO_3)_2Fe](ClO_4)_2$. To an argon-purged solution of $L'MoO_3$ (0.5 g) in dry methanol (40 mL) was added $Fe(ClO_4)_2 \cdot 6H_2O$ (0.25 g). The reaction mixture was stirred under an argon atmosphere for 1 h and kept in the refrigerator at 0 °C for 3 days. A light yellow solid separated out, which was filtered off, washed with ether, and dried over $CaCl_2$. The compound is air-stable and insoluble in all common solvents (yield 0.15 g). Anal. Calcd for $[((C_9H_{21}N_3)MoO_3)_2Fe](ClO_4)_2$: C, 24.42; H, 4.78; N, 9.49. Found: C, 24.34; H, 5.0; N, 9.4.

$[(L'MoO_3)_4Fe](ClO_4)_3$. To a solution of $Fe(ClO_4)_3 \cdot 9H_2O$ (0.4 g) dissolved in dry methanol (5 mL) was added slowly a methanolic solution (20 mL) of $L'MoO_3$ (0.5 g) with stirring at room temperature. A colorless precipitate separated out, which was filtered off, washed with dry methanol, and dried in vacuo over fused $CaCl_2$. The compound is hygroscopic. Anal. Calcd for $[((C_9H_{21}N_3)MoO_3)_4Fe](ClO_4)_3$: C, 26.67; H, 5.24; N, 10.40. Found: C, 26.4; H, 5.2; N, 10.5.

Physical Measurements. Magnetic susceptibilities of powdered samples were measured by the Faraday method (Sartorius microbalance, Bruker B-E10C8 research magnet and B-VT 1000 automatic temperature control) in the temperature range 110–293 K. Diamagnetic corrections were applied with use of Pascal's constants.[16]

The NMR spectra were recorded in the FT mode with a Bruker AM-400 spectrometer at a magnetic field of 9.395 T (^{95}Mo, ^{183}W, and ^{17}O frequencies 26.08, 16.67, and 54.24 MHz, respectively). All the spectra were obtained from samples in 10 mm diameter tubes at 70 °C. ^{95}Mo chemical shifts were measured relative to a separate sample of 1 M Na_2MoO_4 in D_2O at pH 12. Sweep widths of 5000–15 151.5 Hz were used with acquisition times of 3.277–0.017 s. The pulse length was 30 μs (90° tip angle). For ^{183}W the chemical shifts were measured relative to external 2 M Na_2WO_4 in D_2O. The sweep width was 166 666.667 Hz, the acquisition time was 0.049 μs, and typically 79 400 transients were obtained for the spectra; the pulse length was 5.0 μs (~15° tip angle). ^{17}O NMR spectra were obtained with the same equipment as the ^{95}Mo and ^{183}W NMR spectra, and the chemical shifts were measured from the D_2O solvent line. A pulse width of 25 μs provided the 90° tip angle used throughout the experiments. Sweep widths of 50 000–100 000 Hz were used with acquisition times of 0.041–0.026 s, and more than 10^5 transients were obtained for each spectrum.

Table I. Metal–Oxygen Stretching Frequencies of the Complexes (Infrared, KBr Disk)

complex	$\nu(M{=}O)$,[a] cm^{-1}	ref
$(dien)MoO_3$	839 (s)[b]	21
$LMoO_3$	850 (s), 820 (s)	this work
$L'MoO_3$	862 (sh), 851 (s)	this work
LWO_3	830 (s), 800 (s)	this work
$L'WO_3$	864 (s), 838 (s)	this work
$[(L'MoO_3)_2Fe^{II}](ClO_4)_2$	900 (s), 755 (sh),[a] 746 (s)[c]	this work
$[(LMoO_3)_4Fe](ClO_4)_3$	900 (s), 786 (sh),[c] 746 (s)[c]	this work
$[(L'MoO_3)_4Co](ClO_4)_2$	885 (s), 830 (s)	this work
$[(L'WO_3)_4Co](ClO_4)_2$	880 (s), 840 (s)	this work
$[L'_2Mo_2O_5](Br_3)_2$	930 (s), 905 (s), 770 (s)[c]	6
$[L'_2W_2O_5](PF_6)_2$	960 (s), 915 (s), 800 (s)[c]	13

[a] Legend: s = strong; sh = shoulder. [b] The A_1 and E (Mo=O) stretching modes are accidentally degenerate.[21] [c] ν(M—O—M') stretching frequencies.

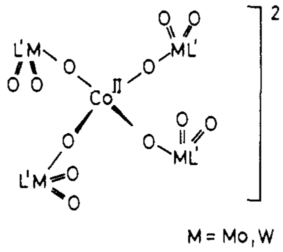

Figure 1. Proposed structure of $[(L'MO_3)_4Co]^{2+}$ dications (M = Mo, W).

Electronic spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer, and the infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer (KBr disks).

Results

Syntheses and Characterization of Complexes. Air-stable solutions of $LM(CO)_3$ and $L'M(CO)_3$ (M = Mo, W) in tetrahydrofuran (thf) react readily with 30% hydrogen peroxide at moderate temperature (<50 °C) to yield brown solutions with effervescence of CO (oxidative decarbonylation). At prolonged reaction times the solution eventually becomes colorless. Reduction of the volume of the reaction mixture under reduction pressure and addition of thf afforded colorless solids of the composition $LMO_3 \cdot xH_2O$ and $L'MO_3 \cdot xH_2O$ (x = 2, 3). The water molecules of crystallization are only weakly bonded in these solids since they are slowly lost on storage in dry air or faster in vacuo over P_2O_5 or $CaCl_2$. The neutral complexes are moderately soluble in water, methanol, acetone, and acetonitrile without detectable ligand dissocitation, contrasting in this respect with $(dien)MoO_3$ and $(dien)WO_3$ (dien = diethylenetriamine). In the infrared region two $\nu(M{=}O)$ stretching frequencies are observed in the range 800–850 cm^{-1} (Table I), in agreement with the C_{3v} local symmetry (A_1 + E) of the N_3MO_3 core of LMO_3 and $L'MO_3$ complexes.

The stability of $L'MO_3$ complexes toward ligand dissociation in solution and their solubility in methanol and water allowed the investigation of the ligating properties of the MO_3 moiety toward other transition-metal centers.

The reaction of $L'MO_3$ (M = Mo, W) dissolved in dry methanol with $Co(ClO_4)_2 \cdot 6H_2O$ at room temperature yielded a beautiful deep blue solution, from which blue crystals of the composition $[(L'MoO_3)_4Co](ClO_4)_2$ and $[(L'WO_3)_4Co](ClO_4)_2 \cdot 4H_2O$ slowly precipitated, respectively (eq 3). If the same reaction was carried

$$4L'MO_3 + Co^{2+} \xrightarrow{CH_3OH} [(L'MO_3)_4Co]^{2+} \quad (3)$$
$$M = Mo, W$$

out in water, only the formation of pink $[Co(H_2O)_6]^{2+}$ was observed. This indicates that LMO_3 units are weaker donor ligands than water but stronger than methanol. Although it is possible

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Table II. Electronic Spectra and Magnetic Properties of the Complexes

complex	color	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})	magnetic moment, μ_B	Θ, K
$[(L'MoO_3)_4Co](ClO_4)_2$	blue	680 (596), 620 (sh), 600 (sh)^{a,b}	5.21^c	−40
$[(L'WO_3)_4Co]ClO_4)_2\cdot 4H_2O$	blue	658 (784), 610 (sh), 580 (sh), 560 (sh)^{a,b}	5.05^c	−30
$[(L'MoO_3)_2Fe](ClO_4)_2$	yellow	417^a	5.02	−7
$[(L'MoO_3)_4Fe](ClO_4)_3$	colorless	483 (sh), 462 (7), 429 (28) *b*	6.12	0

^{a}Reflection spectrum (KBr disk). ^{b}Measured in CH_3CN. ^{c}Uncorrected for temperature-independent paramagnetism.

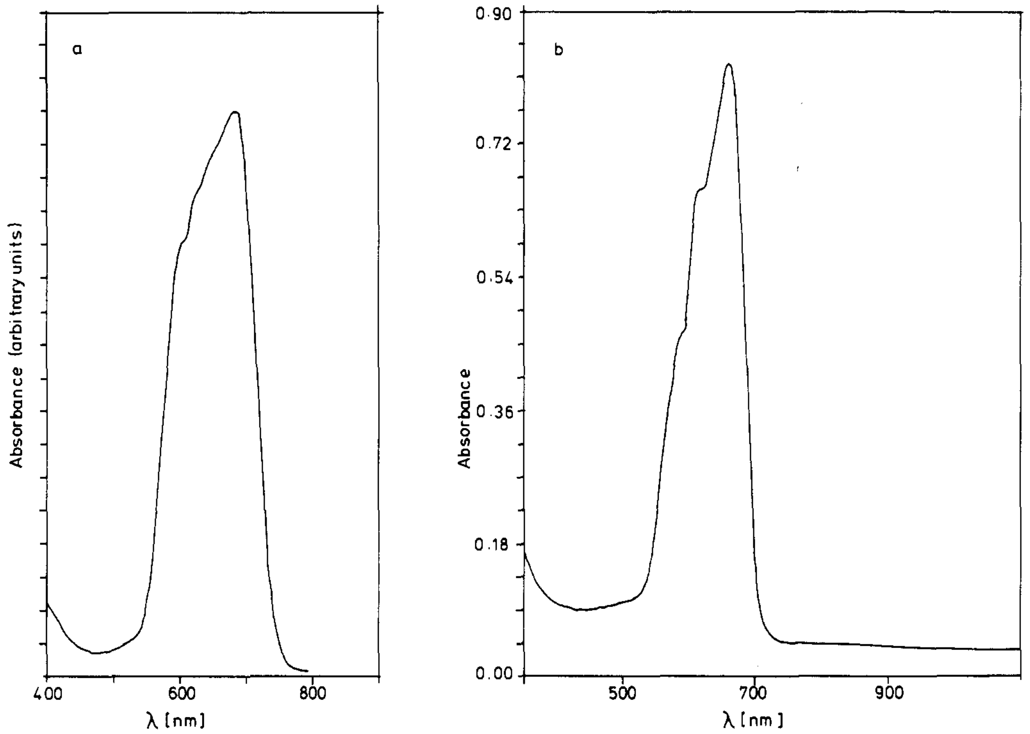

Figure 2. Electronic spectra of (a) $[(L'MoO_3)_4Co](ClO_4)_2$ (reflectance spectrum) and (b) $[(L'WO_3)_4Co](ClO_4)_2$ in solution (acetonitrile).

to recrystallize these materials from methanol or acetonitrile or to prepare the corresponding blue hexafluorophosphate salts by addition of $NaPF_6$ to such solutions, we have not been able to grow single crystals suitable for a single-crystal X-ray diffraction study. The structure of the dications $[(L'MO_3)_4Co]^{2+}$ is nevertheless readily deduced from their spectroscopic and magnetic properties to be as depicted in Figure 1. It is proposed that the central cobalt(II) ion is tetrahedrally surrounded by four oxygen atoms, one from each coordinated LMO_3 unit, which function as monodentate neutral ligands. In the infrared spectrum two ν(M=O) stretching frequencies are again observed (Table I), which are assigned to the ν_{as}(M=O) and the ν_s(M=O) vibrations of the resulting *cis*-MO_2 group with two terminal oxygen atoms, after one oxygen atom of the *cis*-MO_3 unit has been coordinated to the Co(II) center.

The electronic spectra of $[(LMO_3)_4Co](ClO_4)_2$ species both in solution (acetonitrile) and in the solid state are in agreement with a tetrahedral CoO_4 core. One multicomponent band around 630 nm with a molar absorption coefficient of ~700 L mol^{-1} cm^{-1} has been observed (Table II; Figure 2), which is associated with the $^4A_2 \rightarrow {}^4T_1(P)$ transition in tetrahedral symmetry.

It is expected that a "normal" tetrahedral CoO_4 unit provides a magnetic moment in the range 4.5–4.7 μ_B and exhibits a strong absorption band (ϵ 10^2–10^3 L mol^{-1} cm^{-1}) at 600–700 nm.[17-20]

The magnetic data of $[(LMO_3)_4Co]^{2+}$ complexes are given in Table II: Both compounds (M = Mo, W) exhibited satisfactory dependence on the Curie–Weiss law, $\chi_M = C/(T - \Theta)$, in the temperature range 100–293 K, and magnetic moments were calculated from the relation $\mu = 2.84C^{1/2}$. χ_M represents the measured magnetic susceptibility corrected for diamagnetism only. Magnetic moments of 5.21 and 5.05 μ_B for the molybdenum and tungsten complexes, respectively, appear to be too large for a tetrahedral arrangement around cobalt(II). In fact they appear to be more typical for hexacoordinated high-spin Co(II), where magnetic moments between 4.7 and 5.2 μ_B are observed. When the measured susceptibility values were corrected for diamagnetism *and* temperature-independent paramagnetism (TIP),[19] the magnetic moments exhibit somewhat reduced values (4.89 μ_B for the molybdenum complex and 4.83 μ_B for its tungsten analogue), which are more typical for tetrahedral cobalt(II).[27] The LMO_3 groups must be considered to be very bulky ligands, and the oxygens are very weak donor atoms. Therefore, the Co–O bond distances may be unusually long and the LMO_3 ligands provide a small *Dq* value comparable with that of Cl^- or I^-. That steric effects may be of some consequence upon the Co–O distances has been shown for the two complexes $[Co(Me_3PO)_4]^{2+}$ and $[Co(Ph_3PO)_4]^{2+}$, which have magnetic moments of 4.34 and 4.72 μ_B,

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Table III. ^{17}O NMR Data of the Complexes

complex	chem shift,[a] ppm	ref	complex	chem shift,[a] ppm	ref
Na_2MoO_4	532	22	LWO_3	541	this work
Na_2WO_4	426	this work	$L'WO_3$	560	this work
$LMoO_3$	689	this work	$[MoO_3(nta)]^{3-}$	701	22
$L'MoO_3$	576	this work	$[MoO_3(ida)]^{2-}$	698	22

[a] Downfield from solvent D_2O.

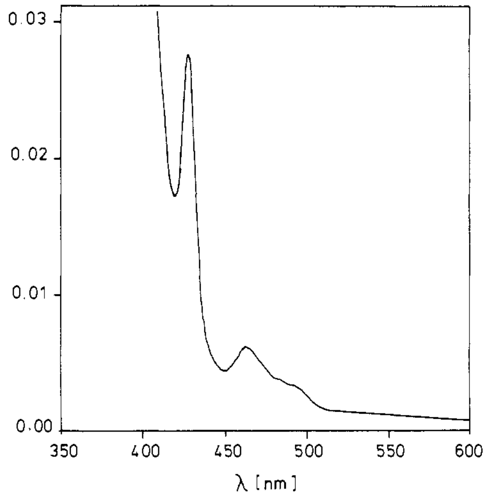
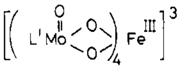


Figure 3. Electronic spectrum of $[(L'MoO_3)_4Fe](ClO_4)_3$ measured in acetonitrile solution.

respectively.[18] As will be shown from ^{17}O NMR data (see below), the oxygen atoms in $L'MoO_3$ are less basic than those of $L'WO_3$. In agreement with this observation is the fact that the magnetic moment of $[(L'WO_3)_4Co]^{2+}$ is smaller than that of the corresponding molybdenum complex, since the orbital contribution increases with decreasing ligand field splitting (i.e. donor strength of the ligand). In accordance with this interpretation is the fact that in the electronic spectrum the principal absorption band of $[(L'WO_3)_4Co]^{2+}$ is observed at a wavelength shorter than that of $[(L'MoO_3)_4Co]^{2+}$ (Table II).

The reaction of $L'MoO_3$ with $Fe(ClO_4)_2{\cdot}6H_2O$ in dry methanol under an argon atmosphere at room temperature afforded after 3 days at 0 °C a light yellow solid of the composition $[(L'MoO_3)_2Fe](ClO_4)_2$, which is insoluble in all common solvents. The temperature-independent (100–300 K) magnetic moment of 5.02 μ_B indicates a high-spin iron(II) center. When the same reaction was carried out with $Fe(ClO_4)_3{\cdot}9H_2O$ as starting material, a colorless solid of the composition $[(L'MoO_3)_4Fe](ClO_4)_3$ was obtained, which is quite hygroscopic. A magnetic moment of 6.12 μ_B is in agreement with a high-spin iron(III) center. The electronic spectrum of the latter material is shown in Figure 3; three weak spin-forbidden d–d transitions are observed. In the infrared spectrum only one $\nu(Mo{=}O)$ stretching frequency is observed at 900 cm^{-1} for both the iron(II) and iron(III) complexes, but in contrast to the case for the cobalt(II) adducts additional strong bands <800 cm^{-1} are detected (Table I), which are assigned to $\nu(Mo{-}O{-}Fe)$ vibrations. It is tempting to propose that the $L'MoO_3$ units act as bidentate ligands, forming a polymeric structure in case of the iron(II) species and a monomeric species with an octacoordinate iron(III) center



but this proposal rests entirely on infrared spectroscopic evidence, which of course is not sufficient. We have as yet not been able to grow suitable single crystals for a single-crystal X-ray diffraction study.

^{17}O, ^{95}Mo, and ^{183}W NMR Spectroscopy. The results for ^{17}O NMR measurements are presented in Table III and those for ^{95}Mo and ^{183}W NMR experiments in Table IV. No spin coupling was observed between ^{17}O and either ^{95}Mo or ^{97}Mo. For $[MoO_4]^{2-}$ Miller and Wentworth[22] have reported spin coupling between ^{95}Mo and ^{17}O with a coupling constant of 40 ± 1 Hz. The ^{17}O NMR spectra of LMO_3 and $L'MO_3$ (M = Mo, W) dissolved in D_2O did not show the presence of any appreciable amounts of $[MoO_4]^{2-}$ or $[WO_4]^{2-}$, whose signals would have easily been detected under our experimental conditions. This is good evidence for the stability of these species in solution toward ligand dissociation and is in contrast to the behavior of species like $(dien)MO_3$, $[MoO_3(ida)]^{2-}$, and $[MoO_3(nta)]^{3-}$ (ida = iminodiacetate, nta = nitrilotriacetate) in aqueous solution, where signals due to $[MoO_4]^{2-}$ have been observed.[22]

Table IV. ^{95}Mo and ^{183}W NMR Data of the Complexes

complex	chem shift,[a] ppm	solvent	line width, Hz	ref
$LMoO_3$	86	D_2O	280	this work
$L'MoO_3$	98	D_2O	267	this work
$[(MoO_3)_2(edta)]^{4-}$	63		290	24
$[MoO_3(ida)]^{2-}$	66		130	24
$[MoO_3(nta)]^{3-}$	67		160	24
$L'WO_3$	−98	D_2O	<5	this work
$WO_2(ONEt_2)_2$	−330	$CDCl_3$		26
$WO_2(ONC_5H_{10})_2$	−338	$CDCl_3$		26

[a] See Experimental Section for details.

Interestingly, the oxo atoms in $LMoO_3$ and $L'MoO_3$ are slightly more shielded as compared to those in their anionic analogues $[MoO_3(ida)]^{2-}$ and $[MoO_3(nta)]^{3-}$ and, consequently, the Mo centers are more deshielded in the first two compounds than in the last two (Table IV). Comparison of $LMoO_3$ with $M'MoO_3$ shows that the terminal oxo atoms in the former are more deshielded than in the later and the molybdenum center in $LMoO_3$ is more shielded than in $L'MoO_3$. These results clearly show that the terminal oxo groups in $LMoO_3$ and $L'MoO_3$ are more basic than in their anionic analogues and that in $L'MoO_3$ they are slightly more basic than in $LMoO_3$; i.e., $L'MoO_3$ has the most pronounced ligating properties toward other metal centers within this series of structurally similar molybdenum complexes. Furthermore, the oxo atoms in the tungsten complexes LWO_3 and $L'WO_3$ are even more basic than those in their molybdenum counterparts.

It has been shown that the ^{95}Mo chemical shifts for a large number of six-coordinate molybdenum(VI) complexes containing a *cis*-MoO_2 moiety covers a range of about 900 ppm and are sensitive to apparently minor ligand variations.[23] In contrast, information available on monomeric six-coordina'e MoO_3 species is restricted to a few anionic complexes, all of which feature one tertiary amine and two carboxylate ligands in addition to the MoO_3 unit.[24,25] They resonant at 66 ± 4 ppm (Table IV).

$LMoO_3$ and $L'MoO_3$ exhibit a single resonance at 86 and 98 ppm, respectively. Thus the molybdenum(VI) centers are more deshielded than in their anionic analogues.

^{183}W chemical shifts for monomeric six-coordinate tungsten(VI) species containing a WO_3 unit have not been reported previously. LWO_3 has not been successfully investigated due to its prohibitively low solubility, but $L'WO_3$ resonates at −98 ppm, which may be compared with values of −330 and −338, ppm reported for $WO_2(ONEt_2)_2$ and $WO_2(ONC_5H_{10})_2$,[26] both of which contain two N,O-coordinated hydroxylamido derivatives and a *cis*-dioxotungsten(VI) center.

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