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Molybdenum Oxo Nitrosyl Complexes. 2. ^{95}Mo NMR Studies of Defect and Complete Lindqvist-Type Derivatives. Crystal and Molecular Structure of $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{17}(\text{OCH}_3)(\text{NO})]$

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Reaction of $(n\text{-Bu}_4\text{N})_3[\text{Mo}_6\text{O}_{18}(\text{NO})]$ (**1**) with dimethyl sulfate in methanol gives $(n\text{-Bu}_4\text{N})_2[\text{SMo}_{12}\text{O}_{40}]$ and $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{17}(\text{OCH}_3)(\text{NO})]$ (**2**). Compound **2** has been characterized by X-ray diffraction. Crystal data for **2**: monoclinic space group $P2_1/c$, $a = 9.514(3)$ Å, $b = 18.066(5)$ Å, $c = 15.418(4)$ Å, $\beta = 105.25(2)°$, $Z = 2$; 2451 reflections, $R = 0.037$. The anion $[\text{Mo}_6\text{O}_{17}(\text{OCH}_3)(\text{NO})]^{2-}$ is structurally related to $[\text{Mo}_6\text{O}_{18}(\text{NO})]^{3-}$ and to $[\text{Mo}_6\text{O}_{19}]^{2-}$; however, due to its location on an inversion center, structural parameters for only a disorder-averaged anion were obtained. Compounds **1**, **2**, and $(n\text{-Bu}_4\text{N})_2[\text{Mo}_5\text{O}_{13}(\text{OCH}_3)_4(\text{NO})\{\text{Na}(\text{CH}_3\text{OH})\}\cdot 3\text{MeOH}$ (**3**) have been studied by ^{95}Mo solution NMR spectroscopy. For all species, the expected numbers of Mo signals were observed although much effort was required to reveal the $\text{Mo}^{\text{II}}(\text{NO})$ signal. The very high deshielding of the Mo(II) resonances has been ascribed to paramagnetic shifts for the most part. The possible activation of $[\text{Mo}_6\text{O}_{19}]^{2-}$ upon nitrosylation has been discussed on the basis of ^{17}O NMR data; the charge distribution on the surface oxygen atoms in the anions of **1** and **2** appears to result from the electron-withdrawing effect of the nitrosyl ligand, which is opposed to the overall increase in charge of the polyanion.

Introduction

Organodiazenido derivatives of polyoxomolybdates containing $\text{Mo(NNAr)}_2{}^{2+}$ or Mo(NNAr)^{3+} units have been known for some time.[1–3] More recently we have described some nitrosyl derivatives of polyoxomolybdates containing the Mo(NO)^{3+} group;[4–6] two other oxo–nitrosyl compounds have been reported by Zhang et al.[7] These two families of compounds combine hard strong π-donor oxo ligands and soft, noninnocent,[8] π-acceptor RN_2 or NO ligands. In all the derivatized polyoxomolybdates characterized to date, the (aryldiazenido)molybdenum geometry is best described as singly bent (Mo–N–N = *ca.* 180°, N–N–C = *ca.* 120°) and the nitrosyl ligand is coordinated in a linear fashion. The short Mo–N, N–N, or N–O bond distances, and the linearity of the Mo–N–N or Mo–N–O moieties, suggest extensive delocalization and significant multiple bond character throughout the MoNNAr and MoNO units. In such coordination modes, aryldiazenido and nitrosyl ligands are commonly considered as $\text{RN}_2{}^+$ and NO^+ species. According to this formalism, Mo(NNAr)^{3+} and Mo(NO)^{3+} would contain Mo(II) centers while $\text{Mo(NNAr)}_2{}^{2+}$ would contain Mo(0) centers. The presence of reduced centers is consistent with electrochemical studies, which reveal that $[\text{Mo}_6\text{O}_{18}(\text{NNAr})]^{3-}$ and $[\text{Mo}_6\text{O}_{18}(\text{NO})]^{3-}$ exhibit one-electron oxidations. Nevertheless, the description of the electronic structure of these complexes is still disputed. Some improvement might be expected from multinuclear NMR studies. Recently, (organodiazenido)polyoxomolybdates have been studied by ^{95}Mo NMR spectroscopy; however no unambiguous assignment of the Mo signals was possible because the expected numbers of signals were not observed.[1b] We have now succeeded in observing all the Mo signals, including that of the reduced Mo center, in three nitrosyloxomolybdates, namely $[\text{Mo}_6\text{O}_{18}(\text{NO})]^{3-}$, $[\text{Mo}_6\text{O}_{17}(\text{OMe})(\text{NO})]^{2-}$, and $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\{\text{Na}(\text{MeOH})\}]^{2-}$. Furthermore, the two first compounds have also been characterized by ^{17}O NMR spectroscopy in order to assess the possible activation of the surface oxygen atoms in these functionalized hexamolybdates. We report here the results of these studies together with the crystal structure of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_6\text{O}_{17}(\text{OMe})(\text{NO})]$.

Experimental Section

The following chemicals were used as received from Aldrich: hydroxylamine hydrochloride, dimethyl sulfate, 1 M methanolic tetra-*n*-butylammonium hydroxide, and reagent grade solvents. Tetra-*n*-butylammonium tetrafluoroborate (Fluka) was recrystallized twice from H_2O and dried at 80 °C. $(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$ was prepared as described in the literature.[9] The synthesis of $(n\text{-Bu}_4\text{N})_2[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\{\text{Na}(\text{MeOH})\}]\cdot 3\text{MeOH}$ (**3**) was described previously.[4,6] Infrared spectra were recorded from KBr pellets with a Perkin-Elmer Model 597 spectrometer. Electronic absorption spectra were recorded with a Kontron Model Uvikon 820 spectrophotometer. Elemental analyses were performed by the Service Central d'Analyse of the CNRS (Vernaison, France).

Synthesis of $(n\text{-Bu}_4\text{N})_3[\text{Mo}_6\text{O}_{18}(\text{NO})]$ (1). $(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$ (5.91 g, 7.5 mmol) and $(\text{NH}_3\text{OH})\text{Cl}$ (0.52 g, 7.5 mmol) were dissolved in MeCN (25 mL), and the solution was boiled under reflux for 2 h, giving a brown microcrystalline powder, which was isolated after cooling. A further crop of crystals of **1** was obtained within 1 day; then crystals of $(n\text{-Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$ grew from the filtrate. Yield: 2.6 g (64%). Anal. Calcd for $\text{C}_{48}\text{H}_{108}\text{N}_4\text{Mo}_6\text{O}_{19}$: C, 35.56; H, 6.72; N, 3.46; Mo, 35.51. Found: C, 35.2; H, 6.6; N, 3.6; Mo, 35.6 IR (cm^{-1}, KBr pellet): 1570 (s), ν(NO); 965 (w), 940 (s), $\nu(\text{MoO}_t)$; 795 (s), ν(MoOMo). ^{95}Mo NMR ($\text{CH}_3\text{CN}/\text{CD}_3\text{COCD}_3$, 323 K): 146, 212 ($\text{Mo}^{\text{VI}}$), 878 ($\text{MO}^{\text{II}}$). ^{17}O NMR

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Table I. Summary of X-ray Diffraction Data for $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{17}(\text{OCH}_3)(\text{NO})]$ (**2**)

formula	$C_{33}H_{75}N_3Mo_6O_{19}$	V, Å^3	2557
fw	1393.6	Z	2
system	monoclinic	T, °C	20
space group	$P2_1/c$	λ, Å	0.710 69
a, Å	9.514(3)	μ(Mo Kα), cm^{-1}	14.58
b, Å	18.066(5)	ρ_{calc}, g cm^{-3}	1.81
c, Å	15.418(4)	R^a	0.037
β, deg	105.25(2)	$R_w{}^b$	0.038

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$ ($w = 1.0$).

(CH_3CN/CD_3CN 90/10, 297 K): −41 (O_c), 526, 563, 603 (O_b), 871, 886 (O_t). ^{14}N NMR (CH_3CN/CD_3CN 90/10, 297 K): 15.6 (*N*O).

Synthesis of $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{17}(\text{OMe})(\text{NO})]$ (2). $(n\text{-Bu}_4\text{N})_3[\text{Mo}_6\text{O}_{18}(\text{NO})]$ (0.4 g, 0.25 mmol) and $(\text{MeO})_2\text{SO}_2$ (0.023 mL, 0.25 mmol) were mixed in MeCN (10 mL), and the solution was boiled under reflux for 3 h and then cooled to room temperature. Dark-brown needles of $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{17}(\text{OMe})(\text{NO})]$ formed and were collected by filtration after 4 h. Yellow crystals of a mixture of $(n\text{-Bu}_4\text{N})_2[\text{SMo}_{12}\text{O}_{40}]$ (**4**) and $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$ subsequently grew from the filtrate. Yield of **2**: 0.11 g (31%). Anal. Calcd for $C_{33}H_{75}N_3Mo_6O_{19}$: C, 28.44; H, 3.02; N, 5.42; Mo, 41.31. Found: C, 28.6; H, 3.1; N, 5.4; Mo, 41.4. IR (cm^{-1}, KBr pellet): 1615 (s), ν(NO); 1005 (w), ν(O–CH$_3$); 980 (w), 960 (s), ν(MoO$_t$); 800 (s), ν(MoOMo). ^{95}Mo NMR (CH_3CN/CD_3COCD_3, 323 K): 134 (1), 182 (1), 191 (1), 203 (2) (Mo^{VI}), 1107 (1) (Mo^{II}). ^{17}O NMR (CH_3CN/CD_3CN 90/10, 297 K): −38 (O_c), 539, 555, 571, 575, 577, 633, 651 (O_b), 907, 913, 917, 949 (O_t). ^{14}N NMR (CH_3CN/CD_3CN 90/10, 297 K): 19.3 (NO). ^{13}C NMR (CD_3CN): 58.7 (O*C*H$_3$). ^{1}H NMR (CD_3CN): 4.7 (O–C*H*$_3$).

X-ray Crystallographic Study of $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{17}(\text{OMe})(\text{NO})]$. X-ray data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Lattice parameters were obtained from a least-squares fit of the setting angles of 25 automatically centered reflections in the range $14 \le \theta \le 14.2°$. Crystal data are summarized in Table I. All computations were performed on a Micro-VAX II using the CRYSTALS system.[10] The structure was solved by direct methods.[11] Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms of the cations were located on difference Fourier maps and introduced as fixed contributions in idealized positions (C–H = 0.95 Å). An empirical absorption correction was applied using DIFABS.[12] Neutral-atom scattering factors were used, with an anomalous dispersion correction applied.[13] Final atomic coordinates are listed in Table II.

Electrochemical Studies. Cyclic voltammetry was carried out on a PAR Model 273 instrument. A standard three-electrode cell was used, which consisted of platinum working and auxiliary electrodes and a saturated calomel electrode (SCE) as the reference. Measurements were made at room temperature under nitrogen in DMF. Solution concentrations were 1 mM for the compounds under study and 0.1 M for the supporting electrolyte, n-Bu$_4$NBF$_4$.

NMR Studies. The ^{1}H and ^{13}C NMR spectra were obtained at 300 and 75.5 MHz respectively, on a Bruker AC 300 spectrometer (7.1 T): the Bruker quattro nuclei probe allows one to obtain the spectra of both nuclei on the same CD_3CN solution in 5 mm o.d. tubes.

The ^{95}Mo NMR spectra were registered at 32.6 MHz (11.8 T) on a Bruker AM 500 apparatus operating on the Fourier mode. About 2 mL of a nearly saturated solution in the appropriate solvent (acetonitrile for **1** and **2**, methanol for **3**) was mixed with 0.22 mL of acetone-d_6 for field-frequency lock and put in a conventional 10 mm o.d. NMR tube. The high-temperature measurements were made using the internal Bruker BVT-1000 temperature control unit driven by a copper–constantan thermocouple. The spectra were obtained using the commercial broadband Bruker VSP probehead, without any special modification. In order to search for the unknown Mo(II) resonance, we had to scan a very large frequency range and therefore had to use very large spectral widths with the unavoidable consequence of a rolling base line (probe ringing) and the eventuality of missing the Mo(II) resonance.[14] As the pulse sequences designed to minimize this effect introduce relatively large delays between the end of the first excitation pulse and the beginning of the acquisition,[15] most of the signal could be lost in the case of quickly relaxing resonances; therefore the spectra were registered using the simple "one pulse" excitation (10 μs, about 20° flip angle) and a preacquisition delay ranging between 10 and 100 μs. Chemical shifts are given according to the IUPAC convention, with respect to an external aqueous alkaline Na_2MoO_4 solution (replacement method without bulk magnetic susceptibility correction).

Table II. Atomic Positional Parameters[a] and Temperature factors[b] for $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{17}(\text{OMe})\text{NO}]$ (**2**)

atom	x/a	y/b	z/c	U(eq), Å^2
Mo(1)	−0.18735(8)	0.08239(4)	−0.02593(5)	0.0379
Mo(2)	0.16138(9)	0.10120(4)	0.02510(6)	0.0457
Mo(3)	−0.00724(9)	0.00212(5)	−0.15197(5)	0.0443
O(1)[c]	−0.426(2)	0.1896(9)	−0.0491(9)	0.0697
O(2)	0.2890(7)	0.1673(4)	0.0416(5)	0.0659
O(3)	−0.0156(7)	0.0018(4)	−0.2617(4)	0.0591
O(121)	−0.2924(6)	−0.0101(4)	−0.0373(4)	0.0540
C(121)[c]	−0.445(2)	−0.017(1)	−0.008(1)	0.0592
O(122)	−0.0136(7)	0.1498(3)	−0.0009(5)	0.0461
O(123)[c]	0.00000	0.00000	0.00000	0.0358
O(131)	−0.1592(6)	0.0697(3)	−0.1441(4)	0.0461
O(132)	−0.1379(6)	0.0697(3)	0.1039(4)	0.0472
O(231)	0.1479(6)	0.0761(3)	0.1421(4)	0.0454
O(232)	0.1273(7)	0.0785(4)	−0.1028(4)	0.0507
N(1)	−0.3240(8)	0.1465(4)	−0.0417(5)	0.0384
N(2)	0.7094(7)	0.2402(4)	0.2223(5)	0.0407
C(1)	0.650(1)	0.1619(5)	0.2075(7)	0.0523
C(2)	0.603(1)	0.1284(6)	0.2864(8)	0.0680
C(3)	0.539(1)	0.0527(7)	0.263(1)	0.0849
C(4)	0.481(2)	0.0179(8)	0.332(1)	0.1027
C(5)	0.604(1)	0.2923(5)	0.2499(7)	0.0518
C(6)	0.459(1)	0.3010(7)	0.1836(9)	0.0796
C(7)	0.359(1)	0.3420(8)	0.231(1)	0.0897
C(8)	0.218(2)	0.354(1)	0.176(2)	0.1622
C(9)	0.736(1)	0.2640(5)	0.1339(7)	0.0536
C(10)	0.794(1)	0.3404(6)	0.1305(7)	0.0621
C(11)	0.808(2)	0.3556(7)	0.0371(9)	0.0905
C(12)	0.859(2)	0.4315(9)	0.025(1)	0.1109
C(13)	0.848(1)	0.2442(5)	0.2994(6)	0.0506
C(14)	0.972(1)	0.1934(6)	0.2909(9)	0.0673
C(15)	1.103(1)	0.2083(8)	0.372(1)	0.0981
C(16)	1.222(2)	0.161(1)	0.377(1)	0.1339

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] $U(\text{eq}) = [U(11)\cdot U(22)\cdot U(33)]^{1/3}$. [c] Occupancy factor 0.5.

The ^{17}O NMR spectra (67.8 MHz) were obtained at the natural abundance (0.037%) on the Bruker AM 500 spectrometer, using 10 mm o.d. tubes in the VSP probehead. The samples were dissolved in acetonitrile with 10% deuterated acetonitrile; the chemical shifts are given with respect to water. The ^{14}N NMR spectra were registered in the same conditions at 36.1 MHz; the chemical shifts are given relative to acetonitrile acting as an internal reference and recalculated with respect to neat liquid nitromethane ($\delta_{\text{CH}_3\text{CN}} = +135.83$ ppm).[16]

Results

Synthesis and Characterization. Compound **1** was originally obtained by spontaneous transformation of **3** in MeCN or CH_2Cl_2.[4] Reductive nitrosylation of $(n\text{-Bu}_4\text{N})_2[\text{Mo}_2\text{O}_7]$ with hydroxylamine chlorhydrate in MeCN now provides a more straightforward synthesis of **1**. The reaction of 1 equiv of **1** with 1 equiv of $(\text{MeO})_2\text{SO}_2$ in MeCN then results in the formation

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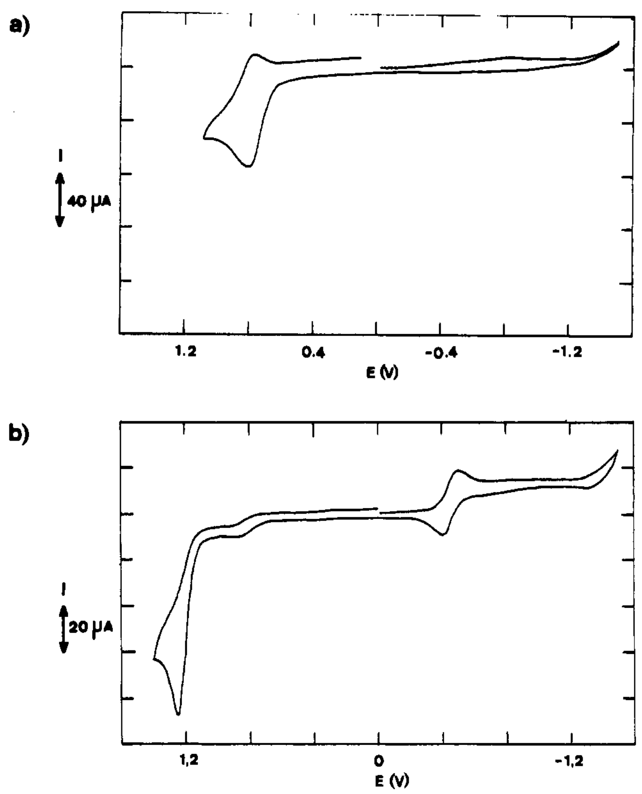

Figure 1. Cyclic voltammograms in 0.1 M n-Bu$_4$NBF$_4$/DMF solutions of **1** (a) and **2** (b) recorded at 0.1 V/s.

of a mixture of (n-Bu$_4$N)$_2$[Mo$_6$O$_{17}$(OMe)(NO)] (**2**), (n-Bu$_4$N)$_2$[SMo$_{12}$O$_{40}$] (**4**), and (n-Bu$_4$N)$_2$[Mo$_6$O$_{19}$]. Compounds **1** and **2** were characterized by chemical analysis, IR spectroscopy, and X-ray crystallographic analysis. A preliminary X-ray study of **4** has confirmed that the anion has the Keggin structure which was inferred from the IR spectrum. This compound had been recently obtained from a 0.05 M Mo(VI)–0.2 M H$_2$SO$_4$/CH$_3$COCH$_3$ mixture (1:1 v/v) containing traces of V(V).[17] Compound **2** was obtained in relatively low yield (*ca.* 30%). It was observed that crystals of (n-Bu$_4$N)$_2$[Mo$_6$O$_{19}$] progressively form at the expense of **2** when the latter is kept in its mother solution for more than 1 day. Prolonged boiling of the reaction mixture resulted in a decrease in the yield of **2** and in an increase in that of **4**, which was separated by hot filtration after 7h. Increase in the (MeO)$_2$SO$_2$:1 ratio also lowered the yield in **2** and raised that in **4**. Compound **4** was also obtained (50% yield) from the reaction of dimethyl sulfate in excess (5 mmol) with (n-Bu$_4$N)$_2$[Mo$_6$O$_{19}$] (0.5 mmol) in CH$_3$CN (15 mL). The formation of [Mo$_6$O$_{17}$(OCH$_3$)(NO)]$^{2-}$ likely occurs by direct methylation of [Mo$_6$O$_{18}$(NO)]$^{3-}$ although an indirect pathway involving cluster dissociation and subsequent reaggregation cannot be ruled out.

The IR spectra of **1** and **2** are very similar except for the presence of a weak band arising from the C–O stretching vibration at 1005 cm^{-1} in **2** and the shift of the NO and MoO stretching vibrations, respectively, from 1570 and 940 cm^{-1} in **1** to 1615 and 960 cm^{-1} in **2**. Both electronic spectra of [Mo$_6$O$_{18}$(NO)]$^{3-}$ and [Mo$_6$O$_{17}$(OMe)(NO)]$^{2-}$ are characterized by a strong band at *ca.* 320 nm (ϵ *ca.* 9000 L mol^{-1} cm^{-1}), which is assigned to an oxygen to Mo(VI) charge-transfer transition by comparison with [Mo$_6$O$_{19}$]$^{2-}$.[18] In addition, they display a shoulder at *ca.* 665 nm (ϵ *ca.* 60 L mol^{-1} cm^{-1}), which is most likely associated with a $d_{xy} \leftarrow d_{xz},d_{yz}$ transition within the Mo^{II}(NO) unit.

Cyclic voltammograms for **1** and **2** are shown in Figure 1. **1** is characterized by a quasi-reversible one-electron oxidation process at +0.83 V, while oxidation of **2** occurs at +1.25 V and is irreversible. These processes are obviously associated with the MoNO unit. The anodic shift in the oxidation potential on going from **1** to **2** can be attributed to the decrease in the negative charge of the cluster. In addition, [Mo$_6$O$_{17}$(OMe)(NO)]$^{2-}$ is characterized by one quasi-reversible one-electron reduction process at –0.45 V, while [Mo$_6$O$_{18}$(NO)]$^{3-}$ is not reducible at potentials up to –1.5 V. Again, the difference is readily explained on electrostatic grounds. It is noteworthy that the reduction potential of [Mo$_6$O$_{17}$(OMe)(NO)]$^{2-}$ is very close to that of [Mo$_6$O$_{19}$]$^{2-}$, which suggests that the LUMO of the cluster is not significantly altered by the MoNO unit.

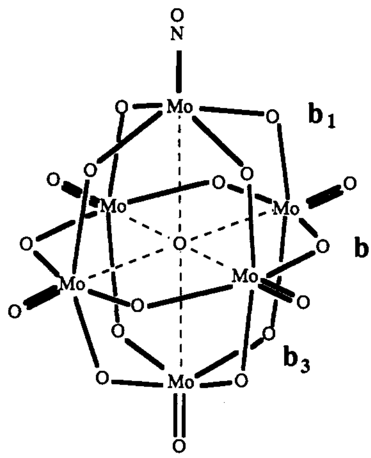

Figure 2. Idealized representation of the [Mo$_6$O$_{18}$(NO)]$^{3-}$ anion showing the three distinct bridging positions.

Solid-State Structure of 2. Single crystals of **2** are composed of discrete n-Bu$_4$N$^+$ cations and [Mo$_6$O$_{17}$(OMe)(NO)]$^{2-}$ anions. The latter are structurally related to the well-known [Mo$_6$O$_{19}$]$^{2-}$ anion[19] and to the previously characterized [Mo$_6$O$_{18}$(NO)]$^{3-}$ anion.[4] The unit cell contains two anions, which are located on inversion centers. The asymmetric unit contains one half-anion and one cation. The location of the monomethylated anion on an inversion center implies some kind of disorder. A similar situation has been already observed for **1**.[4]

Following a common practice, the three different types of oxo ligands in the Linqvist[20] structure will be termed O$_t$ (terminal), O$_b$ (bridging), and O$_c$ (central). Methylation of the [Mo$_6$O$_{18}$(NO)]$^{3-}$ anion could occur at three distinct bridging sites, labeled as b$_1$, b$_2$, and b$_3$ in Figure 2, giving rise to three isomers termed B$_1$, B$_2$, and B$_3$, respectively. Difference Fourier maps reveal no significant peak in the vicinity of equatorial oxygen atoms, which rules out isomer B$_2$. Unfortunately, because of the location of the anion on an inversion center, the X-ray crystallographic analysis does not allow one to make the distinction between isomers B$_1$ and B$_3$ and even to ascertain the formation of a single isomer. However, NMR studies support the formation of a single methylated isomer (*vide infra*).

Because of the disorder in the solid-state structures of both **1**[4] and **2**, structural parameters for only disorder-averaged anions were obtained. Thus, neither of the X-ray studies can totally reveal the effect of the Mo(NO)$^{3+}$ unit on the geometry, hence, on the electronic structure of the cluster. Owing to the analogy between the formally isoelectronic nitrosyl and diazenido ligands, structural parameters for the [Mo$_6$O$_{18}$(NO)]$^{3-}$ anion are expected to be similar to those of the [Mo$_6$O$_{18}$(NNAr)]$^{3-}$ anions (Ar =

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C_6H_5[1a] and C_6F_5[1b]), where the central oxygen atom is significantly displaced toward the reduced Mo center. In this respect, it is worthwhile to point out that the observed Mo_{ax}–O_c bond length (2.254 and 2.279 Å, respectively, in each of the two independent anions of **1**) is significantly shorter than the average value for Mo_{eq}–O_c (2.342 and 2.331 Å, respectively) while the Mo_{ax}–O_b bond length (1.96 and 1.94 Å) is larger than the average value for Mo_{eq}–O_b (1.89 and 1.90 Å), where O_b refers to b_1 and b_3 bridging oxygen atoms only.

NMR Studies. Although the ^{95}Mo resonances of the Mo(VI) atoms in **1**–**3** were easily obtained at room temperature in the expected region (100–200 ppm), strenuous efforts were required to observe the signal from the MoNO group. As the reported ^{95}Mo chemical shifts for mononuclear nitrosylmolybdenum(II) complexes span a very large scale (>3000 ppm),[21] the preliminary spectra were recorded with the largest spectral width allowed by the analog digital converter, i.e. 125 kHz (3800 ppm at 32.6 MHz). Owing to the very distorted base line, no other resonance than the relatively narrow signals from the Mo(VI) centers (a few hundred Hz) could be detected. By increasing the preacquisition delay or by using special pulse sequences[15] derived for minimizing the consequences of probe ringing, we could obtain flat base lines without however any new resonance from the Mo(II) center.

The nuclear spin relaxation of ^{95}Mo is essentially governed by the quadrupolar mechanism,

$$T_{2q}{}^{-1} = \pi\Delta\nu_{1/2} = \frac{3\pi^2}{10}\frac{(2I+3)}{I^2(2I-1)}\left[\frac{e^2q_{zz}Q}{h}\right]^2(1 + {}^1/_3\eta^2)\tau_c$$

where q_{zz} and η are respectively the largest component and the asymmetry parameter of the electric field gradient (efg) tensor at the resonant nucleus and eQ is the nuclear quadrupole moment. The correlation time for molecular tumbling is expressed as $\tau_c = 4\pi r^3\eta_s/(3kT)$ with respect to the radius r of the species under study and to the viscosity η_s of the medium.

The Mo(II) resonances in mononuclear Mo(II) nitrosyl complexes have been reported as broad to very broad (up to 1800 Hz);[21] in the present case of polynuclear complexes a further broadening could be expected due to the size of the species (large r) and to the unsymmetrical geometrical environment of the Mo nucleus (large efg); the observation of the Mo(II) resonance was further hindered by the relatively low solubility of our compounds (about 10^{-2} M).

As already noted for ^{17}O NMR spectroscopy,[22] the temperature is expected to have a dramatic effect on the relaxation time and consequently on the line width of the resonance: as far as allowed by the stability of the species and the physical properties of the solvent, raising the temperature induces a lowering of the correlation time τ_c, both directly and indirectly through a lowering of η_s. Owing to this fact, the search for the Mo(II) signal was pursued at 70 °C with the most favorable species *i.e.*, **1**, which presents the highest solubility and stability in a low-viscosity solution (acetonitrile/acetone-d_6). With a systematic progressive variation of the offset frequency, a reduced spectral width (10 kHz), and using a 90° flip angle, we were able to detect a significant signal at +878 ppm ($\Delta\nu_{1/2} \approx 500$ Hz). Once localized, this line could be observed even at lower temperature, however, with a significant broadening (50 °C, $\Delta\nu_{1/2} \approx 600$ Hz; 25 °C $\Delta\nu_{1/2} \approx 800$ Hz; see Table III). For the two other species, the signal from the Mo(NO) group was searched at 50 °C, in the same δ region, with similar experimental conditions and was finally observed at 1107 ppm ($\Delta\nu_{1/2} \approx 600$ Hz) and 758 ppm ($\Delta\nu_{1/2} \approx 1800$ Hz) for **2** and **3**, respectively. The spectra presented in Figure 3 were obtained under the following conditions: in order to circumvent offset problems the carrier frequency was fixed approximatively in the middle of the spectral window of about 45 kHz (≈1300 ppm) and the pulse width was reduced to 10 μs, corresponding to a flip angle of about 20°; moreover for quantitative purposes, *i.e.*, to obtain a reliable integration of the different resonance signals, the preacquisition delay was chosen relatively short (down to 10 μs for **3**) and the baseline was corrected using the Bruker software, after Fourier transformation. Under these conditions, the spectra of the three species display the predicted number of lines with the expected relative intensities. The anions of **1** and **3** present respectively three lines (intensity ratio 1:4:1) and two lines (1:4) in agreement with their high symmetry in solution (C_{4v}). The spectrum of **2** displays one deshielded resonance (intensity 1) and four lines (2:1:1:1) in the shielded part of the spectrum; these observations are consistent with the existence in solution of a unique isomer of symmetry C_s, *i.e.* B_1 or B_3 (*vide supra*; Figure 2).

Table III. ^{95}Mo NMR Data[a,b]

anion	$\delta_{Mo^{II}}$[c]	$\delta_{Mo^{VI}}$[c]
$[Mo_6O_{19}]^{2-}$		123 126[d]
$[Mo_6O_{18}(NNC_6H_5)]^{3-}$ [d]		−23 −57.9
$[Mo_6O_{18}(NO)]^{3-}$	878 (1; 600)	212 (4; 250) 146 (1; 350)
$[Mo_6O_{17}(OCH_3)(NO)]^{2-}$	1107 (1; 600)	203 (2; 135) 191 (1; 325) 182 (1; 140) 134 (1; 250)
$[Mo_5O_{13}(OCH_3)_4(NO)]^{3-}$	758 (1; 1800)	61 (4; 425)

[a] Spectra recorded at 323 K. [b] ^{95}Mo chemical shifts (in ppm) referred to external Na_2MoO_4 in D_2O at pH 11. [c] Relative intensity and line width (in Hz) in parentheses. [d] Reference 1b; data at 292 K.

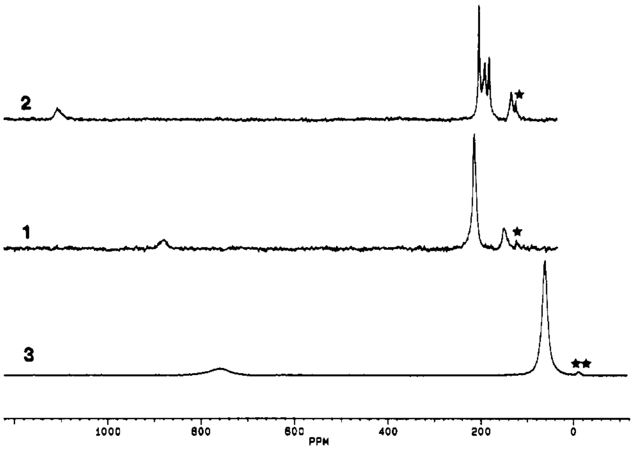

Figure 3. ^{95}Mo NMR spectra of molybdenum oxo nitrosyl complexes recorded at 323 K: $[Mo_6O_{18}(NO)]^{3-}$ (**1**) and $[Mo_6O_{17}(OCH_3)(NO)]^{2-}$ (**2**) in CH_3CN/CD_3COCD_3; $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ (**3**) in CH_3OH/CD_3COCD_3 (* = $[Mo_6O_{19}]^{2-}$; ** = unidentified impurity).

The natural-abundance ^{17}O spectrum of **1** exhibits the six lines expected from the oxo ligands: according to the literature data, they can be assigned to two deshielded O_t (4:1) around 870 ppm, three O_b (4:4:4) around 560 ppm, and one shielded O_c at about −41 ppm. The ^{17}O resonance from the nitrosyl ligand could not be detected, likely because of the coupling with the spin-1 ^{14}N nucleus (Table IV). For the less symmetrical $[Mo_6O_{17}(OMe)(NO)]^{2-}$ anion, four lines in approximate intensity ratio 1:2:1:1 appear in the 900 ppm region, which correspond to the four types of O_t; the seven lines between 540 and 650 ppm, in approximate intensity ratio 1:2:1:2:2:2:1, could be assigned to the seven types of O_b, and finally the broad resonance at about −38 ppm could be due to O_c. The resonances from both the nitrosyl and the methoxy groups were not recognized.

The ^{14}N resonances from the nitrosyl group are relatively

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Table IV. ^{17}O NMR Data[a,b]

anion	δ_{O_t}[c] OMo^{VI}	$\delta_{O_{b1}}$[c] OMMo^{VI} [d]	$\delta_{O_{b2,b3}}$[c] OMo$^{VI}{}_2$	δ_{O_c}[c] OMMo$^{VI}{}_5$ [d]
$[Mo_6O_{19}]^{2-}$ [e]	940		565	−37
$[Mo_6O_{18}(NO)]^{3-}$	886 (4)	603 (4)	563 (4)	−41 (1)
	871 (1)		526 (4)	
$[Mo_6O_{17}(OCH_3)(NO)]^{2-}$	949 (1)	651 (1)	577 (1)	−38 (1)
	917 (2)	633 (2)	575 (2)	
	913 (1)		571 (2)	
	907 (1)		555 (2)	
			539 (1)	
$[Mo_5O_{18}Ti(C_5H_5)]^{3-}$ [f]	863	641	535	5
	834		516	
$[Mo_6O_{18}(NNC_6F_5)]^{3-}$ [e]	930	645	602	29
	914		567	

[a] Spectra recorded at 297 K. [b] ^{17}O chemical shifts (in ppm) referred to external $^{17}OH_2$. [c] Relative intensity in parentheses. [d] M = Mo^{II}, Ti^{4+}. [e] Reference 1b; data at 297 K. [f] Reference 25.

Table V. ^{14}N NMR Data[a]

anion	δ[b] (ppm)	$\Delta\nu_{1/2}$ (Hz)	intensity[c]
$[Mo_6O_{18}(NO)]^{3-}$	15.6	15	0.3
$[Mo_6O_{17}(OCH_3)(NO)]^{2-}$	19.3	40	0.5

[a] Spectra recorded at 297 K. [b] ^{14}N chemical shifts referred to neat CH_3NO_2. [c] Relative intensity to $(n\text{-}Bu_4N)^+$.

narrow, and the ^{14}N chemical shifts for compounds **1** and **3** are in the usual range for linear Mo(NO) groups.[21] In both cases, the integration with respect to the n-Bu_4N^+ resonance (−315 ppm) agrees with the chemical composition (Table V).

Discussion

^{95}Mo NMR spectroscopy has proved to be a useful tool for characterizing molybdenum oxo nitrosyl complexes. The data allow to make a clear distinction between Mo^{VI} centers and the reduced nitrosyl-Mo center. ^{95}Mo chemical shifts of Mo^{VI} sites are consistent with the values obtained for underivatized polyoxomolybdates, while those of the reduced site fall in the range observed for six-coordinate nitrosylmolybdenum(II) complexes.[14,21] As a matter of fact, the latter span a large range; nevertheless, NMR data for compounds **1**–**3** support their description as mixed-valence Mo(VI)/Mo(II) complexes. To the best of our knowledge, this is the first report of the assignment of distinct localized oxidation states in a polyoxomolybdate by means of ^{95}Mo NMR spectroscopy. However, there is a precedent in tungsten chemistry. Indeed, ^{183}W NMR spectroscopy has allowed the localization of both W(VI) and W(IV) centers in six-electron reduced heteropolytungstates, $[BW^{IV}{}_3W^{VI}{}_9O_{40}H_6]^{5-}$, $[SiW^{IV}{}_3W^{VI}{}_9O_{40}H_6]^{4-}$, and $[H_2W^{IV}{}_3W^{VI}{}_9O_{40}H_6]^{6-}$.[23] A look at Table III reveals that the missing signal in the ^{95}Mo NMR spectrum of $[Mo_6O_{18}(NNPh)]^{3-}$ is very likely that of the (organodiazenido)molybdenum unit. The very high deshielding of Mo(II) resonances in nitrosyl-containing oxomolybdates might arise from paramagnetic shifts for the most part; indeed these compounds are characterized by the presence of low-energy charge-transfer transitions. However, this deshielding might also be indicative of some electron deficiency at the Mo(II) center, which achieves a 16-electron configuration at best.

It was anticipated that ^{17}O NMR spectroscopy could bring some insight into the possible activation of surface oxygen atoms upon nitrosylation of $[Mo_6O_{19}]^{2-}$. Indeed, for some oxomolybdenum(VI) compounds,[24] a correlation has been observed among ^{17}O chemical shifts, Mo–O bond lengths, and the π-bond order, which can be formulated as follows: the larger the Mo–O bond length, the greater the negative charge and the greater the ^{17}O shielding.[9b] Hence, for $[Mo_5O_{18}Ti(C_5H_5)]^{3-}$ the low-frequency shift of all the *O*Mo (O_t) and *O*Mo$_2$ (O_{b2}, O_{b3}; see figure 2) ^{17}O resonances, in comparison with $[Mo_6O_{19}]^{2-}$, is indicative of an increase in charge on the entire hexametalate framework as Mo^{VI}O^{4+} is replaced by a Ti^{IV}(C$_5$H$_5$)$^{3+}$ unit.[25] For the heterobridging *O*TiMo atom, however, the large deshielding with respect to the *O*Mo$_2$ in $[Mo_6O_{19}]^{2-}$ cannot be interpreted with such a simple approach because of different bonding environments for the oxygen atoms in both anions.

For $[Mo_6O_{18}(NO)]^{3-}$ as for the other monosubstituted Lindqvist anions ($[Mo_5O_{18}Ti(C_5H_5)]^{3-}$, $[VMo_5O_{19}]^{3-}$, $[VW_5O_{19}]^{3-}$),[8b,25a] we can assume that, among the three bridging oxygen resonances, the high-frequency one (δ +603 ppm) could be assigned to OMo^{II}-Mo^{VI} (O_{b1}). Within the frame of this approximation, the OMo^{VI} and OMo$_2{}^{VI}$ external oxygen atoms of $[Mo_6O_{18}(NO)]^{3-}$ are significantly shielded with respect to $[Mo_6O_{19}]^{2-}$, though to a less extent than in $[Mo_5O_{18}Ti(C_5H_5)]^{3-}$.[25] Quite obviously, the electron-withdrawing effect of the nitrosyl ligand is opposed to the overall increase in charge of the hexametalate framework. In $[Mo_6O_{18}(NNC_6F_5)]^{3-}$, the bridging oxygen resonances are shifted to high frequency with respect to $[Mo_6O_{19}]^{2-}$, which indicates a reduction in charge on the corresponding oxygen atoms. Although ^{17}O NMR spectroscopy does not provide any definitive evidence for the activation of $[Mo_6O_{18}(NO)]^{3-}$ with respect to $[Mo_6O_{19}]^{2-}$, such an activation is supported by the observation that $[Mo_6O_{18}(NO)]^{3-}$ can be methylated by dimethyl sulfate while surface oxygen atoms of the $[Mo_6O_{19}]^{2-}$ anion are known to be quite nonbasic[26] and unreactive.

Finally, we return to the question of the site of methylation in the $[Mo_6O_{18}(NO)]^{3-}$ anion. Steric effects are not expected to be important here, so direct methylation should occur at the most basic site. Comparison of the ^{95}Mo NMR spectrum of $[Mo_6O_{17}(OMe)(NO)]^{2-}$ with that of $[Mo_6O_{18}(NO)]^{3-}$ (Figure 3 and Table III) shows that the Mo(II) resonance is strongly deshielded through methylation. This observation could agree with the methylation in the b_1 site. However, the rules governing the metal chemical shifts in polyoxometalates are not yet clearly understood; for example, in vanadium-substituted polyoxotungstates, ^{183}W chemical shift variations of the same amplitude have been observed for tungsten nuclei either adjacent to or largely remote from the substitution site.[27] At the state of our knowledge, it seems that ^{95}Mo NMR cannot give us a definitive answer to the question of the site of methylation in $[Mo_6O_{18}(NO)]^{3-}$.

^{17}O NMR could be helpful to decide what is the location of the methoxo group: for the $[Nb_2W_4O_{19}]^{4-}$ anion it has been observed that the methylation of one *O*Nb$_2$ bridging oxygen does not dramatically affect the other bridging oxygen resonances; *i.e.*, the O_b resonances fall in three relatively well-separated regions, which were assigned to *O*Nb$_2$, *O*NbW, and *O*W$_2$, respectively.[28] One can assume that in the $[Mo_6O_{17}(OCH_3)(NO)]^{2-}$ anion also the ^{17}O resonance of the bridging oxygen *O*MM′ is primarily determined by M and M′ and that the methylation on a remote oxygen acts only as a perturbation; we expect therefore two different kinds of O_b corresponding to the four oxygen b_1 (*O*Mo^{II}Mo^{VI}) and to the eight oxygen b_2 and b_3 (*O*Mo^{VI}Mo^{VI}). Actually the two lines at 651 and 633 ppm, respectively, are well separated from the five other ones between 577 and 539 ppm (Table IV): the former could be then tentatively assigned to the b_1 resonances; the number of lines as well as their relative intensities (1:2) are in favor of the B_1 isomer, for which one expects a missing ^{17}O resonance (OMe group) in the b_1 region. The same conclusion may be drawn from the IR data. The high-frequency shift of the ν(NO) vibration in **2** compared to **1** is

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consistent with the replacement of an oxo ligand by the weaker π-donor methoxo ligand; however, it could arise in part from the decrease in charge on the cluster so the argument is somewhat less conclusive. Finally, it may be added that our assumption is in agreement with previous studies on other substituted hexametalates incorporating trivalent units, which have shown that the most reactive bridging oxygens are usually the $OM^{VI}M'$ sites (M = Mo, W; M' = Nb, V, Ti).[25,28]

Concluding Remarks

^{95}Mo NMR spectroscopy has proved to be an useful tool for characterizing derivatized polyoxomolybdates, providing all expected resonances could be observed. Although the high deshielding of the Mo(II) nucleus in the $Mo(NO)^{3+}$ fragment is likely due to a prevailing contribution of the paramagnetic term, the large $\delta_{^{95}Mo}$ variation through methylation is not clearly understood and further ^{95}Mo NMR investigations on other derivatized polyoxomolybdates are required to shed more light into the problem of the activation of the surface oxygen of these species. On the other hand, even at the natural abundance, ^{17}O NMR brings more direct information, which is however limited by the lack of observing all signals, *i.e.*, those from the methoxo and the nitrosyl groups.

Supplementary Material Available: Tables giving crystal data, anisotropic thermal parameters, bond lengths, and bond angles for $(n\text{-}Bu_4N)_2[Mo_6O_{17}(OCH_3)(NO)]$ (2) (7 pages). Ordering information is given on any current masthead page.