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Lindqvist-Type Oxo Nitrosyl Complexes. Syntheses, Vibrational, Multinuclear Magnetic Resonance (^{14}N, ^{17}O, ^{95}Mo, and ^{183}W), and Electrochemical Studies of $[M_5O_{18}\{M'(NO)\}]^{3-}$ Anions (M, M′ = Mo, W)

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The whole series of Lindqvist-type nitrosyl derivatives $(n\text{-}Bu_4N)_3[M_5O_{18}\{M'(NO)\}]$ (M, M′ = Mo, W) has been synthesized through the reaction of $[Mo(NO)\{MeC(NH_2)NO\}(acac)_2]$ or $[W(NO)Cl_3(MeCN)_2]$ with $(n\text{-}Bu_4N)_2[Mo_2O_7]$ or $(n\text{-}Bu_4N)_2[WO_4]$ in MeCN. The electronic features of the $[M_5O_{18}\{M'(NO)\}]^{3-}$ anions have been investigated by vibrational, electronic and multinuclear (^{14}N, ^{17}O, ^{95}Mo, and ^{183}W) magnetic resonance spectroscopy, and by electrochemistry. A full assignment of the NMR spectra has been achieved. Chemical shifts are dominated by the paramagnetic term of the shielding. ^{17}O NMR data and electrochemical reduction data show that the expected effect of the whole charge increase with respect to the parent oxoanions $[M_6O_{19}]^{2-}$ is partly offset by the electron-withdrawing effect of the nitrosyl ligand. All four species are essentially localized mixed-valence complexes, with five d^0-M(VI) centers and one d^4-M′(II) center; however, some electronic delocalization is supported by ^{95}Mo and ^{183}W NMR data and by electrochemical data.

Introduction

Most of the current interest in polyoxometalates derives its impetus from their relevance to catalysis, biology, medecine, geochemistry, material science, and topology.[2] Our group is currently involved in the functionalization of polyoxometalates,[3−8] with the aim to (i) tune their properties for the design of improved catalytic systems, (ii) stabilize novel molecular architectures, and (iii) model the reactions and properties of catalytic oxides. These are exemplified by the nitrosyl derivatives.[3] Indeed, $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$, which can be viewed as a defect Lindqvist-type derivative, is fairly stable whereas the parent $[Mo_5O_{18}]^{6-}$ anion has not yet been described.[4] Activation of $[Mo_6O_{18}(NO)]^{3-}$ with respect to $[Mo_6O_{19}]^{2-}$ is supported by the observation that $[Mo_6O_{18}(NO)]^{3-}$ can be methylated by dimethyl sulfate,[5] while surface oxygen atoms of $[Mo_6O_{19}]^{2-}$ are known to be quite nonbasic[9] and unreactive.

These molybdenum oxo nitrosyl complexes contain a $Mo(NO)^{3+}$ unit which can be written as $\{MoNO\}^4$ using the formalism of Enemark and Feltham.[10] The short Mo−N distance and the linearity of the Mo−N−O moiety support extensive delocalization and significant multiple bond character within the Mo(NO) unit.[4−6] In such a case, the nitrosyl ligand is commonly considered as NO^+; thus the linear $Mo(NO)^{3+}$ would contain a d^4-Mo(II) center. Indeed, according to spectroscopic data, $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ and $[Mo_6O_{18}(NO)]^{3-}$ are properly described as localized mixed-valence Mo(VI)/Mo(II) complexes.[5] However, in the case of $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$, a nitrosyl Keggin derivative, ^{183}W NMR data also support some delocalization of the Mo(II) d-electrons onto the polytungstate framework.[6] We have now achieved the synthesis and characterization of the whole series of Lindqvist-type oxo nitrosyl complexes $[M_5O_{18}\{M'(NO)\}]^{3-}$ (M, M′ = Mo, W), which allows one to specify the interaction between the $M'(NO)^{3+}$ unit and the $M_5O_{18}{}^{6-}$ ligand. The discussion will address the following questions: (i) the extent of d-electron delocalization over the Mo(NO) moiety and M_5O_{18} framework, (ii) the influence of the metal, *i.e.* Mo *vs* W, and (iii) the influence of the structure, *i.e.* Lindqvist *vs* Keggin derivatives.

Experimental Section

Starting Materials and Reagents. $(n\text{-}Bu_4N)_2[Mo_2O_7]$,[11a] $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$,[11b] $(n\text{-}Bu_4N)_2[W_6O_{19}]$,[11c] $[Mo(NO)\{MeC(NH_2)NO\}(acac)_2]$,[12] $[W(NO)Cl_3(MeCN)_2]$,[13] $[Mo(NO)_2(acac)_2]$,[14] and $[W(NO)_2(acac)(MeCN)_2](BF_4)$[15] have been prepared as described in the literature. The synthesis of $(n\text{-}Bu_4N)_2[WO_4]$ followed that of Klemperer and coworkers,[16] except that it was carried out in methanol instead of water.

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Reagent-grade MeCN, HPLC-grade DMF, 1 M methanolic n-Bu_4NOH, n-Bu_4NHSO_4, $NaBF_4$, and hydroxylamine chlorhydrate were purchased from Aldrich. Acetonitrile was distilled over calcium hydride and stored under an argon atmosphere over activated 3-Å molecular sieves. n-Bu_4NBF_4 was synthesized from n-Bu_4NHSO_4 and $NaBF_4$ and dried overnight under vacuum.

The synthesis of $(n\text{-}Bu_4N)_3[Mo_6O_{18}(NO)]$ has been described elsewhere.[5]

Synthesis of $(n\text{-}Bu_4N)_3[W_5O_{18}\{Mo(NO)\}]$. A mixture of $(n\text{-}Bu_4N)_2[WO_4]$ (3.66 g, 5 mmol) and $[Mo(NO)\{MeC(NH_2)NO\}(acac)_2]$ (1.2 g, 3 mmol) in 25 mL of MeCN was refluxed for 4 h. The resulting deep-brown solution was filtered while hot and allowed to stand at ambient temperature. Light-green crystals of $(n\text{-}Bu_4N)_3[W_5O_{18}\{Mo(NO)\}]$ immediately began to grow. After a few days, they were collected by filtration and washed with diethyl ether. Yield: 1.19 g (57% based on $(n\text{-}Bu_4N)_2[WO_4]$). Anal. Calcd for $C_{48}H_{108}N_4MoO_{19}W_5$: C, 27.98; H, 5.28; N, 2.72; Mo, 4.66; W, 44.61. Found: C, 28.2; H, 5.3; N, 2.7; Mo, 4.8; W, 44.4. IR (cm^{-1}, KBr pellet): 1580 (s), 975 (w), 960 (vs), 885 (w), 830 (m), 800 (vs), 615 (w), 570 (w), 460 (m), 440 (m), 425 (m).

Synthesis of $(n\text{-}Bu_4N)_3[W_5O_{18}\{W(NO)\}]$. To $[W(NO)Cl_3(MeCN)_2]$ (0.402 g, 1 mmol) in 15 mL of distilled MeCN was added $(n\text{-}Bu_4N)_2[WO_4]$ (5.496 g, 7.5 mmol). The mixture immediately turned darker. After being refluxed for 4 h, the dark green mixture was filtered while hot, giving a nonidentified white solid which was discarded. Dark green crystals of $(n\text{-}Bu_4N)_3[W_5O_{18}\{W(NO)\}]$ formed from the filtrate within a few days. They were collected by filtration and air-dried. Yield: 0.39 g (18% based on $[W(NO)Cl_3(MeCN)_2]$). Anal. Calcd for $C_{48}H_{108}N_4O_{19}W_6$: C, 26.83; H, 5.07; N, 2.61; W, 51.34. Found: C, 27.7; H, 5.2; N, 2.8; W, 48.4. IR (cm^{-1}, KBr pellet): 1530 (s), 980 (w), 960 (vs), 885 (w), 830 (m), 800 (vs), 790 (s), 740 (w), 630 (w), 595 (w), 570 (w), 455 (m), 440 (m), 420 (m).

Synthesis of $(n\text{-}Bu_4N)_3[Mo_5O_{18}\{W(NO)\}]$. Mixing $(n\text{-}Bu_4N)_2[Mo_2O_7]$ (1.97 g, 2.5 mmol) and $[W(NO)Cl_3(MeCN)_2]$ (0.201 g, 0.5 mmol) in 15 mL of distilled acetonitrile produced a dark solution, which was refluxed for 4 h and then filtered to remove any insoluble particule. After this was allowed to stand for a few days at room temperature, brown crystals of $(n\text{-}Bu_4N)_3[Mo_5O_{18}\{W(NO)\}]$ were collected and washed with diethyl ether. Yield: 0.47 g (55% based on $[W(NO)Cl_3(MeCN)_2]$). Anal. Calcd for $C_{48}H_{108}N_4Mo_5O_{19}W$: C, 33.74; H, 6.37; N, 3.28; Mo, 28.07; W,10.76. Found: C, 33.9; H, 6.4; N, 3.4; Mo, 27.8; W, 11.4. IR (cm^{-1}, KBr pellet): 1520 (s), 965 (w), 940 (vs), 885 (w), 790 (vs), 770 (s), 620 (w), 570 (w), 475 (w), 395 (w), 370 (w).

If necessary, $(n\text{-}Bu_4N)_3[M_5O_{18}\{M'(NO)\}]$ (M, M′ = Mo, W) compounds can be easily recrystallized at room temperature in reagent-grade DMF.

Analyses. Elemental analyses were performed by the Service Central d'Analyse of the CNRS (Vernaison, France).

Physical Measurements. Infrared spectra were recorded from KBr pellets on a Bio-Rad FT 165 spectrometer. Electronic absorption spectra were recorded as MeCN solutions with a Shimadzu model UV-2101 spectrophotometer.

Electrochemistry. All measurements were carried out in DMF under argon at room temperature, using a standard three-electrode cell, which consisted of the working electrode, an auxiliary platinum electrode, and an aqueous saturated calomel electrode (SCE) equipped with a double junction. Solution concentrations were *ca.* 1 mM for the compound under study and 0.1 M for the supporting electrolyte, n-Bu_4NBF_4. Polarograms at a dropping mercury electrode or at a rotating platinum electrode were recorded at 0.15 or 0.30 $V\cdot min^{-1}$ on a Tacussel PRG3 device. Cyclic voltammograms at a platinum electrode were recorded at 0.1 V s^{-1} on a device made of a Tacussel PRT 100−1X potentiostat, a Tacussel GSTP4 waveform generator, and an IFELEC IF 2502 X-Y plotter.

NMR Studies. NMR spectra were measured on solutions with Bruker AC 300, MSL 400, and AM 500 spectrometers operating in the Fourier mode. High-temperature measurements were made using the internal Bruker BVT-1000 temperature control unit driven by a copper−constantan thermocouple. ^{95}Mo and ^{14}N NMR spectra were recorded on an AM 500 apparatus, at 32.6 and 36.1 MHz, respectively. Natural abundance ^{17}O NMR spectra were obtained at either 54.2 MHz (MSL 400) or 67.8 MHz (AM 500). ^{183}W spectra were obtained at either 12.5 MHz (AC 300), 16.7 MHz (MSL 400), or 20.8 MHz (AM 500). ^{95}Mo, ^{17}O, and ^{14}N NMR data were measured without lock, at 333 K, on nearly saturated solutions in MeCN, while the ^{183}W NMR data were obtained at 298 K on nearly saturated solutions in DMF containing about 10% v/v acetone-d_6 for field-frequency lock. Conventional 10 mm o.d. sample tubes were used. Chemical shifts in ppm were referenced to the appropriate standard: external aqueous alkaline Na_2MoO_4 solution for ^{95}Mo NMR, external Na_2WO_4 solution in D_2O for ^{183}W, external H_2O for ^{17}O, and internal MeCN for ^{14}N. The ^{14}N chemical shifts were recalculated with respect to neat liquid nitromethane ($\delta_{MeCN/MeNO_2} = -135.83$ ppm).[17]

X-ray Diffraction. Lattice parameters were obtained from a least-squares fit of the setting angles of 25 automatically centered reflections with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation.

Results

Syntheses. Molybdenum oxo nitrosyl complexes can be obtained through reductive nitrosylation of polyoxomolybdates in non-aqueous solvents; *e.g.* $(n\text{-}Bu_4N)_3[Mo_6O_{18}(NO)]$ is conveniently prepared by the reaction of hydroxylamine chlorhydrate on $(n\text{-}Bu_4N)_2[Mo_2O_7]$ in MeCN,[5] while free NH_2OH reacts with $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ to yield $(n\text{-}Bu_4N)_3[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot xMeOH$.[4a,b] However, the reductive nitrosylation of polyoxomolybdates is not quite general, *e.g.* Keggin-type molybdenum oxo−nitrosyl complexes could not be obtained through reaction of hydroxylamine with molybdenum Keggin anions,[6] and the reaction does not extend to polyoxotungstates. An alternative strategy for the synthesis of derivatized-polyoxometalates is based upon the condensation of the appropriate precursors.[16,18] Thus it was expected that the $[M_5O_{18}\{M'(NO)\}]^{3-}$ complexes could be obtained by reaction of a Mo(II) or W(II) nitrosyl complex with either $(n\text{-}Bu_4N)_2[Mo_2O_7]$ or $(n\text{-}Bu_4N)_2[WO_4]$. Among the numerous Mo(II) nitrosyl complexes reported in the literature,[19] we have selected $[Mo(NO)\{MeC(NH_2)NO\}(acac)_2]$, which is conveniently obtained by reductive nitrosylation of $[MoO_2(acac)_2]$ with acetamidoxime in MeOH[12] and which reacts with $(n\text{-}Bu_4N)_2[WO_4]$ in acetonitrile to give $(n\text{-}Bu_4N)_3[W_5O_{18}\{Mo(NO)\}]$. On the other hand, comparatively few nitrosyl W(II) complexes exist, among which $[W(NO)\{HB(Me_2pz)_3\}X_2]$,[20] $[W(NO)(OR)_3]_n$,[21] $[W(NO)Cl_3(PMe_3)_3]$,[22] and $[W(NO)Cl_3(MeCN)_2]$,[13] have been described.[19] The latter was selected and was found to react with $(n\text{-}Bu_4N)_2[Mo_2O_7]$ or $(n\text{-}Bu_4N)_2[WO_4]$ to give $(n\text{-}Bu_4N)_3[Mo_5O_{18}\{W(NO)\}]$ or $(n\text{-}Bu_4N)_3[W_5O_{18}\{W(NO)\}]$, respectively. In this way, we have achieved the synthesis of the whole series of Lindqvist-type nitrosyl derivatives $(n\text{-}Bu_4N)_3[M_5O_{18}\{M'(NO)\}]$ (M, M′ = Mo, W). It is noteworthy that these compounds have been also isolated, though in low yield, from the reactions of dinitrosyl M′(0) complexes, *e.g.* $[Mo(NO)_2(acac)_2]$[14] or $[W(NO)_2(acac)(MeCN)_2](BF_4)$[15] with oxometalates in MeCN.[23] The conversion of the $[M'(NO)_2]^{2+}$ unit into $[M'(NO)]^{3+}$ is precedented.[14a,24]

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Table 1. Lattice Parameters for $(n\text{-Bu}_4\text{N})_3[\text{M}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]$

	M = M′ = W	M = W, M′ = Mo	M = M′ = Mo[a]	M = Mo, M′ = W
system	monoclinic	monoclinic	monoclinic	monoclinic
a (Å)	16.697 (7)	16.724 (4)	16.688 (3)	16.698 (4)
b (Å)	17.28 (1)	17.276 (5)	17.210 (3)	17.280 (3)
c (Å)	24.330 (6)	24.336 (8)	24.267 (4)	24.342 (4)
β (°)	97.53 (3)	97.57 (2)	97.44 (1)	97.35 (2)
V (Å^3)	6957 (26)	6970 (22)	6911 (13)	6972 (15)

[a] Reference 4a.

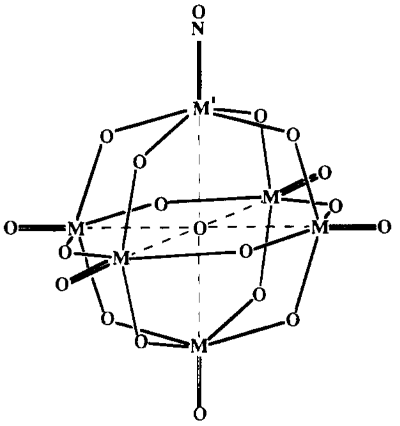

Figure 1. Idealized representation of $[\text{M}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]^{3-}$.

X-ray Diffraction Studies. Lattice parameters are given in Table 1 which reveals that the four $(n\text{-Bu}_4\text{N})_3[\text{M}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]$ compounds are isostructural. It has been previously found that the unit cell of $(n\text{-Bu}_4\text{N})_3[\text{Mo}_5\text{O}_{18}\{\text{Mo}(\text{NO})\}]$ contains two anions, which are located on inversion centers, and six cations.[4a,5] The same features should be exhibited by the crystals of the three other compounds. An idealized representation of the $[\text{M}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]^{3-}$ anion is shown in Figure 1. Throughout the rest of the paper, the different types of oxo ligands will be termed O_t (terminal), O_b (bridging) and O_c (central).

IR and Electronic Spectroscopy. The IR spectra of $(n\text{-Bu}_4\text{N})_3[\text{M}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]$ all display two very strong bands at about 950 and 800 cm^{-1}, which are characteristic of the Lindqvist structure (Table 2). According to valence force field calculations of Lindqvist-type polyoxometalates,[25] the first one can be described as a pure $\text{M}{=}\text{O}_t$ stretching, while the second probably presents some $\text{M}{=}\text{O}_t$ stretching and bending characters in addition to the dominant $\text{M}{-}\text{O}_b$ stretching character. The vibrational spectra of $\text{M}_5\text{M}'$ Lindqvist-type oxoanions can be assigned in idealized O_h symmetry only when M and M′ belong to the same group and present the same oxidation state.[25] In all other cases, more or less marked splittings are observed. In the approximation of separate $\text{M}{=}\text{O}_t$ and $\text{M}'{=}\text{N}$ vibrators, one $\text{M}'{=}\text{N}$ and three $\text{M}{=}\text{O}_t$ IR-active stretching modes would be expected.[7] Actually, a weak band is observed on the high-frequency side of the intense $\nu(\text{M}{=}\text{O}_t)$ band. In the absence of Raman and of metal, oxygen or nitrogen isotopic substitution data, the assignment of this band to either $\nu(\text{M}{=}\text{N})$ or $\nu(\text{M}{=}\text{O}_t)$ would be mostly speculative. The frequencies of the dominant M−O stretching modes are slightly higher for M = W than for M = Mo, reflecting the expected differences in M−O force constants. The weakening of both $\text{M}{-}\text{O}_t$ and $\text{M}{-}\text{O}_b$ bonds with respect to $(n\text{-Bu}_4\text{N})_2[\text{M}_6\text{O}_{19}]$ could arise (i) from a decrease in the cohesion of the M_5O_{18} framework due to the larger M′(II) sphere radius, or (ii) from a redistribution of the potential energy through the oxygen framework due to the overall charge increase. The third dominant band in the IR spectra of $(n\text{-Bu}_4\text{N})_3[\text{M}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]$ corresponds to the NO stretching in the range 1520−1580 cm^{-1}. A common feature of all nitrosyl polyoxometalate derivatives characterized to date,[4−6] is the remarkably low value of ν(NO) for linear nitrosyl groups. The decrease in the NO force constant for W(NO)-containing anions with respect to their Mo(NO) counterparts reflects the increase in π-basicity of tungsten with respect to molybdenum.[26] On the other hand, the slight decrease in ν(NO) from $[\text{W}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]^{3-}$ to $[\text{Mo}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]^{3-}$ suggests that the net electron donation is less from the W_5O_{18} core than from the Mo_5O_{18} core.

Electronic spectral data for $(n\text{-Bu}_4\text{N})_3[\text{M}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]$ are given in Table 3. All spectra display at least one intense band at about 300 nm and a weak absorption in the range 610−680 nm. The former is conceivably an oxygen to M(VI) charge-transfer transition while the latter is associated with the M′(NO) unit: it could be either a $d_{xz},d_{yz} \rightarrow d_{xy}$ transition as previously assumed for $(n\text{-Bu}_4\text{N})_3[\text{Mo}_5\text{O}_{18}\{\text{Mo}(\text{NO})\}]$[4b,5] or a $d_{xz},d_{yz} \rightarrow \pi^*(\text{NO})$ transition. This band is quite broad and splits into two components for $(n\text{-Bu}_4\text{N})_3[\text{W}_5\text{O}_{18}\{\text{W}(\text{NO})\}]$ in DMF solution, so that both transitions could be actually involved. It is obscured by the broad O → Mo charge-transfer transition in the case of $(n\text{-Bu}_4\text{N})_3[\text{Mo}_5\text{O}_{18}\{\text{W}(\text{NO})\}]$.

NMR Studies. All $(n\text{-Bu}_4\text{N})_3[\text{M}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]$ compounds are more soluble in DMF than in MeCN. Due to the low receptivity of the tungsten-183 nucleus, the ^{183}W NMR spectra were measured in DMF at room temperature on nearly saturated solutions. However, such solutions are rather viscous and give broad lines in ^{95}Mo NMR. Since the quadrupolar relaxation rate can be reduced through an increase in temperature and a decrease in solvent viscosity, the ^{95}Mo ($I = {}^5/_2$) NMR spectra were obtained at 333K from MeCN solutions.[5]

According to the idealized C_{4v} symmetry of the $[\text{M}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]^{3-}$ anions, the metal centers belong to three types, *e.g.* one M′(II), four equatorial M(VI) (M_{eq}) and one axial M(VI) (M_{ax}). All three expected resonances, with relative intensities 1:4:1, have been observed for the homometallic species $[\text{Mo}_5\text{O}_{18}\{\text{Mo}(\text{NO})\}]^{3-}$ [5] and $[\text{W}_5\text{O}_{18}\{\text{W}(\text{NO})\}]^{3-}$ (Figure 2). On the other hand, both the ^{95}Mo NMR spectrum of $[\text{Mo}_5\text{O}_{18}\{\text{W}(\text{NO})\}]^{3-}$ and the ^{183}W spectrum of $[\text{W}_5\text{O}_{18}\{\text{Mo}(\text{NO})\}]^{3-}$ present two lines with relative intensities 4:1, which are respectively assigned to the four M_{eq} and to the unique M_{ax}. In both cases, the expected resonance of the M′(II) center has been observed in the relevant NMR spectrum (respectively ^{183}W and ^{95}Mo).

The results have been gathered in Table 4. As previously noticed for the Mo(II) resonance in $[\text{Mo}_5\text{O}_{18}\{\text{Mo}(\text{NO})\}]^{3-}$,[5] the W(II) resonance in $[\text{W}_5\text{O}_{18}\{\text{W}(\text{NO})\}]^{3-}$ and $[\text{Mo}_5\text{O}_{18}\{\text{W}(\text{NO})\}]^{3-}$, lying at about 600 ppm, is highly deshielded with respect to those of the W(VI) centers at about 160 ppm. This was previously ascribed to an enhanced contribution of the paramagnetic term in shielding,[5] which is supported by the presence of low-lying magnetically active excited states in the $[\text{M}_5\text{O}_{18}\{\text{M}'(\text{NO})\}]^{3-}$ species. Furthermore, the M(II) resonance is much broader than the M(VI) lines whether M = Mo or W. Such a broadening could arise (i) from the unsymmetrical environment of the nitrosyl-bearing metal center, resulting in fast relaxation of the corresponding ^{95}Mo or ^{183}W nucleus (quadrupolar or chemical shift anisotropy—CSA—mechanism), and/or (ii) from the partially coalesced coupling with the spin-1 ^{14}N nucleus of the nitrosyl ligand (scalar relaxation of the second

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(25) (a) Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Fouassier, M. *Inorg. Chem.* **1982**, *21*, 30. (b) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *J. Mol. Struct.* **1984**, *114*, 49. (c) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Spectrosc. Lett.* **1986**, *19*, 765.

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Table 2. Selected IR Data[a,b]

	ν(NO)	$\nu(MO_t)$		$\nu(MO_bM)$			
$[W_6O_{19}]^{2-}$		975 vs			815 vs		740 w
$[W_5O_{18}\{W(NO)\}]^{3-}$	1530 s	980 w	960 vs	830 m	800 vs	790 s	740 w
$[W_5O_{18}\{Mo(NO)\}]^{3-}$	1580 s	975 w	960 vs	830 m	800 vs		
$[Mo_6O_{19}]^{2-}$		955 vs			800 vs		740 w
$[Mo_5O_{18}\{Mo(NO)\}]^{3-}$	1570 s	960 w	940 vs		790 vs		
$[Mo_5O_{18}\{W(NO)\}]^{3-}$	1520 s	965 w	940 vs		790 vs	770 s	

[a] Spectra recorded as KBr pellets of tetrabutylammonium salts. [b] ν in cm^{-1}.

Table 3. Electronic Spectral Data[a]

	λ^b (ϵ)^c	λ^b (ϵ)^c
$[W_6O_{19}]^{2-}$	280 (14500)	
$[W_5O_{18}\{W(NO)\}]^{3-}$	280 (14900)	610 (90)
$[W_5O_{18}\{Mo(NO)\}]^{3-}$	265 (14800) 320 (5300)^d	680 (20)
$[Mo_6O_{19}]^{2-}$	260 (17600) 325 (9000)	
$[Mo_5O_{18}\{Mo(NO)\}]^{3-}$	325 (13400)	665 (45)
$[Mo_5O_{18}\{W(NO)\}]^{3-}$	310 (9600)	*e*

[a] Spectra recorded in MeCN. [b] λ in nm. [c] ϵ in mol^{-1} L cm^{-1}. [d] Shoulder. [e] See text.

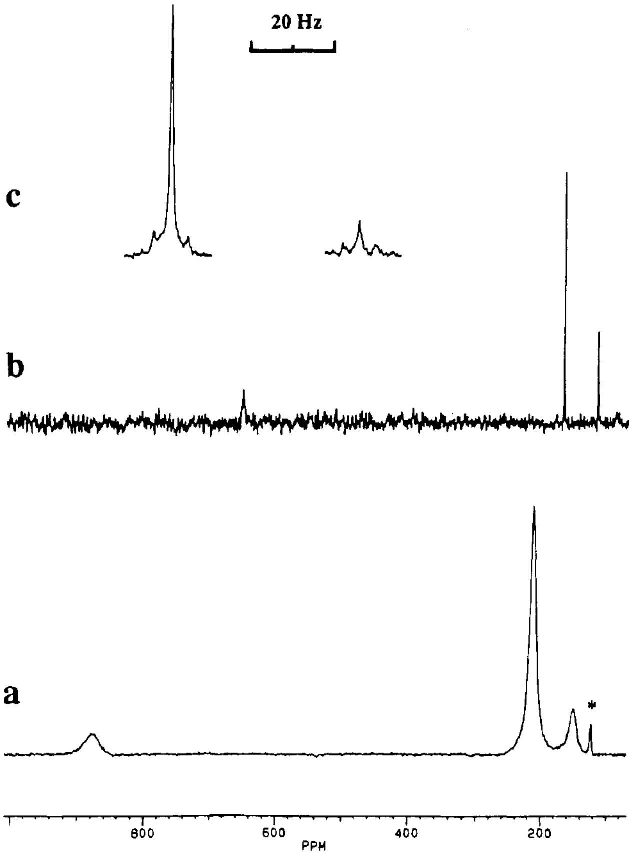

Figure 2. NMR spectra of the homometallic $[M_6O_{18}(NO)]^{3-}$ anions recorded at 298K: (a) 32.6 MHz ^{95}Mo spectrum of $[Mo_6O_{18}(NO)]^{3-}$ in MeCN; (b) 20.8 MHz ^{183}W spectrum of $[W_6O_{18}(NO)]^{3-}$ in DMF/ CD_3COCD_3 (c) abscissa expansion of the W(VI) resonances showing the tungsten satellites due to mutual homonuclear $^2J(W_{eq}^{VI} - W_{ax}^{VI})$ coupling.

Table 4. ^{95}Mo and ^{183}W NMR Data for Lindqvist-Type Polyanions[a]

	δ (ppm)			$J_{W_{eq}-W_{ax}}$ (Hz)
	M′ ^{b}	M_{eq} ^{b}	M_{ax} ^{b}	
$[W_6O_{19}]^{2-}$		59		
$[W_5O_{18}\{MoO\}]^{2-}$ ^{c}		66.5	59.3	9.3
$[W_5O_{18}\{W(NO)\}]^{3-}$	653 (80)	168 (1)	116.5 (1.5)	8.3
$[W_5O_{18}\{Mo(NO)\}]^{3-}$	938 (750)	166,5 (1)	129 (1)	7.8
$[Mo_6O_{19}]^{2-}$		124		
$[Mo_5O_{18}\{WO\}]^{2-}$ ^{c}	65.2			
$[Mo_5O_{18}\{Mo(NO)\}]^{3-}$ ^{d}	878 (600)	212 (250)	146 (350)	
$[Mo_5O_{18}\{W(NO)\}]^{3-}$	614 (90)	228 (180)	150 (230)	

[a] ^{95}Mo chemical shifts referred to external Na_2MoO_4 in D_2O; ^{183}W chemical shifts referred to external Na_2WO_4 in D_2O. [b] Line width (in Hz) in parentheses. [c] Reference 29. [d] Reference 5.

kind).[27] Scalar $^1J(^{95}Mo-^{14}N)$ coupling has been observed in a few cases, including mononuclear molybdenum nitrosyl complexes[28] and Lindqvist-type phenylimido derivatives $[Mo_6O_{19-x}(NPh)_x]^{2-}$ (x = 1, 2),[7] where the coupling constants lie in the range 40–50 Hz. Therefore, the significant broadening (>600 Hz, see Table 4) of the Mo(II) line for $[W_5O_{18}\{Mo(NO)\}]^{3-}$ and $[Mo_5O_{18}\{Mo(NO)\}]^{3-}$ anions cannot be accounted for by the scalar relaxation mechanism only; thus, the quadrupolar relaxation induced by a large electric field gradient at the resonant ^{95}Mo nucleus should be the dominant relaxation process. On the other hand, the W(II) line width (<100 Hz at 298 K) for both $[Mo_5O_{18}\{W(NO)\}]^{3-}$ and $[W_5O_{18}\{W(NO)\}]^{3-}$ anions is consistent with a dominant scalar relaxation mechanism. Furthermore, the W(II) line width for $[Mo_5O_{18}\{W(NO)\}]^{3-}$ has been found to be nearly independent on the magnetic field ($\Delta\nu_{1/2}$ ~ 80–90 Hz at 7 and 11.8 T), thus a CSA mechanism can be ruled out.

The narrowness of the W(VI) lines allows the observation of the tungsten satellites. The homonuclear $^2J(W_{eq}^{VI}-W_{ax}^{VI})$ coupling constants of about 8 Hz are hardly significantly smaller than in the parent $[W_5O_{18}MoO]^{2-}$ oxoanion where $^2J(W_{eq}-W_{ax})$ = 9.3 Hz,[29] which indicates that the geometry of the W_5O_{18} framework is not markedly affected upon the substitution of $M'(NO)^{3+}$ for MoO^{4+}. Note that the$W_{eq}^{VI}-W^{II}$ coupling could not be observed, due to the rapid relaxation of the W(II) nucleus.

The natural-abundance ^{17}O NMR spectra of $(n\text{-}Bu_4N)_3[M_5O_{18}\{M'(NO)\}]$ have been measured on MeCN solutions at 333 K in order to reduce the relaxation rate,[30] hence the signal linewidth. All spectra display a pattern of five lines with relative intensities 4:1:4:4:4 (Figure 3). According to the acknowledged correlation between O–M bond strengths and ^{17}O chemical shifts, the first two deshielded lines (δ > 700 ppm) are assigned to the five terminal oxo ligands and the three other lines (600 ppm > δ > 400 ppm) to the 12 bridging oxo ligands. Note that the two most shielded resonances merge into one single line, with relative intensity 8, for $[W_5O_{18}\{Mo(NO)\}]^{3-}$. A high repetition rate (10–20 Hz) was intentionally selected in order to reduce the accumulation time of these natural-abundance ^{17}O NMR spectra. It follows that the relaxation of the central oxo ligand could not be achieved, thus the O_c resonance could not be detected. Moreover, the O–N resonance was not observed,

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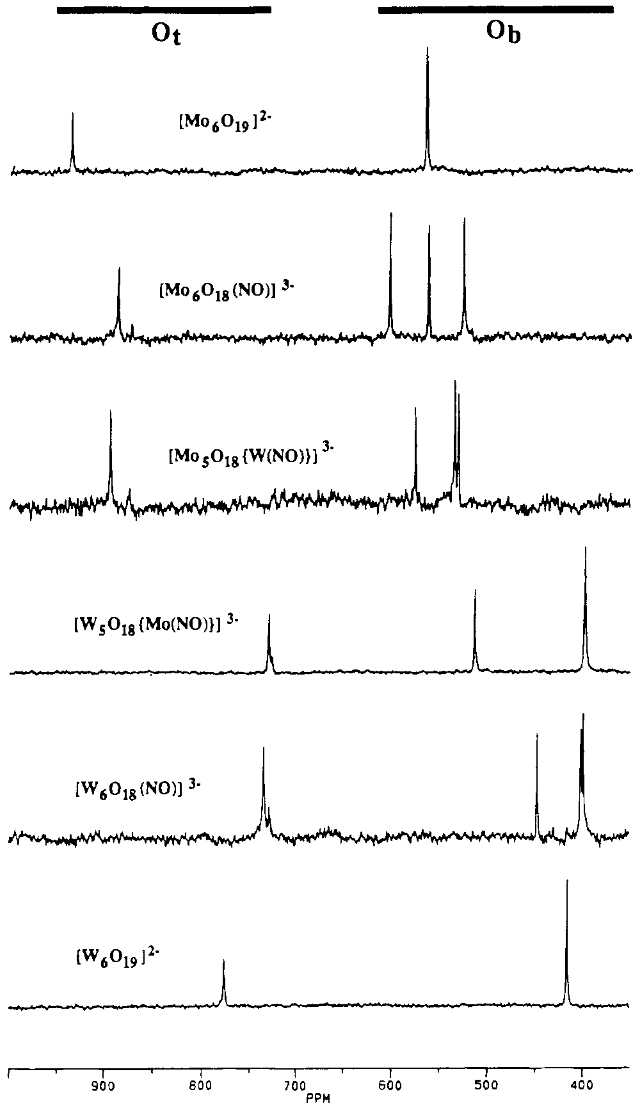

Figure 3. Natural-abundance ^{17}O NMR spectra of all $[M_5O_{18}\{M'(NO)\}]^{3-}$ anions and of the parent oxoanions $[M_6O_{19}]^{2-}$ (M, M′ = Mo, W) recorded at 333 K on MeCN solutions, either at 54.2 MHz (MSL400, $[W_6O_{19}]^{2-}$, $[W_5O_{18}\{Mo(NO)\}]^{3-}$, $[Mo_6O_{19}]^{2-}$) or at 67.8 MHz (AM500, $[W_6O_{18}(NO)]^{3-}$, $[Mo_5O_{18}\{W(NO)\}]^{3-}$, $[Mo_6O_{18}(NO)]^{3-}$).

Table 5. ^{17}O NMR Data for Lindqvist-Type Hexametalates[a,b]

	δ_{O_t}[c]		δ_{O_b}[c]		
			OMM′	OM$_2$	
$[W_6O_{19}]^{2-}$	775 (6)			415 (12)	
$[W_5O_{18}\{W(NO)\}]^{3-}$	734 (4)	728 (1)	448 (4)	402 (4)	399 (4)
$[W_5O_{18}\{Mo(NO)\}]^{3-}$	730 (4)	727 (1)	514 (4)	399 (8)	
$[Mo_6O_{19}]^{2-}$	935 (6)			564 (12)	
$[Mo_5O_{18}\{Mo(NO)\}]^{3-}$[d]	886 (4)	871 (1)	603 (4)	563 (4)	526 (4)
$[Mo_5O_{18}\{W(NO)\}]^{3-}$	894 (4)	874 (1)	534 (4)	575 (4)	530 (4)

[a] Spectra recorded at 333 K in MeCN. [b] ^{17}O chemical shifts referred to external OH$_2$. [c] δ in ppm; relative intensity in parentheses. [d] Reference 5.

likely because of the $^{17}O-^{14}N$ coupling. Chemical shifts values, referred to external OH$_2$, are given in Table 5.

For the homometallic derivatives $[W_5O_{18}\{W(NO)\}]^{3-}$ and $[Mo_5O_{18}\{Mo(NO)\}]^{3-}$, the δ_{O_b} range is rather narrow (49 and 77 ppm respectively) and the center of gravity of the three lines lies close to the O$_b$ line for the parent oxo anion, respectively $[W_6O_{19}]^{2-}$ and $[Mo_6O_{19}]^{2-}$. Thus, the O$_b$ resonances are only slightly shifted upon the substitution of $M(NO)^{3+}$ for MO^{4+}. On the contrary, δ_{O_b} strongly depends upon M. Tungsten-bounded ^{17}O nuclei are highly shielded with respect to similar molybdenum-bounded ^{17}O nuclei, *e.g.* W–O$_b$–W oxo ligands are shielded by about 150 ppm with respect to Mo–O$_b$–Mo ligands, while Mo–O$_b$–W resonances lie between those of W–O$_b$–W and Mo–O$_b$–Mo in mixed $[Mo_{6-x}W_xO_{19}]^{2-}$ species.[29] Thus, δ_{O_b} for the $[M_5O_{18}\{M'(NO)\}]^{3-}$ species should be arranged in the order: $Mo^{II}-O_b-Mo^{VI} \gg Mo^{II}-O_b-W^{VI} \approx W^{II}-O_b-Mo^{VI} \gg W^{II}-O_b-W^{VI}$. For a given M_5O_{18} moiety, the $M'^{II}-O_b-M^{VI}$ line can be identified as the most deshielded O$_b$ line upon the replacement of W(II) by Mo(II). Thus, the line at 448 ppm for $[W_5O_{18}\{W(NO)\}]^{3-}$ can be assigned to the $W^{II}-O_b-W^{VI}$ resonance since it shifts to 514 ppm for $[W_5O_{18}\{Mo(NO)\}]^{3-}$, whereas the two other O$_b$ lines are nearly unchanged. Similarly, the line at 534 ppm for $[Mo_5O_{18}\{W(NO)\}]^{3-}$ can be assigned to the $W^{II}-O_b-Mo^{VI}$ resonance since it shifts to 603 ppm for $[Mo_5O_{18}\{Mo(NO)\}]^{3-}$, whereas the locations of the two other lines compare well in both complexes. It follows that $\delta(W^{II}-O_b-W^{VI}) > \delta(W^{VI}-O_b-W^{VI})$ and $\delta(Mo^{II}-O_b-W^{VI}) > \delta(W^{II}-O_b-W^{VI})$, and accordingly $\delta(Mo^{II}-O-Mo^{VI}) > \delta(Mo^{VI}-O-Mo^{VI})$, and $\delta(Mo^{II}-O_b-Mo^{VI}) > \delta(W^{II}-O_b-Mo^{VI})$. Concerning $\delta_{OMM'}$, the deshielding effect upon the substitution of Mo for W is then about 85–90 ppm for the M_5O_{18} core, and about 70 ppm for the M′(NO) unit.

Table 6. ^{14}N NMR Data[a,b]

	δ (ppm)[c]
$[W_5O_{18}\{W(NO)\}]^{3-}$	11.1 (50)
$[W_5O_{18}\{Mo(NO)\}]^{3-}$	22.6 (5)
$[Mo_5O_{18}\{Mo(NO)\}]^{3-}$ [d]	15.2 (15)
$[Mo_5O_{18}\{W(NO)\}]^{3-}$	−24.1 (20)

[a] Spectra recorded in MeCN at 333 K. [b] ^{14}N Chemical shifts referred to neat MeNO$_2$. [c] Line width in parentheses. [d] Reference 5.

The ^{14}N NMR chemical shifts of $[M_5O_{18}\{M'(NO)\}]^{3-}$ anions are within the range for linear nitrosyl ligands,[31–33] and follow the same general shielding pattern as the M′-NMR chemical shift. The nitrogen shielding increases from M′ = Mo to M′ = W, as the excitation energy increases. On the other hand, the nitrogen shielding decreases from $[Mo_5O_{18}\{M'(NO)\}]^{3-}$ to $[W_5O_{18}\{M'(NO)\}]^{3-}$ for a given M′(NO) unit. This is consistent with the apparent decrease in the HOMO-LUMO gap (Table 3).

Electrochemical Studies. The electrochemical behavior of the four compounds has been studied in DMF (Table 7). Although none of them is reducible at a platinum electrode, all display a reduction wave at a dropping mercury electrode. Comparison with the $(n\text{-}Bu_4N)_2[M_6O_{19}]$ parents suggests that this is a one-electron reduction process, as expected in aprotic media. For both $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ and $(n\text{-}Bu_4N)_2[W_6O_{19}]$, the second reduction wave is altered by a maximum so that an accurate value of $E_{1/2}$ cannot be determined; estimated values are −1.40 and −2.15 V respectively. All four nitrosyl derivatives also display an oxidation wave at a rotating platinum electrode. This oxidation process was shown to be reversible according to cyclic voltammetry, which also supports a one-electron process. $(n\text{-}Bu_4N)_3[W_5O_{18}\{W(NO)\}]$ and $(n\text{-}Bu_4N)_3[Mo_5O_{18}\{W(NO)\}]$ further exhibit a second irreversible, multi-electron-oxidation process, at respectively +1.43 and +1.25 V.

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Table 7. Electrochemical Data[a] for $[M_5O_{18}\{M'(NO)\}]3-$ anions in DMF[b]

	$E_{1/2}$[c]	$E_{1/2}$[d]	E_{p_a}[c,e]	E_{p_c}[c,e]	$(E_{p_a} + E_{p_c})/2$	$E_{p_a} - E_{p_c}$
$[W_6O_{19}]^{2-}$		−1.02				
		∼ −2.15[f]				
$[W_5O_{18}\{W(NO)\}]^{3-}$	∼1.43[f]					
	0.51		0.59	0.49	0.54	0.1
		−1.74				
$[W_5O_{18}\{Mo(NO)\}]^{3-}$	0.85		0.95	0.85	0.90	0.1
		−1.39				
$[Mo_6O_{19}]^{2-}$		−0.47				
		∼ −1.40[f]				
$[Mo_5O_{18}\{Mo(NO)\}]^{3-}$	0.76		0.79	0.71	0.75	0.08
		−1.22				
$[Mo_5O_{18}\{W(NO)\}]^{3-}$	∼1.25[f]					
	0.38		0.45	0.36	0.41	0.09
		−1.15				

[a] $E_{1/2}$ (half-wave potential), E_{p_a} (anodic peak potential) and E_{p_c} (cathodic peak potential) in V *vs* SCE. [b] 0.1M in n-Bu_4NBF_4. [c] Platinum electrode. [d] Dropping mercury electrode. [e] Scan rate: 0.1 V s^{-1}. [f] See text.

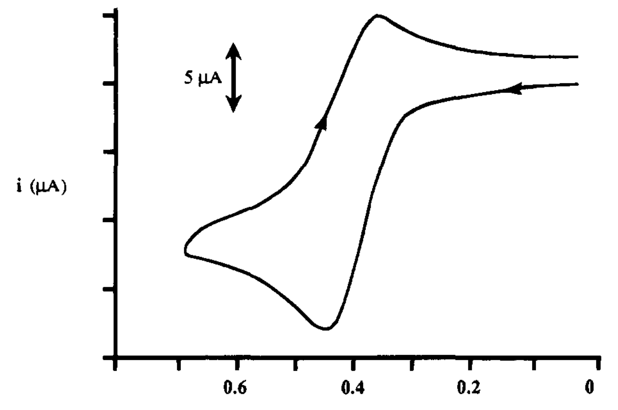

Figure 4. Cyclic voltammogram of $(n\text{-}Bu_4N)_3[Mo_5O_{18}\{W(NO)\}]$ at a platinum electrode in DMF. Concentration: 10^{-3} M. Scan rate: 0.1 V/s

Discussion

The extent of electronic interaction between $M'(NO)^{3+}$ and oxometalate moieties can be assessed by considering the following effects: (i) the overall anion charge increase, which should mainly affect the charge density on peripheral oxo ligands, hence the ^{17}O rather than the ^{183}W or ^{95}Mo resonances within the M_5O_{18} framework, (ii) the delocalization of the M'(II) d-electrons onto the adjacent M(VI) centers, which should be reflected in the ^{183}W or ^{95}Mo rather than in the ^{17}O NMR spectra, (iii) the electron-withdrawing effect of the nitrosyl ligand, which should be inferred from ^{14}N, ^{17}O, and ^{183}W or ^{95}Mo NMR, as well as from IR data, (iv) the substitution of W for Mo, and (v) a change in the structure, *e.g.* Lindqvist- *vs* Keggin-type, by comparison with previous results.[7] Let us recall that in reduced polyoxoanions, the extent of electronic delocalization is higher in tungstates than in molybdates and higher in Keggin-type than in Lindqvist-type oxometalates.[34]

Let us characterize the M_5O_{18} framework of a given $[M_5O_{18}\{M'(NO)\}]^{3-}$ species by an average M(VI) chemical shift defined as $\langle\delta\rangle = [4\delta_{M_{eq}} + \delta_{M_{ax}}]/5$ (M = Mo or W). The calculated values are given in Table 8 together with those for a number of related compounds. It can be inferred from the comparison of $[Mo_6O_{19}]^{2-}$ with $[Mo_5O_{18}\{VO\}]^{3-}$,[35a] and from that of $[W_6O_{19}]^{2-}$ with $[W_5O_{18}\{MoO\}]^{2-}$ [29] and $[W_5O_{18}\{VO\}]^{3-}$,[35b] that the replacement of one metallic M(VI) center by another one d^0-center induces only a small shift on the M(VI) resonances whether the whole charge remains constant or not. On the contrary, these resonances are significantly deshielded in $[M_5O_{18}\{M'(NO)\}]^{3-}$ with respect to the $[M_6O_{19}]^{2-}$ parents. It is also noteworthy that the splitting resulting from the $O_h \rightarrow C_{4v}$ correlation is much larger for d^4-nitrosyl than for d^0-oxo derivatives. These features are reminiscent of those displayed by the ^{183}W NMR spectra of diamagnetic $[PW_{11}O_{39}\{Ru^{II}(L)\}]^{5-}$ where the tungsten atoms adjacent to the Ru(II) center are strongly deshielded with respect to the Zn analogue.[36a] According to Rong and Pope,[36a] electrochemical and spectral data for the Ru(II) derivatives are clearly indicative of partial delocalization of Ru π-electron density on the adjacent tungsten atoms, which is consistent with the deshielding of these atoms: indeed, ^{183}W NMR of diamagnetic reduced heteropolyanions has shown that the signals of the W atoms bearing the added electrons are consistently high frequency shifted with respect to the corresponding signals in the nonreduced anion. This has been ascribed to a dominant paramagnetic contribution to the nuclear shielding.[28,36] Therefore, the significant deshielding of the M(VI) centers in $[M_5O_{18}\{M'(NO)\}]^{3-}$ with respect to $[M_6O_{19}]^{2-}$ could be likewise assigned to a partial delocalization of the M'(II) d-electrons onto the M_5O_{18} framework. A similar analysis has been done previously for $[PW_{11}O_{39}\{Mo(NO)\}]^{4-}$.[7] The deshielding magnitude is approximately the same in Lindqvist- as in Keggin-type nitrosyl derivatives, but is much less than in $[PW_{11}O_{39}\{Ru^{II}(L)\}]^{5-}$.

Table 8. Average ^{183}W or ^{95}Mo Chemical Shifts for Lindqvist-Type Polyanions

	$\delta_{M_{eq}}$	$\delta_{M_{ax}}$	$\Delta\delta$	$\langle\delta\rangle$[a]	$\langle\delta\rangle - \delta_{[M_6O_{19}]^{2-}}$
$[W_6O_{19}]^{2-}$	59		0	59	0
$[W_5O_{18}\{MoO\}]^{2-}$[b]	66.5	59.3	7.2	65.1	6.1
$[W_5O_{18}\{VO\}]^{3-}$[c]	76.4	75.9	0.5	76.3	17.3
$[W_5O_{18}\{W(NO)\}]^{3-}$	168	116.5	51.5	157.7	98.7
$[W_5O_{18}\{Mo(NO)\}]^{3-}$	166.5	129	37.5	159	100
$[Mo_6O_{19}]^{2-}$	124		0	124	0
$[Mo_5O_{18}\{VO\}]^{3-}$[d]				128	4
$[Mo_5O_{18}\{Mo(NO)\}]^{3-}$	212	146	66	198.8	74.8
$[Mo_5O_{18}\{W(NO)\}]^{3-}$	228	150	78	212.4	88.4

[a] $\langle\delta\rangle = [4\delta(M_{eq}) + \delta(M_{ax})]/5$. [b] Reference 29. [c] Reference 35b. [d] Reference 35a; aqueous solution.

^{183}W chemical shifts and $^2J_{W-W}$ coupling constants for $[W_5O_{18}\{W(NO)\}]^{3-}$ and $[W_5O_{18}\{Mo(NO)\}]^{3-}$ are very similar, and so are ^{95}Mo chemical shifts for $[Mo_5O_{18}\{W(NO)\}]^{3-}$ and $[Mo_5O_{18}\{Mo(NO)\}]^{3-}$. Thus it appears that the substitution of

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Table 9. Average ^{17}O Chemical Shifts for Some Linqvist-Type Polyanions

	$\langle\delta_{O_t}[OMo^{VI}]\rangle^a$	$\langle\delta_{O_b}[OMo^{VI}_2]\rangle^a$		$\langle\delta_{O_t}[OW^{VI}]\rangle$	$\langle\delta_{O_b}[OW^{VI}_2]\rangle$	$\Delta\langle\delta_{O_t}[OM^{VI}]\rangle^b$	$\Delta\langle\delta_{O_b}[OM^{VI}_2]\rangle^c$
$[Mo_6O_{19}]^{2-}$	935	564	$[W_6O_{19}]^{2-}$	775	415	160	149
$[Mo_5O_{18}\{VO\}]^{3-\ d}$	885	536	$[W_5O_{18}\{VO\}]^{3-\ d}$	731	392	154	144
	−50	*−28*		*−44*	*−23*		
			$[W_5O_{18}\{NbO\}]^{3-\ e}$	731.6	393		
				-43.4	*−22*		
			$[W_5O_{18}\{TaO\}]^{3-\ e}$	732.6	393.5		
				−42.4	*−21.5*		
			$[W_5O_{18}\{NbS\}]^{3-\ f}$	758.4	402		
				−16.6	*−13*		
			$[W_5O_{18}\{TaS\}]^{3-\ f}$	756	404.5		
				−19	*−10.5*		
$[Mo_5O_{18}\{Mo(NO)\}]^{3-}$	883	544.5	$[W_5O_{18}\{Mo(NO)\}]^{3-}$	729.4	399	153.6	145.5
	−52	*−19.5*		*−45.6*	*−16*		
$[Mo_5O_{18}\{W(NO)\}]^{3-}$	890	552.5	$[W_5O_{18}\{W(NO)\}]^{3-}$	732.8	400.5	157.2	131.5
	−45	*−11.5*		*−42.2*	*−14.5*		
$[PMo_{12}O_{40}]^{3-\ d}$	936	583	$[PW_{12}O_{40}]^{3-\ d}$	769	431	167	152
		550			405		145
$[SiMo_{12}O_{40}]^{4-\ d}$	928	580	$[SiW_{12}O_{40}]^{4-\ d}$	761	427	167	153
		555			405		150

[a] The value of $\langle\delta\rangle - \delta_{\text{oxo parent}}$ is given in italics. [b] $\Delta\langle\delta_{O_t}\rangle = \langle\delta_{O_t}[OMo^{VI}]\rangle - \langle\delta_{O_t}[OW^{VI}]\rangle$. [c] $\langle\delta_{O_b}\rangle = \langle\delta_{O_b}[OMo^{VI}_2]\rangle$ - $\langle\delta_{O_b}[OW^{VI}_2]\rangle$. [d] Reference 38. [e] Reference 39. [f] Reference 40.

$W(NO)^{3+}$ for $Mo(NO)^{3+}$ has no significant effect on the M_5O_{18} core. Then, we will consider the replacement of a Mo_5O_{18} by a W_5O_{18} core. Although the magnitude of the overall deshielding, defined as $\langle\delta\rangle - \delta_{\text{parent}}$ is larger for M = W than for M = Mo (Table 8), the difference in δ-sensitivity must be taken into account. Indeed, the expected correlation between ^{95}Mo and ^{183}W chemical shifts for closely related polyoxoanions,[37] *e.g.* $[Mo_6O_{19}]^{2-}$ and $[W_6O_{19}]^{2-}$, $[Mo_5O_{18}(VO)]^{3-}$ [35a] and $[W_5O_{18}(VO)]^{3-}$,[35b] $[Mo_5O_{18}\{W(NO)\}]^{3-}$ and $[W_5O_{18}\{W(NO)\}]^{3-}$, and $[Mo_5O_{18}\{Mo(NO)\}]^{3-}$ and $[W_5O_{18}\{Mo(NO)\}]^{3-}$, is actually observed. Thus, ^{95}Mo and ^{183}W NMR data hardly reveal any significant difference between the accepting properties of the M_5 cores.

The ^{17}O NMR spectrum of any $[M_5O_{18}\{M'(NO)\}]^{3-}$ anion is globally shielded with respect to that of the oxo parent $[M_6O_{19}]^{2-}$. This shielding has been calculated as $\langle\delta\rangle - \delta_{\text{parent}}$ for both terminal and bridging ligands, and is given in italics in Table 9 where it can be seen that the values for d^4-$[M_5O_{18}\{M'(NO)\}]^{3-}$ (M' = Mo, W) and for d^0-$[M_5O_{18}\{M'O\}]^{3-}$ (M' = V, Nb, Ta)[38,39] anions are quite similar. Therefore, the shielding may be primarily ascribed to the increase of the overall anion charge. However, the data for $[W_5O_{18}\{M'S\}]$ (M' = Nb, Ta)[40] anions point out that some ligand effect cannot be definitely ruled out. Thus, the net shielding could result from a balance of the charge increase, the electron delocalization, and the electron-withdrawing effect of the nitrosyl ligand.

Now, if we consider the effect of the replacement of Mo by W in the M_5O_{18} core, it appears that the ^{17}O NMR spectra of $[W_5O_{18}\{M'(NO)\}]^{3-}$ anions are shielded with respect to those of $[Mo_5O_{18}\{M'(NO)\}]^{3-}$ anions. This expected trend originates from the paramagnetic contribution to the shielding which should decrease in tungstates with respect to molybdates as the energy of the $O \rightarrow M(VI)$ charge-transfer bands increases (see Table 3). This effect is quantified in Table 9 as $\Delta\langle\delta_{O_t}\rangle = \langle\delta_{O_t}[OMo^{VI}]\rangle - \langle\delta_{O_t}[OW^{VI}]\rangle$ and $\Delta\langle\delta_{O_b}\rangle = \langle\delta_{O_b}[OMo^{VI}_2]\rangle - \langle\delta_{O_b}[OW^{VI}_2]\rangle$ for pairs of related species. The calculated values do not deviate markedly from a mean value of ~150 ppm.

Electrochemical data for $[M_5O_{18}\{M'(NO)\}]^{3-}$ species should depend on all five effects listed above. Let us first consider the reduction process: it appears that the nitrosyl derivatives are less reducible than their oxo parents, which is consistent with the overall anion charge increase. However, the reduction potential (E_{red}) of a given $[M_5O_{18}\{M'(NO)\}]^{3-}$ anion is less negative than that of the parent one-electron reduced $[M_6O_{19}]^{3-}$ anion with the same charge. The same trend has been previously observed for Keggin derivatives.[7] It can be ascribed to the electron-withdrawing character of the nitrosyl ligand. With regard to the relative π-acceptor properties of the M_5O_{18} cores, data appear conflicting since $[W_5O_{18}\{W(NO)\}]^{3-}$ is less easily reduced than $[W_5O_{18}\{Mo(NO)\}]^{3-}$ while $[Mo_5O_{18}\{W(NO)\}]^{3-}$ is more easily reduced than $[Mo_5O_{18}\{Mo(NO)\}]^{3-}$.

Now let us turn to the oxidation process, which is associated with the M'(NO) unit. The oxidation of a given $[M_5O_{18}\{W(NO)\}]^{3-}$ anion is clearly easier than that of the related $[M_5O_{18}\{Mo(NO)\}]^{3-}$ anion. On the other hand, $[Mo_5O_{18}\{W(NO)\}]^{3-}$ is more easily oxidized than $[W_5O_{18}\{W(NO)\}]^{3-}$, and $[Mo_5O_{18}\{Mo(NO)\}]^{3-}$ is more easily oxidized than $[W_5O_{18}\{Mo(NO)\}]^{3-}$. As the oxidation potential of the M'(II) center should increase as electron delocalization onto the adjacent M(VI) centers increases, these data suggest that delocalization is larger in $[W_5O_{18}\{M'(NO)\}]^{3-}$ than in $[Mo_5O_{18}\{M'(NO)\}]^{3-}$ for a given M'(NO) unit. Furthermore, it can be inferred from the comparison of $(n\text{-}Bu_4N)_3[W_5O_{18}\{Mo(NO)\}]$ with $(n\text{-}Bu_4N)_4[PW_{11}O_{18}\{Mo(NO)\}]$, which displays on oxidation wave at +1.25 V,[7] that electron delocalization is favoured in Keggin- over Lindqvist-type species.

Concluding Remarks. The combination of various techniques, including vibrational, electronic and multinuclear magnetic resonance spectroscopy, and electrochemistry, has allowed the description of the electronic structure of the $[M_5O_{18}\{M'(NO)\}]^{3-}$ anions (M, M' = Mo, W). The expected effect of the whole charge increase with respect to the parent oxoanions $[M_6O_{19}]^{2-}$ is partly offset by the electron-withdrawing effect of the nitrosyl ligand. All four species are essentially localized mixed-valence complexes, with five d^0-M(VI) centers and one d^4-M'(II) center; however, some electronic delocalization is supported by ^{95}Mo and ^{183}W NMR data and by electrochemical data. Moreover, electrochemical data suggest that the extent of delocalization is larger in tungsten than in molybdenum complexes.

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