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Molybdenum Oxo Nitrosyl Complexes. 1. Defect Lindqvist Compounds of the Type $[Mo_5O_{13}(OR)_4(NO)]^{3-}$ (R = CH_3, C_2H_5). Solid-State Interactions with Alkali-Metal Cations

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Reactions of hydroxylamine with isopolyoxomolybdates in methanol or ethanol yield nitrosylpolyoxomolybdates of the type $[Mo_5O_{13}(OR)_4(NO)]^{3-}$ (R = Me, Et). The structures of $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot 3MeOH$ (**1**), $K_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)(MeOH)\}]$ (**2**), $(Me_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)\}]$ (**3**), and $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(DMF)\}]$ (**4**) have been determined by X-ray crystallography. Crystal data for **1**: monoclinic space group $P2_1/a$, $a = 23.325(7)$ Å, $b = 15.917(5)$ Å, $c = 18.433(7)$ Å, $\beta = 105.82(6)°$, $Z = 4$; structure refinement based on 5281 reflections ($I > 3\sigma(I)$; Mo Kα radiation $\lambda = 0.710\,69$ Å in all cases), $R = 0.059$. Crystal data for **2**: triclinic space group $P\bar{1}$, $a = 9.897(1)$ Å, $b = 9.993(2)$ Å, $c = 12.548(2)$ Å, $\alpha = 94.17(1)°$, $\beta = 90.06(1)°$, $\gamma = 100.18(1)°$, $Z = 2$; 3701 reflections, $R = 0.055$. Crystal data for **3**: monoclinic space group $P2_1/n$, $a = 16.733(1)$ Å, $b = 13.855(2)$ Å, $c = 13.934(5)$ Å, $\beta = 107.8(2)°$, $Z = 4$; 3048 reflections, $R = 0.044$. Crystal data for **4**: monoclinic space group $P2_1/c$, $a = 19.437(9)$ Å, $b = 13.818(6)$ Å, $c = 22.920(9)$ Å, $\beta = 106.93(3)°$, $Z = 4$; 5461 reflections, $R = 0.045$. The $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anion has an approximate C_{4v} symmetry; it contains a linear $Mo^{II}(NO)^{3+}$ unit and may be viewed as deriving from the hitherto unknown lacunar $[Mo_5O_{18}]^{6-}$ Lindqvist anion. The sixth position is occupied by a sodium cation, which interacts with the four terminal axial oxygen atoms of the anion and attains coordination numbers of 5, 6, and 7, in **1** and **4**, **3**, and **2**, respectively, by further ligation to solvent molecules and to an oxygen atom from a second anion. Solutions of **1** in methanol are quite stable, while the ethoxo derivative transforms easily into $(n\text{-}Bu_4N)_3[Mo_6O_{18}(NO)]$. The defect $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ species is a convenient starting material for the synthesis of a number of other nitrosyl-containing polyoxometalates.

Introduction

The coordination chemistry of polyoxometalates is an area of increasing interest owing to the structural analogy of these species to metal oxide surfaces.[1] Specific interest in organic derivatives of polyoxometalates derives from the expectation that their chemistry will provide some insight into the mechanisms of heterogeneous catalytic processes employing metal oxides.[2,3a,4] An interesting development in this area has been the synthesis of polyoxomolybdate coordination complexes with branched polydentate oxygen donor ligands, in particular alkoxy compounds.[3,5] Besides polynuclear oxomolybdenum complexes with chelating and bridging chelating ligands, the area of derivatized polyoxometalates, where some terminal oxo groups are replaced by inorganic or organic ligands, is rapidly expanding. Representative examples include methoxy,[3a] formyl,[6] and pyridine[7] derivatives of octamolybdates and cyclopentadienyl,[8,11b] organoimido,[4a] organodiazenido,[9] and organohydrazido(2–)[10] derivatives of $[M_6O_{19}]^{2-}$ anions (M = Mo, W). The neutral $[W_6O_{17}(Cp^*)_2]^8$ is remarkable among a broad range of organometallic oxides.[11a] The chemistry of molybdenum oxo organoimido complexes has been investigated as part of modeling studies of the SOHIO ammoxidation process,[4] while the organodiazenido and organohydrazido groups are of interest as potential models of NNH and NNH_2, which are intermediates in the conversion of coordinated dinitrogen into ammonia and are also postulated to be involved in enzymatic nitrogen fixation.[12]

As a part of our continuing interest in derivatized polyoxometalates and in the chemistry of Mo–N multiple bonds,[13,14] we have explored the chemistry of nitrosyl derivatives of polyoxomolybdates with the aim of (i) assessing the change in the electronic structure of oxomolybdate clusters arising from the replacement of a terminal π-donor oxo ligand by the very strong

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π-acceptor nitrosyl ligand and (ii) looking for models for catalytic oxygenation of NO_x on metal oxides. Despite the obvious analogy[15] between RN_2^+ and NO^+ and a number of reports of organodiazenido derivatives of isopolymolybdates,[9,16] nitrosyl derivatives of oxomolybdates were unknown until the report of $[Mo_{36}O_{110}(NO)_4(H_2O)_{14}]\cdot 42H_2O$ by Zhang et al. in 1986.[17] A variety of mononuclear nitrosylmolybdenum(II) complexes had been previously characterized by the groups of Müller[18] and Wieghardt.[19] Most of them are diamagnetic mononuclear complexes containing the $Mo(NO)^{3+}$ or $Mo(NO)_2^{2+}$ moieties, while a few contain the paramagnetic $Mo(NO)^{2+}$ unit. A few polynuclear nitrosylmolybdenum(II) complexes had also been characterized.[20] However, MoO_4^{2-} and $NH_2OH{\cdot}HCl$ in the absence of any other reagents are known to afford a poorly characterized polymeric nitrosyl complex, which has been used as a starting material for the preparation of a number of mononuclear nitrosyl complexes.[19a,21]

We have recently found that the reaction of hydroxylamine with isopolymolybdates in nonaqueous solution provides a convenient route to nitrosyl derivatives of polyoxomolybdates, and we have now succeeded in preparing a fairly large number of molybdenum oxo nitrosyl complexes. Some of them, such as the Lindqvist or Keggin derivatives, may be viewed as derivatives of known iso- or heteropolyoxomolybdates, while others, such as nitrosyldecamolybdates, have no counterpart in classical polyoxomolybdate chemistry. The keystone in this area is the species $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$, which is a convenient starting material for the synthesis of other oxo nitrosyl derivatives; moreover, it behaves like an inorganic porphyrin and exhibits a varied coordination chemistry. We report here the synthesis of $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ in the presence of alkali-metal cations. A preliminary account of these results has been published,[22] and a short review of our current work on molybdate oxo nitrosyl complexes is available.[23]

Experimental Section

Starting Materials and Reagents. Fumaronitrile, ammonium molybdate tetrahydrate, tetrabutylammonium bromide, n-Bu_4NBr, and hydroxylamine chlorhydrate were purchased from Aldrich and used without further purification. Tetrabutylammonium tetrafluoroborate, n-Bu_4NBF_4, (Fluka) was recrystallized twice from H_2O and dried at 80 °C under vacuo. Reagent grade solvents (Merck or Aldrich) were used as received. $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$[24] and $K_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 40H_2O$[25] were prepared as described in the literature. An approximately 1 molar solution of NH_2OH in methanol saturated in NaCl was prepared from $(NH_3OH)Cl$, which was poured into a methanolic solution of sodium methoxide; then the precipitate of NaCl was removed by filtration.

Synthesis of $N{\equiv}CCH{=}CHC(NH_2)NOH$. The monoamidoxime of fumaronitrile was prepared in a way similar to that described for the diamidoxime.[26] Fumaronitrile (5 g, 0.064 mol), $(NH_3OH)Cl$ (4 g, 0.057 mol), and Na_2CO_3 (3.4 g, 0.032 mol) were dissolved in water (40 mL); after stirring of the mixture for *ca.* 20 min, a while solid began to precipitate and the mixture suddenly got thicker. After filtration, the crude solid was extracted with ether. The mixture was filtered to remove the insoluble diamidoxime, and the solvent was removed in vacuo to give a white solid. Yield: 4.2 g (59%). Anal. Calcd for $C_4H_5N_3O$: C, 43.24; H, 4.54; N, 37.84. Found: C, 43.1; H, 4.6; N, 37.8.

Syntheses of Complexes. $(n\text{-}Bu_4N)_2[Mo_4O_{12}\{NCCHCHC(NH_2)NO\}_2]$. A mixture of $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ (46 g) and fumaroamidoxime (9.5 g) in methanol (200 mL) was refluxed for 1 h. After initial darkening, the mixture cleared up when a white solid began to precipitate. The crude solid was collected by filtration. Yield: 39 g (71%). Then, crystals of the same compound slowly grew from the filtrate (additional crop: 0.5 g). Anal. Calcd for $C_{40}H_{80}N_{10}Mo_4O_{14}$: C, 37.51; H, 6.29; N, 8.75; Mo, 29.96. Found: C, 37.2; H, 6.4; N, 8.5; Mo, 30.9.

$(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot 3MeOH$ (1). Method 1. Methanolic NH_2OH (80 mL, *ca.* 80 mmol) was added to a suspension of $(n\text{-}Bu_4N)_2[Mo_4O_{12}\{NCCHCHC(NH_2)NO\}_2]$ (32 g, 25 mmol) in methanol (20 mL). The mixture was refluxed for 3 h to give a dark solution. After cooling at room temperature and standing for *ca.* 12 h, the solution afforded 5 g of **1** as violet plate crystals (yield: 18%).

Method 2. Methanolic NH_2OH (40 mL, *ca.* 40 mmol) was added to a suspension of $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ (13.45 g, 6.25 mmol) in methanol (50 mL), and the mixture was refluxed for 7 h upon which its color turned yellow, then brown, and finally violet. The hot mixture was filtered, giving a light-brown solid, which was discarded. When the filtrate was kept at room temperature for 24 h, violet crystals of **1** were obtained, which were separated and washed with diethyl ether. Yield: 8 g (59%). Anal. Calcd for $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]$: C, 32.16; H, 6.42; N, 3.04; Mo, 34.72; Na, 1.66. Found: C, 32.1; H, 6.4; N, 3.2; Mo, 34.9; Na, 1.9. IR (cm^{-1}, KBr pellet): 1635 (s), $\nu(NO)$; 1040 (s), $\nu(O{-}C)$; 945 (sh), 930 (s), 900 (s), 875 (sh), $\nu(MoO_t)$; 700 (s), $\nu(MoOMo)$.

$K_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)(MeOH)\}]$ (2). Methanolic NH_2OH (25 mL, *ca.* 25 mmol) was added to a suspension of $K_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 40H_2O$ (0.543 g, 0.08 mmol) in methanol (20 mL). After being refluxed for 7 h, the mixture was filtered while hot, giving a light-brown solid, which was discarded. A small quantity of rose-violet plate crystals of $K_2[Mo_5O_{13}(OCH_3)_4(NO)\{Na(H_2O)(MeOH)\}]$ (**2**) formed from the filtrate within a few days. IR (cm^{-1}, KBr pellet): 1625 (s), $\nu(NO)$; 1030 (s), $\nu(O{-}C)$; 935 (s), 920 (s), 900 (w), 890 (w), 865 (w), $\nu(MoO_t)$; 705 (s), $\nu(MoOMo)$.

$(Me_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)\}]$ (3). Addition of methanolic NH_2OH (19.2 mL, *ca.* 19.2 mmol) to a suspension of $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ (6.5 g, 3 mmol) and Me_4NBr (3.08 g, 20 mmol) in methanol (100 mL) led to the formation of a yellow precipitate, which dissolved upon heating while a new violet precipitate appeared. After being refluxed for 7 h, the hot mixture was filtered, giving **3** as a rose powder, which was washed with Et_2O (4.3 g, 87% yield). The crude product later proved to be contaminated with Me_4NBr. Rose-violet hexagonal plate crystals of **3** suitable for an X-ray study were obtained from the reaction of NH_2OH with a sample of $(n\text{-}Bu_4N)_3[VMo_5O_{19}]$ that contained a small percentage of Me_4N^+ cations. Anal. Calcd for $C_{12}H_{38}N_3Mo_5NaO_{19}$: C, 13.98; H, 3.71; N, 4.08. Found: C, 14.3; H, 3.7; N, 4.2. IR (cm^{-1}, KBr pellet): 1605 (s), $\nu(NO)$; 1040 (s), $\nu(O{-}C)$; 955 (w), 940 (w), 930 (s), 895 (s), 875 (sh), $\nu(MoO_t)$; 700 (s), $\nu(MoOMo)$.

$(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(DMF)\}]$ (4). Violet crystals of **4** were obtained initially from the reaction of **1** with $(n\text{-}Bu_4N)_4[SiMo_{12}O_{40}]$ and n-Bu_4NOH in DMF, which failed to yield the expected nitrosyl Keggin derivative $[SiMo_{12}O_{39}(NO)]^{5-}$. Then it was found that **4** can be

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Table I. Summary of X-ray Diffraction Data for Compounds **1–4**

	compd			
	1	**2**	**3**	**4**
fw	1477.93	993.07	1031.13	1422.86
space group	$P2_1/a$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a, Å	23.325(7)	9.897(1)	16.733(1)	19.437(9)
b, Å	15.917(5)	9.993(2)	13.855(2)	13.818(6)
c, Å	18.433(7)	12.548(2)	13.934(5)	22.920(9)
α, deg	90	94.17(1)	90	90
β, deg	105.82(6)	90.06(1)	107.8(2)	106.93(3)
γ, deg	90	100.18(1)	90	90
V, Å^3	6584(8)	1218(3)	3076	5889(48)
Z	4	2	4	4
T, °C	20	20	20	20
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69
μ(Mo Kα), cm^{-1}	9.73	28.89	20.27	10.82
ρ_{calc}, g cm^{-3}	1.49	2.71	2.23	1.61
R[a]	0.059	0.055	0.044	0.045
R_w[b]	0.063	0.064	0.049	0.048

[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).

obtained by recrystallization of **1** in DMF with methanolic n-Bu$_4$NOH added. IR (cm^{-1}, KBr pellet): 1615 (s), ν(NO); 1045 (s), ν(O–C); 945 (sh), 925 (s), 910 (s), 890 (s), ν(MoO$_t$); 700 (s), ν(MoOMo).

$(n\text{-Bu}_4\text{N})_2[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\{\text{Li}(\text{MeOH})\}]\cdot x\text{MeOH}$ (5). LiOH (0.17 g) was added to the solution of (NH$_3$OH)Cl (0.44 g, 6.4 mmol) in MeOH (10 mL). $(n\text{-Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$ (2.15 g, 1 mmol) was then added to this cloudy solution. After the mixture was boiled under reflux for 7 h, a brown solid was separated by hot filtration. Violet crystals of **5** were obtained from the refrigerated filtrate. Yield: 0.7 g (32%). Anal. Calcd for $(n\text{-Bu}_4\text{N})_2[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\{\text{Li}(\text{MeOH})\}]$: C, 32.54; H, 6.49; N, 3.08; Mo, 35.12; Li, 0.51. Found: C, 32.6; H, 6.6; N, 3.6; Mo, 34.6; Li, 0.4. IR (cm^{-1}, KBr pellet): 1630 (s), ν(NO); 1040(s), ν(O–C); 930 (s), 895 (s), 880 (s), ν(MoO$_t$); 700 (s), ν(MoOMo).

$(n\text{-Bu}_4\text{N})_2[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\{\text{Na}(\text{EtOH})\}]\cdot x\text{EtOH}$ (6). Methanolic NH$_2$OH (3.2 mL, *ca.* 3.2 mmol) was added to a suspension of $(n\text{-Bu}_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$ (1.075 g, 0.5 mmol) in ethanol (10 mL). After being refluxed for 7 h, the mixture was filtered while hot, giving a light-brown precipitate, which was discarded. Violet crystals of **6** grew from the filtrate within 1 day. Yield: 0.26 g (23%). Anal. Calcd for $(n\text{-Bu}_4\text{N})_2[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\{\text{Na}(\text{EtOH})\}]$: C, 34.74; H, 6.80; N, 2.89. Found: C, 33.2; H, 6.7; N, 3.0. IR (cm^{-1}, KBr pellet): 1635 (s), ν(NO); 1050 (s), ν(O–C); 945 (sh), 930 (s), 900 (s), 880 (sh), ν(MoO$_t$); 700 (s), ν(MoOMo).

Physical Studies. Infrared spectra (KBr pellets) were recorded with a Perkin-Elmer 597 spectrophotometer. Electronic absorption spectra were recorded on a Shimadzu UV 160A spectrophotometer. Cyclic voltammetry was carried out on a PAR Model 273 instrument. A standard three-electrode cell was used, which consisted of a platinum or carbon working electrode, an auxiliary platinum electrode, and a saturated calomel reference electrode (SCE). Measurements were made at room temperature in CH$_3$CN under nitrogen. Solution concentrations were 1 mM for the compounds under study and 0.1 M for the supporting electrolyte, n-Bu$_4$NBF$_4$.

X-ray Structure Determinations. Data were recorded at room temperature either on a Philips PW1100 diffractometer (**1** and **3**) or on an Enraf Nonius CAD4 diffractometer (**2** and **4**) using graphite-monochromated Mo Kα radiation. A crystal of **1** was sealed in a thin-walled capillary containing a few drops of the mother solution, while crystals of **2–4** were mounted on glass fibers and sealed with an epoxy cement. Lattice parameters and the orientation matrix were obtained from a least-squares fit of the setting angles of 25 automatically centered reflections. The intensities of two standard reflections were monitored every 1 h; a linear decay was observed for **1** while no significant change was observed in the course of data collection for **2–4**. Crystal data are summarized in Table I. Data processing was performed on a MicroVAX II using the CRYSTALS system.[27] Intensities were corrected for Lorentz and polarization effects. Reflections with $I \geq 3\sigma(I)$ were kept in further calculations. The structures were solved by direct methods (SHELXS 86),[28] which gave the coordinates of the Mo atoms and most of the oxygen atoms of the anion. The remaining non-hydrogen atoms were located through subsequent Fourier syntheses and least-squares refinement. Because only some of the hydrogen atoms could be located on difference

Table II. Atomic Positional[a] Parameters and Temperature Factors[b] for $(n\text{-Bu}_4\text{N})_2[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\{\text{Na}(\text{MeOH})\}]\cdot 3\text{MeOH}$ (**1**)

atom	x/a	y/b	z/c	U(eq), Å^2
Mo(1)	0.89076(4)	–0.05077(5)	0.32236(5)	0.0608
Mo(2)	0.76907(4)	0.01805(5)	0.37679(5)	0.0626
Mo(3)	0.74788(4)	–0.12309(5)	0.24425(5)	0.0620
Mo(4)	0.82724(4)	0.14330(5)	0.27690(5)	0.0634
Mo(5)	0.80709(4)	0.00170(5)	0.14433(5)	0.0625
N(1)	0.9604(4)	–0.0944(6)	0.3678(6)	0.0857
O(1)	1.0080(4)	–0.1263(6)	0.4002(6)	0.1147
O(10)	0.8055(2)	0.0009(3)	0.2711(3)	0.0453
O(12)	0.8619(3)	–0.0365(4)	0.4139(3)	0.0667
O(13)	0.8449(3)	–0.1579(4)	0.3019(4)	0.0715
O(14)	0.9128(3)	0.0706(4)	0.3298(3)	0.0659
O(15)	0.8949(3)	–0.0537(4)	0.2153(4)	0.0692
O(21)	0.7010(3)	0.0587(5)	0.3285(4)	0.0795
O(22)	0.7673(4)	0.0170(5)	0.4683(4)	0.0890
O(23)	0.7517(3)	–0.0968(4)	0.3470(3)	0.0658
O(24)	0.8151(3)	0.1173(4)	0.3725(4)	0.0687
O(31)	0.6825(3)	–0.0705(5)	0.2034(4)	0.0822
O(32)	0.7288(4)	–0.2264(5)	0.2378(4)	0.0855
O(35)	0.7829(3)	–0.1097(4)	0.1623(3)	0.0657
O(41)	0.7564(3)	0.1739(4)	0.2319(4)	0.0778
O(42)	0.8665(4)	0.2339(4)	0.2942(4)	0.0870
O(45)	0.8476(3)	0.1017(4)	0.1883(4)	0.0617
O(51)	0.7363(3)	0.0459(5)	0.1111(4)	0.0807
O(52)	0.8330(4)	–0.0100(5)	0.0677(4)	0.0936
C(12)	0.8948(6)	–0.049(1)	0.4907(6)	0.0976
C(13)	0.8586(6)	–0.2319(7)	0.3484(8)	0.0979
C(14)	0.9609(6)	0.1082(9)	0.3869(7)	0.0982
C(15)	0.9264(6)	–0.1170(9)	0.1864(8)	0.0980
Na(1)	0.6765(2)	0.0764(3)	0.1942(3)	0.0953
O(101)	0.5930(4)	0.1556(8)	0.1370(7)	0.1344
C(101)	0.589(1)	0.204(2)	0.074(2)	0.2114
O(102)	0.6150(8)	0.066(1)	0.413(1)	0.2087
C(102)	0.633(1)	0.118(2)	0.477(2)	0.2339
O(103)	0.4998(6)	0.2044(9)	0.1856(8)	0.1654
C(103)	0.491(2)	0.158(2)	0.244(1)	0.2261
O(104)	0.4689(5)	0.3684(8)	0.1933(7)	0.1337
C(104)	0.5123(9)	0.430(1)	0.213(1)	0.1561
N(2)	0.8490(4)	0.2901(6)	0.5422(6)	0.0889
C(21)	0.8482(5)	0.1975(7)	0.5627(7)	0.0884
C(22)	0.8042(8)	0.1793(8)	0.6106(8)	0.1101
C(23)	0.821(1)	0.091(1)	0.643(1)	0.1564
C(24)	0.786(2)	0.066(2)	0.697(2)	0.3060
C(31)	0.7890(5)	0.3260(8)	0.5063(7)	0.0878
C(32)	0.7570(6)	0.2817(8)	0.4317(7)	0.0935
C(33)	0.6965(8)	0.326(1)	0.401(1)	0.1286
C(34)	0.6629(8)	0.288(1)	0.324(1)	0.1420
C(41)	0.8739(6)	0.3455(9)	0.6124(8)	0.0963
C(42)	0.9355(8)	0.322(1)	0.657(1)	0.1374
C(43)	0.956(1)	0.382(2)	0.728(1)	0.1783
C(44)	0.952(2)	0.320(2)	0.788(2)	0.2794
C(51)	0.8934(6)	0.294(1)	0.4935(9)	0.1008
C(52)	0.8955(9)	0.385(1)	0.461(1)	0.1433
C(53)	0.949(1)	0.381(2)	0.423(2)	0.1661
C(54)	0.948(2)	0.471(2)	0.385(2)	0.2375
N(3)	0.8132(4)	0.2638(7)	0.0057(6)	0.0914
C(61)	0.7613(7)	0.235(1)	–0.0618(8)	0.1100
C(62)	0.7342(9)	0.151(1)	–0.045(1)	0.1245
C(63)	0.700(1)	0.114(1)	–0.124(2)	0.2089
C(64)	0.648(1)	0.172(2)	–0.139(3)	0.2559
C(71)	0.7924(7)	0.278(1)	0.0778(8)	0.1144
C(72)	0.7408(8)	0.344(1)	0.064(1)	0.1286
C(73)	0.733(1)	0.359(1)	0.141(1)	0.1545
C(74)	0.676(1)	0.418(2)	0.128(1)	0.2071
C(81)	0.8361(6)	0.3457(9)	–0.0213(8)	0.1025
C(82)	0.8834(7)	0.389(1)	0.0385(9)	0.1161
C(83)	0.9061(7)	0.465(1)	–0.003(1)	0.1197
C(84)	0.952(1)	0.516(2)	0.062(2)	0.2483
C(91)	0.8642(6)	0.200(1)	0.0282(8)	0.1061
C(92)	0.8884(7)	0.178(1)	–0.037(1)	0.1327
C(93)	0.938(1)	0.114(1)	–0.008(1)	0.1591
C(94)	0.971(1)	0.102(2)	–0.066(2)	0.2264

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

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Table III. Atomic Positional Parameters[a] and Temperature Factors[b] for $K_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)(MeOH)\}]$ (**2**)

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å²
Mo(1)	−0.2754(1)	−0.3259(1)	0.36149(9)	0.0318
Mo(2)	−0.4181(1)	−0.2099(1)	0.14599(9)	0.0334
Mo(3)	−0.2765(1)	−0.4796(1)	0.10706(9)	0.0335
Mo(4)	−0.1337(1)	−0.0315(1)	0.24571(9)	0.0311
Mo(5)	0.0102(1)	−0.2993(1)	0.20367(9)	0.0334
N(1)	−0.319(1)	−0.371(1)	0.4916(9)	0.0406
O(1)	−0.345(1)	−0.404(1)	0.5802(8)	0.0613
O(10)	−0.2161(9)	−0.2663(9)	0.2042(7)	0.0335
O(12)	−0.4528(9)	−0.275(1)	0.3166(7)	0.0373
C(12)	−0.539(2)	−0.208(2)	0.385(1)	0.0528
O(13)	−0.325(1)	−0.5070(9)	0.2834(7)	0.0343
C(13)	−0.316(2)	−0.634(1)	0.330(1)	0.0511
O(14)	−0.208(1)	−0.129(1)	0.3971(7)	0.0357
C(14)	−0.203(2)	−0.054(2)	0.499(1)	0.0567
O(15)	−0.0813(9)	−0.3507(9)	0.3637(7)	0.0346
C(15)	0.007(2)	−0.328(2)	0.459(1)	0.0528
O(21)	−0.359(1)	−0.166(1)	0.0231(8)	0.0444
O(22)	−0.582(1)	−0.187(1)	0.1487(9)	0.0512
O(23)	−0.4393(9)	−0.402(1)	0.1198(7)	0.0349
O(24)	−0.3270(9)	−0.0484(9)	0.2233(7)	0.0362
O(31)	−0.230(1)	−0.418(1)	−0.0143(8)	0.0468
O(32)	−0.336(1)	−0.648(1)	0.0816(8)	0.0471
O(35)	−0.0951(9)	−0.4742(9)	0.1633(7)	0.0375
O(41)	−0.089(1)	0.0062(9)	0.1163(7)	0.0375
O(42)	−0.091(1)	0.118(1)	0.3193(8)	0.0436
O(45)	0.0202(9)	−0.1188(9)	0.2704(7)	0.0334
O(51)	0.042(1)	−0.245(1)	0.0779(8)	0.0433
O(52)	0.159(1)	−0.343(1)	0.2454(9)	0.0492
Na(1)	−0.1142(6)	−0.1797(6)	−0.0491(4)	0.0418
O(100)	−0.065(1)	−0.322(1)	−0.2021(8)	0.0465
O(200)	−0.228(1)	−0.056(1)	−0.1695(8)	0.0491
C(200)	−0.351(2)	−0.119(2)	−0.226(1)	0.0534
K(1)	−0.3350(4)	−0.4835(4)	−0.2202(3)	0.0483
K(2)	−0.2777(4)	0.1155(3)	0.0100(3)	0.0459

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

Table IV. Atomic Positional Parameters[a] and Temperature Factors[b] for $(Me_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)\}]$ (**3**)

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å²
Mo(1)	0.32239(6)	−0.16561(8)	−0.07303(8)	0.0208
Mo(2)	0.19158(7)	0.01156(8)	−0.03116(9)	0.0243
Mo(3)	0.23035(7)	−0.18000(8)	0.11436(7)	0.0243
Mo(4)	0.11895(7)	−0.13338(9)	−0.22297(8)	0.0256
Mo(5)	0.15894(7)	−0.32333(8)	−0.07809(8)	0.0242
N(1)	0.4220(6)	−0.1802(8)	−0.0902(8)	0.0280
O(1)	0.4887(6)	−0.1954(8)	−0.1056(8)	0.0429
O(10)	0.1990(5)	−0.1563(6)	−0.0555(6)	0.0220
O(12)	0.3205(5)	−0.0237(6)	−0.0516(6)	0.0223
C(12)	0.3691(9)	0.046(1)	−0.085(1)	0.0351
O(13)	0.3539(5)	−0.1863(6)	0.0733(6)	0.0266
C(13)	0.428(1)	−0.235(1)	0.134(1)	0.0376
O(14)	0.2555(5)	−0.1473(6)	−0.2168(6)	0.0263
C(14)	0.279(1)	−0.152(1)	−0.307(1)	0.0360
O(15)	0.2901(5)	−0.3061(6)	−0.0925(6)	0.0214
C(15)	0.315(1)	−0.368(1)	−0.162(1)	0.0396
O(21)	0.0919(5)	0.0138(6)	−0.0164(7)	0.0300
O(22)	0.2247(6)	0.1295(7)	−0.0136(8)	0.0362
O(23)	0.2493(5)	−0.0448(6)	0.0987(6)	0.0269
O(24)	0.1588(5)	−0.0052(6)	−0.1719(6)	0.0263
O(31)	0.1283(6)	−0.1716(7)	0.1157(7)	0.0345
O(32)	0.2872(6)	−0.1971(7)	0.2374(6)	0.0386
O(35)	0.2233(6)	−0.3091(6)	0.0622(6)	0.0270
O(41)	0.0265(5)	−0.1232(6)	−0.1931(7)	0.0294
O(42)	0.0934(7)	−0.1157(8)	−0.3488(7)	0.0419
O(45)	0.1312(5)	−0.2715(6)	−0.2104(6)	0.0277
O(51)	0.0624(5)	−0.3055(7)	−0.0605(7)	0.0358
O(52)	0.1650(7)	−0.4453(7)	−0.0935(8)	0.0428
Na(1)	0.0047(3)	−0.1369(4)	−0.0321(4)	0.0375
O(100)	−0.1151(7)	−0.2367(8)	−0.0616(9)	0.0536
N(2)	0.0635(7)	−0.4440(8)	0.2048(8)	0.0324
C(21)	0.135(1)	−0.380(1)	0.260(1)	0.0430
C(31)	0.035(1)	−0.501(1)	0.279(1)	0.0450
C(41)	−0.008(1)	−0.383(1)	0.142(1)	0.0474
C(51)	0.093(1)	−0.513(1)	0.136(1)	0.0570
N(3)	0.3794(7)	0.4438(9)	0.1404(8)	0.0364
C(61)	0.453(1)	0.393(1)	0.210(1)	0.0469
C(71)	0.3466(9)	0.518(1)	0.202(1)	0.0444
C(81)	0.403(1)	0.497(1)	0.059(1)	0.0539
C(91)	0.310(1)	0.371(2)	0.095(1)	0.0599

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

Fourier maps, they were not included in the refinement. All atoms were refined anisotropically. There are signs of a slight disorder in the tetrabutylammonium cations of **1**, but no attempt was made to introduce a disorder model in the refinement. An empirical absorption correction was applied using DIFABS.[29] Neutral-atom scattering factors were used, with anomalous dispersion correction applied.[30] Final residuals are given in Table I. Final atomic coordinates are listed in Tables II–V. Selected bond distances and angles are given in Table VI. A view[31] of the anion in **4** is presented in Figure 1. The following numbering scheme has been used for all the compounds containing the $[Mo_5O_{13}(OCH_3)_4(NO)]^{3-}$ unit: the Mo^{II} center is labeled Mo(1), while the Mo^{VI} centers are numbered from Mo(2) up to Mo(5). The nitrosyl ligand is labeled N(1)–O(1). Terminal oxygen atoms (O_t) are labeled O_{ij}, where *i* refers to the number of the Mo atom and $j = 1$ or 2 depending on whether the oxygen atom is axial or equatorial. Bridging oxygen atoms (O_b) are labeled $O_{ii'}$ where *i* and *i'* refer to the numbers of the bridged Mo atoms. The central oxygen atom (O_c) is labeled O(10). Views[31] of one hydrogen-bonded chain in **1** and of the dimeric units in **3** and **2** are given in Figures 2–4, respectively.

Results

Syntheses. Although we had been looking for nitrosyl derivatives of polyoxomolybdates for some time, such a compound was first obtained by serendipity while reacting hydroxylamine with $(n\text{-}Bu_4N)_2[Mo_4O_{12}\{N{\equiv}CCH{=}CHC(NH_2)NO\}_2]$ in methanol with the aim of transforming the pendant cyano groups into amidoxime functions. The mixture was refluxed for a few hours and filtered while hot. The violet crystals which formed immediately from the filtrate were filtered out and identified as $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]\cdot 3MeOH$ (**1**) on the basis of an X-ray structure determination. Quite obviously, the Na^+ cation comes from the hydroxylamine solution. It was soon recognized that this compound can be obtained more conveniently by reacting hydroxylamine with $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ in methanol. Indeed, a variety of polyoxomolybdates can be used as starting materials: $K_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)(MeOH)\}]$ (**2**) is formed when $K_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 40H_2O$ is reacted with hydroxylamine in methanol, and $(Me_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)\}]$ (**3**) has been isolated from the reaction of NH_2OH with $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ in the presence of Me_4NCl. The maximum yield in **1** (*ca.* 60%) has been reached with $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$. Whatever the starting material, the yield is maximum for a ratio of the reactants close to 0.8 mol of NH_2OH *per* Mo atom. The ethoxy derivative $(n\text{-}Bu_4N)_2Na[Mo_5O_{13}(OEt)_4(NO)]\cdot x EtOH$ (**6**) has been similarly prepared by reacting NH_2OH with $(n\text{-}Bu_4N)_2[Mo_4O_{12}\{N{\equiv}CCH{=}CHC(NH_2)NO\}_2]$ or $(n\text{-}Bu_4N)_4[\alpha\text{-}Mo_8O_{26}]$ in ethanol. $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(DMF)\}]$ (**4**) has been obtained by recrystallization of **1** in DMF in the presence of $n\text{-}Bu_4NOH$. Complexes **1**–**6** have been obtained as transparent violet crystals. However crystals of **1** and **6** were found to become quickly opaque when standing in air due to loss of solvent. Chemical analyses of **1**, **5**, and **6** were performed on partially desolvated compounds.

Infrared Spectra. The infrared spectra of compounds **1**–**6** show similar patterns characteristic of the $[Mo_5O_{13}(OR)_4(NO)]^{3-}$ unit: these are a strong band in the range 1605–1635 cm^{-1} assigned to ν(NO), a feature at *ca.* 1040 cm^{-1} arising from the O–C

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Table V. Atomic Positional Parameters[a] and Temperature Factors[b] for $(n\text{-}Bu_4N)_2[Mo_5O_{13}(OMe)_4(NO)\{Na(DMF)\}]$ (4)

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2
Mo(1)	0.19082(4)	0.00849(6)	0.08992(3)	0.0411
Mo(2)	0.14050(5)	0.01327(7)	0.22109(4)	0.0471
Mo(3)	0.21327(5)	–0.18265(6)	0.18875(4)	0.0463
Mo(4)	0.28167(5)	0.13934(6)	0.21803(4)	0.0470
Mo(5)	0.35425(5)	–0.05888(7)	0.18443(5)	0.0540
N(1)	0.1503(5)	0.0373(7)	0.0141(4)	0.0599
O(1)	0.1183(6)	0.0588(8)	–0.0380(4)	0.0897
O(10)	0.2376(3)	–0.0194(4)	0.1847(2)	0.0370
O(12)	0.1062(3)	0.0362(4)	0.1187(3)	0.0476
C(12)	0.0384(6)	0.071(1)	0.0841(6)	0.0876
O(13)	0.1682(3)	–0.1300(4)	0.0885(3)	0.0436
C(13)	0.1114(7)	–0.1780(9)	0.0446(5)	0.0746
O(14)	0.2264(4)	0.1423(4)	0.1161(3)	0.0492
C(14)	0.1994(8)	0.2285(8)	0.0846(7)	0.0853
O(15)	0.2902(3)	–0.0216(5)	0.0868(3)	0.0520
C(15)	0.3232(7)	0.030(1)	0.0475(6)	0.0754
O(21)	0.1851(4)	–0.0100(6)	0.2958(3)	0.0665
O(22)	0.0556(4)	0.0453(6)	0.2205(4)	0.0710
O(23)	0.1284(3)	–0.1187(4)	0.1943(3)	0.0426
O(24)	0.1829(3)	0.1370(5)	0.2163(3)	0.0532
O(31)	0.2557(4)	–0.1972(6)	0.2655(3)	0.0682
O(32)	0.1826(4)	–0.2937(5)	0.1633(4)	0.0675
O(35)	0.2997(3)	–0.1741(5)	0.1634(3)	0.0532
O(41)	0.3167(4)	0.1054(6)	0.2926(3)	0.0666
O(42)	0.2998(4)	0.2598(5)	0.2162(4)	0.0714
O(45)	0.3533(3)	0.0799(5)	0.1890(3)	0.0504
O(51)	0.3850(4)	–0.0780(5)	0.2608(4)	0.0686
O(52)	0.4260(4)	–0.0807(6)	0.1581(5)	0.0816
Na(1)	0.3081(3)	–0.0570(4)	0.3239(2)	0.0819
O(2)	0.3408(7)	–0.111(1)	0.4199(5)	0.1141
N(2)	0.3256(8)	–0.230(1)	0.4793(6)	0.1031
C(1)	0.312(1)	–0.145(1)	0.4549(7)	0.1074
C(2)	0.377(1)	–0.292(2)	0.467(1)	0.2012
C(3)	0.287(1)	–0.267(1)	0.5207(9)	0.1409
N(3)	0.0903(5)	0.3117(7)	0.3079(4)	0.0546
C(31)	0.0600(6)	0.2875(9)	0.2399(4)	0.0596
C(32)	–0.0127(6)	0.3361(9)	0.2102(5)	0.0667
C(33)	–0.0340(8)	0.313(1)	0.1411(6)	0.0848
C(34)	–0.1035(9)	0.364(1)	0.1067(6)	0.1104
C(35)	0.0401(6)	0.2758(9)	0.3447(5)	0.0684
C(36)	0.0334(7)	0.164(1)	0.3434(6)	0.0837
C(37)	–0.0070(8)	0.130(1)	0.3881(7)	0.1095
C(38)	0.034 (1)	0.139(2)	0.4536(8)	0.1376
C(39)	0.0974(7)	0.4209(8)	0.3187(5)	0.0643
C(40)	0.1418(8)	0.474(1)	0.2830(6)	0.0916
C(41)	0.146(1)	0.584(1)	0.2979(8)	0.1148
C(42)	0.192(1)	0.603(1)	0.358(1)	0.1524
C(43)	0.1638(5)	0.2610(9)	0.3272(4)	0.0538
C(44)	0.2053(6)	0.277(1)	0.3953(5)	0.0726
C(45)	0.2694(8)	0.208(1)	0.4125(6)	0.0947
C(461)	0.304(2)	0.185(3)	0.471(2)	0.11(1)
C(462)	0.256(1)	0.121(2)	0.433(1)	0.078(6)
N(5)	0.4023(4)	0.5703(7)	0.2256(5)	0.0641
C(51)	0.4159(6)	0.6671(8)	0.2604(6)	0.0660
C(52)	0.4887(7)	0.670(1)	0.3111(6)	0.0836
C(53)	0.4977(8)	0.767(1)	0.3407(8)	0.0962
C(54)	0.567(1)	0.772(1)	0.3940(8)	0.1217
C(55)	0.4100(7)	0.4825(9)	0.2672(6)	0.0792
C(56)	0.3577(9)	0.487(1)	0.3068(8)	0.1162
C(57)	0.374(1)	0.402(2)	0.351(1)	0.1461
C(58)	0.426(1)	0.423(2)	0.407(1)	0.1667
C(59)	0.3254(6)	0.5784(8)	0.1814(6)	0.0687
C(60)	0.3061(7)	0.493(1)	0.1365(7)	0.0903
C(61)	0.2263(7)	0.506(1)	0.0936(7)	0.0974
C(62)	0.179(1)	0.478(1)	0.1306(9)	0.1263
C(63)	0.4589(6)	0.555(1)	0.1903(6)	0.0761
C(64)	0.4580(8)	0.637(1)	0.1451(7)	0.1093
C(65)	0.510(1)	0.558(2)	0.092(1)	0.1642
C(66)	0.519(1)	0.639(2)	0.096(2)	0.1914

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

Table VI. Selected Bond Lengths and Angles in Compounds **1**–**4**[a]

Bond Lengths (Å)

	1	**2**	**3**	**4**
Mo(1)–N(1)	1.75(1)	1.76(1)	1.77(1)	1.733(8)
Mo(1)–O(10)	2.122(5)	2.154(8)	2.155(8)	2.131(5)
Mo(1)–O(12)	1.992(6)	2.003(9)	1.990(8)	1.979(6)
Mo(1)–O(13)	1.993(7)	1.976(9)	1.965(8)	1.962(6)
Mo(1)–O(14)	1.994(6)	1.980(9)	1.990(8)	2.004(6)
Mo(1)–O(15)	2.003(6)	1.980(9)	2.016(8)	1.997(6)
Mo(2)–O(10)	2.343(5)	2.304(9)	2.359(8)	2.320(5)
Mo(2)–O(12)	2.259(6)	2.291(9)	2.313(8)	2.268(6)
Mo(2)–O(21)	1.720(7)	1.71(1)	1.743(8)	1.709(7)
Mo(2)–O(22)	1.698(7)	1.68(1)	1.719(9)	1.705(7)
Mo(2)–O(23)	1.920(6)	1.90(1)	1.936(9)	1.917(6)
Mo(2)–O(24)	1.924(6)	1.901(9)	1.883(8)	1.915(6)
Mo(3)–O(10)	2.363(5)	2.357(9)	2.286(8)	2.312(6)
Mo(3)–O(13)	2.291(7)	2.291(9)	2.309(8)	2.323(6)
Mo(3)–O(23)	1.917(6)	1.912(9)	1.924(9)	1.907(6)
Mo(3)–O(31)	1.723(8)	1.72(1)	1.717(8)	1.723(7)
Mo(3)–O(32)	1.699(7)	1.69(1)	1.704(9)	1.688(7)
Mo(3)–O(35)	1.915(6)	1.919(9)	1.920(9)	1.934(6)
Mo(4)–O(10)	2.319(5)	2.363(9)	2.330(8)	2.398(6)
Mo(4)–O(14)	2.282(6)	2.263(8)	2.268(8)	2.269(6)
Mo(4)–O(24)	1.905(6)	1.910(9)	1.953(9)	1.910(6)
Mo(4)–O(41)	1.705(7)	1.735(9)	1.726(8)	1.712(7)
Mo(4)–O(42)	1.691(7)	1.68(1)	1.691(9)	1.705(7)
Mo(4)–O(45)	1.937(6)	1.919(9)	1.926(9)	1.897(6)
Mo(5)–O(10)	2.348(5)	2.320(9)	2.404(8)	2.333(5)
Mo(5)–O(15)	2.285(7)	2.260(9)	2.277(8)	2.280(7)
Mo(5)–O(35)	1.917(6)	1.904(9)	1.932(8)	1.895(6)
Mo(5)–O(45)	1.914(6)	1.918(9)	1.900(9)	1.921(6)
Mo(5)–O(51)	1.746(7)	1.716(9)	1.723(9)	1.697(8)
Mo(5)–O(52)	1.691(7)	1.70(1)	1.71(1)	1.701(7)
N(1)–O(1)	1.22(1)	1.20(1)	1.22(1)	1.21(1)
O(12)–C(12)	1.43(1)	1.43(2)	1.43(1)	1.41(1)
O(13)–C(13)	1.44(1)	1.45(2)	1.43(2)	1.42(1)
O(14)–C(14)	1.44(1)	1.43(2)	1.43(1)	1.41(1)
O(15)–C(15)	1.43(1)	1.46(2)	1.46(1)	1.44(1)
Na(1)–O(21)	2,401(9)	2,61(1)	2,52(1)	2,377(9)
Na(1)–O(31)	2,35(1)	2,52(1)	2,48(1)	2,407(9)
Na(1)–O(41)	2,379(9)	2,66(1)	2,39(1)	2,376(1)
Na(1)–O(51)	2,386(9)	2,59(1)	2,60(1)	2,38(1)

Bond Angles (deg)

	1	**2**	**3**	**4**
O(10)–Mo(1)–N(1)	177.8(4)	178.0(5)	176.6(4)	176.5(4)
O(14)–Mo(1)–O(13)	163.1(3)	163.0(3)	162.4(3)	164.0(2)
O(15)–Mo(1)–O(12)	162.8(3)	162.0(3)	163.3(3)	163.4(3)
O(21)–Mo(2)–O(12)	167.0(3)	168.3(4)	168.8(4)	166.7(3)
O(22)–Mo(2)–O(10)	159.5(3)	158.6(4)	158.2(4)	159.2(3)
O(24)–Mo(2)–O(23)	147.8(3)	148.1(4)	145.8(4)	147.7(2)
O(31)–Mo(3)–O(13)	164.9(3)	166.1(4)	166.9(4)	167.4(3)
O(32)–Mo(3)–O(10)	161.1(3)	159.5(4)	160.5(4)	158.2(3)
O(35)–Mo(3)–O(23)	147.1(3)	145.1(4)	149.0(3)	146.6(3)
O(41)–Mo(4)–O(14)	166.1(3)	167.0(4)	164.7(4)	164.7(3)
O(42)–Mo(4)–O(10)	160.4(3)	159.3(4)	160.7(4)	160.6(3)
O(45)–Mo(4)–O(24)	146.9(3)	148.3(4)	148.7(4)	145.3(3)
O(45)–Mo(5)–O(35)	146.1(3)	149.4(4)	147.0(4)	147.0(3)
O(51)–Mo(5)–O(15)	166.2(3)	165.7(4)	165.4(4)	167.1(3)
O(52)–Mo(5)–O(10)	159.6(3)	160.0(4)	160.5(4)	160.1(4)
Mo(1)–N(1)–O(1)	178.3(10)	178.3(12)	175.9(10)	176.1(10)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

stretching vibrations, strong bands in the range 860–955 cm^{-1} characteristic of terminal oxo groups, and a strong band at 700 cm^{-1} assigned to ν(Mo–O–Mo). The structure of the features associated with the MoO_t stretchs displays some variation attributable to differences in the interaction of terminal oxo groups with alkali-metal cations and solvent molecules (*vide infra*). Additional features in the IR spectra arise from the OH stretching and the OH bending modes of the solvent molecules (MeOH in **1**, **2**, and **5**; H_2O in **2** and **3**) and from the CH stretching and CH bending modes of the cations (Me_4N^+ in **3**; $n\text{-}Bu_4N^+$ in other

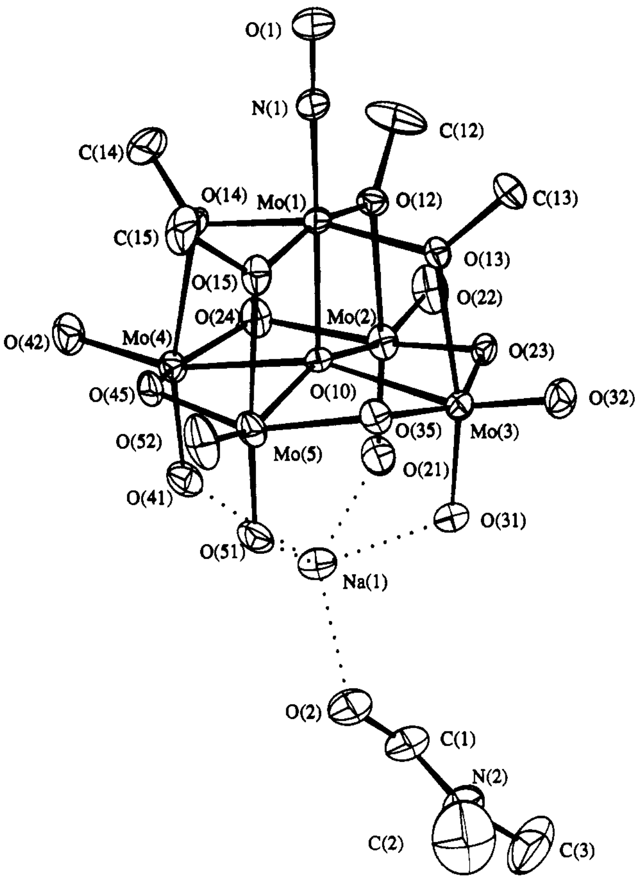


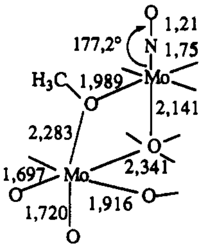
Figure 1. View[31] of the $[Mo_5O_{13}(OCH_3)_4(NO)\{Na(DMF)\}]^{2-}$ anion in **4**, showing the atom-labeling scheme.

compounds). In **4**, a strong band at 1680 cm^{-1} is assigned to the C=O stretching vibration of the DMF molecule.

Electronic Spectroscopy. Compounds **1**–**6** are violet. This color results from an absorption band at 530 nm ($\epsilon \sim 50$ mol^{-1} L cm^{-1} for complexes **1**–**5** in methanol), which appears to be characteristic of the $[Mo_5O_{13}(OR)_4(NO)]^{3-}$ unit. Indeed, all complexes containing this unit, including salts with hydrogen-bonded cations to be described in a subsequent paper, are violet while all other oxo nitrosyl derivatives known at this time are either brown ("complete" Lindqvist derivatives), yellow-green ("complete" Keggin derivatives), or blue (reduced decamolybdates). This band is assigned to the $d_{xy} \leftarrow d_{xz}, d_{yz}$ transition within the Mo^{II}(NO) unit.

^{95}Mo NMR spectroscopy. The ^{95}Mo NMR spectrum of **1** in CH_3OH/acetone-d_6 at 323 K exhibits two lines in intensity ratio 4:1 at 61 and 758 ppm relative to external Na_2MoO_4 in D_2O at pH 11. This is in agreement with the expected C_{4v} symmetry of the anion in solution and support its description as a localized mixed-valence Mo(VI)/Mo(II) species. The high deshielding of the Mo(II) likely arises from paramagnetic shifts. ^{95}Mo NMR spectroscopy of molybdenum oxo nitrosyl complexes will be discussed into details in part 2 of this series of papers.[32]

X-ray Structures. Compounds **1**–**4** all contain the $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ unit. This anion has an approximate C_{4v} symmetry. According to the charge balance, it contains the common $Mo(NO)^{3+}$ unit, which is written as $\{MoNO\}^4$ by using the classification scheme of Enemark and Feltham.[33] This MoNO group displays the expected linear geometry and thus is formally considered as containing a Mo^{II} center and a NO$^+$ species. The $[Mo_5O_{13}(OCH_3)_4(NO)]^{3-}$ anion may be viewed as a functionalized lacunar Lindqvist-type compound,[34] which derives from the hitherto unknown $[Mo_5O_{18}]^{6-}$ anion by replacing the apical MoO^{4+} unit by a $Mo(NO)^{3+}$ unit and replacing the bridging oxygen atoms linking the $Mo(NO)^{3+}$ unit to its four Mo(VI) neighbors by methoxo groups. The sixth position is occupied by a sodium cation which interacts with the four axial O_t atoms of the anion. The four Mo(VI) centers are nearly coplanar (maximum deviation of any Mo atom from the mean plane: 0.012 Å) and the central oxygen atom is displaced by *ca.* 0.4 Å from this plane toward the Mo(II) center. It follows that the Mo(II)–O_c distance (2.141 Å, average for **1**–**4**) is significantly shorter than the Mo(VI)–O_c distance (2.341 Å, average for **1**–**4**). The alkoxo bridges are clearly asymmetrical: Mo(II)–O = 1.99 Å (average for **1**–**4**); Mo(VI)–O = 2.28 Å (average for **1**–**4**). The environment of the methoxo oxygen atoms departs more or less from planarity. The geometrical parameters of the anion, averaged on equivalent bond and angles within the four anions, are given as follows:



In complexes **1**–**4**, the sodium cation is coordinated by either five, six, or seven oxygen atoms, four of which being the axial terminal O_t of a $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anion. In both **1** and **4**, the Na$^+$ displays square pyramidal coordination respectively with a methanol molecule and a DMF molecule in the apical position. In **3**, the Na$^+$ ion attains a coordination number of 6 through further ligation to a water molecule and to an axial O_t of a second $[Mo_5O_{13}(OCH_3)_4(NO)]^{3-}$ anion. In **2**, the Na$^+$ ion shows a coordination number of 7, its surrounding being completed by a water molecule, a methanol molecule, and an axial O_t of a second $[Mo_5O_{13}(OCH_3)_4(NO)]^{3-}$ anion. As expected, the mean Na–O distance increases with the coordination number:

	compd			
	1	**4**	**3**	**2**
coord no. of Na$^+$	5	5	6	7
mean Na–O dist (Å)	2.38	2.39	2.50	2.54

Compounds **1**–**4** differ in intermolecular interactions. While **4** contains discrete $[Mo_5O_{13}(OMe)_4(NO)\{Na(DMF)\}]^{2-}$ anions (Figure 1), the $[Mo_5O_{13}(OMe)_4(NO)\{Na(MeOH)\}]^{2-}$ anions in **1** are linked in chains by methanol molecules. These chains, running along the *a* axis, can be vewied as made up of $[Mo_5O_{13}(OMe)_4(NO)Na]^{2-}$ clusters linked by three hydrogen-bonded methanol molecules, one end of the link being attached to the sodium cation of one cluster and the other one to an equatorial O_b of a second cluster. The fourth methanol molecule in **1** is linked to an axial O_t through an O–H···O bond (Figure 2). More complicated structures are found in **2** and **3**. In both compounds, the Na$^+$ links two $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anions. In compound **3**, the $\{[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)\}]_2\}^{4-}$ dimeric units are held together through hydrogen O–H···O bonds involving the water molecule and equatorial O_t: the water molecule is involved in two hydrogen bonds with two different $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anions. This results in sheets parallel to the $(\vec{a} + \vec{c}, \vec{b})$ plane (Figure 3). In **2**, the $\{[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)(MeOH)\}]_2\}^{4-}$ dimeric units are connected *via* hydrogen and coordination bonds among oxygen anions, water and methanol

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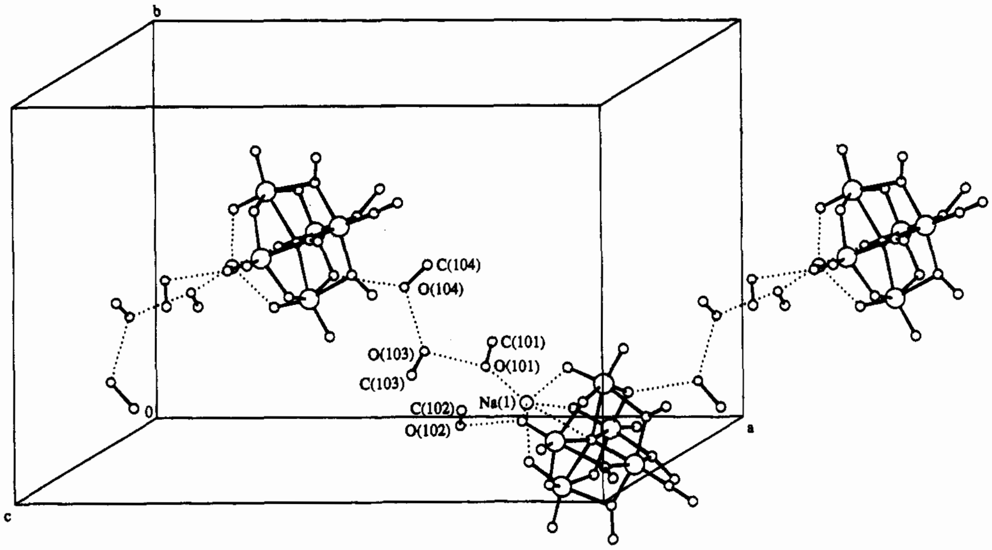

Figure 2. View[31] of a hydrogen-bonded chain in **1**.

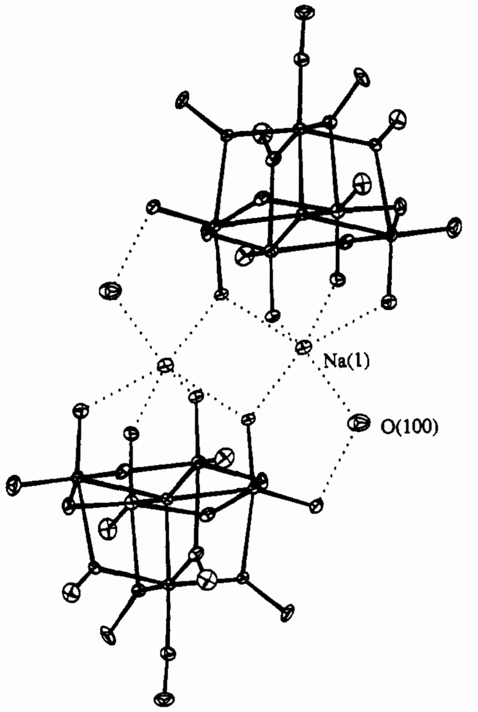

Figure 3. View[31] of a $\{[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)\}]_2\}^{4-}$ unit in **3**.

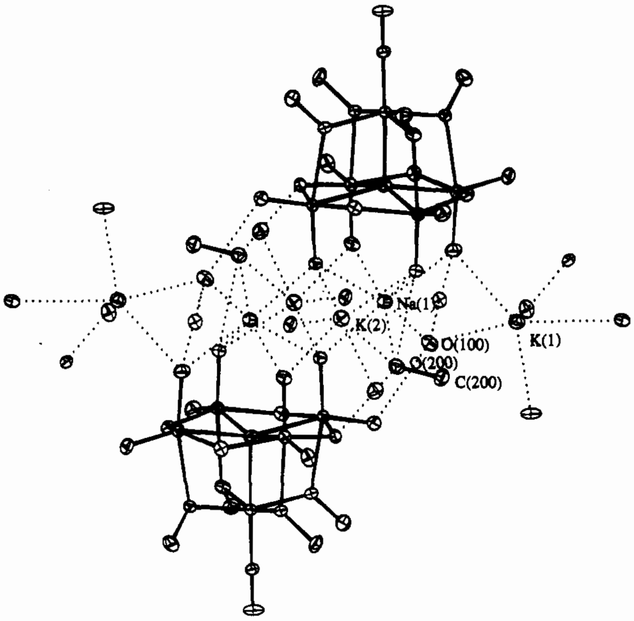

Figure 4. View[31] of a $\{[Mo_5O_{13}(OMe)_4(NO)\{Na(H_2O)(CH_3OH)\}]_2\}^{4-}$ unit in **2**.

molecules, and potassium cations: this results in ribbons running along the *b* axis and connected by K^+ which display irregular surroundings of six oxygen atoms (Figure 4). The distances between the K^+ ions and the coordinated oxygen atoms range from 2.67 to 3.08 Å for K(1) and from 2.63 to 2.83 Å for K(2).

Electrochemistry. The electrochemistry of compound **1** at a platinum electrode has been monitored by cyclic voltammetry in CH_3CN. Under these conditions, the $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ anion is not reducible up to −1.50 V vs SCE. Such a behavior is not unexpected for a *cis*-dioxoisopolyoxomolybdate, *i.e.* a type II compound in the classification of Pope.[35] Otherwise, this compound displays an ill-defined irreversible oxidation peak at +1.09 V vs SCE, associated with the $Mo(NO)^{3+}$ group.

Discussion

Syntheses. The reaction of Mo(VI) oxo anions with hydroxylamine in aqueous solution had been first investigated by Hofmann *et al.*,[36] who described their compounds as hydroxylamine complexes of Mo(VI). It was not until the end of the seventies that it was recognized independently by Müller *et al.*[18] and by Wieghardt *et al.*[19] that the reaction products were nitrosyl complexes of molybdenum(II).

Reductive nitrosylation of oxomolybdenum complexes can also be achieved in nonaqueous solution. For instance, we have found that both acetamidoxime $MeC(NH_2)NOH$[37] and acetone oxime[38] react with $[MoO_2(acac)_2]$ in MeOH to give mononuclear nitrosylmolybdenum(II) complexes $[Mo(NO)(acac)_2\{RC(Y)NO\}]$ (Y = NH_2, CH_3) with a side-on, *N,O*-coordinated oximate ligand. Other amidoximes are generally less reactive than acetamidoxime so that NH_2OH needs to be added to the reacting mixture in order to achieve nitrosylation. In the absence of any additional ligand, NH_2OH reacts on isopolyoxomolybdates in methanol to give nitrosyl-containing polyoxomolybdates. The

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(38) Proust, A.; Roh, S.-G.; Gouzerh, P.; Robert, F. Unpublished results.

initial step of the reaction could be the formation of oxo–methoxo species which subsequently react with hydroxylamine with reaggregation to yield the pentanuclear species. The following scheme have been suggested by Wieghardt for the reductive nitrosylation of Mo(VI) oxo compounds:[39]

$$\mathrm{Mo^{VI}O^{4+} + NH_2OH \Leftrightarrow Mo^{VI}O(NH_2OH)^{4+}}$$

$$\mathrm{Mo^{VI}O(NH_2OH)^{4+} \Rightarrow Mo(NO)^{3+} + H_3O^+}$$

Although the compound isolated by Lassner[21] and by Wieghardt *et al.*[19a] was assumed to be a polymeric Mo(II) nitrosyl complex,[19a] it could be actually an oxo nitrosyl derivative. Indeed, by refluxing of this compound in MeOH in the presence of *n*-Bu$_4$NBr, both (n-Bu$_4$N)$_3$[Mo$_6$O$_{18}$(NO)] and a violet solid tentatively formulated as (n-Bu$_4$N)$_2$(NH$_3$OH)[Mo$_5$O$_{13}$(OMe)$_4$(NO)] on the basis of its infrared spectrum were obtained.

Structures. As previously stated, $[\mathrm{Mo_5O_{13}(OR)_4(NO)}]^{3-}$ complexes can be viewed as defect Lindqvist structures. To the best of our knowledge, the parent $[\mathrm{Mo_5O_{18}}]^{6-}$ anion has not yet been described although its tungsten analogue $[\mathrm{W_5O_{18}}]^{6-}$ has been characterized in cerium(IV)[40] and uranium(IV)[41] complexes. Other related compounds include the organometallic oxide [(Cp)$_5$Y$_5$O(OMe)$_8$],[42] the oxo–alkoxide [Y$_5$O(OPr-*i*)$_{13}$],[43] and the poly(amido imido) nitride [Zr$_5$N(NH)$_4$(NH$_2$)$_4$(OR)$_5$].[44] Strangely enough, the framework of the iodoantimonate $[\mathrm{Sb_5I_{18}}]^{3-}$ [45] also bears distinct resemblance to the defect Lindqvist structure. The enhanced stability of the lacunar $[\mathrm{Mo_5O_{13}(OR)_4(NO)}]^{3-}$ anions compared to $[\mathrm{Mo_5O_{18}}]^{6-}$ probably arises from the electron-withdrawing effect of the nitrosyl ligand and from the decrease in charge resulting from alkylation of the parent oxo anion. The nucleophilicity of the terminal oxygen atoms shows itself in hydrogen bonding to solvent molecules or cations. Indeed, the $[\mathrm{Mo_5O_{13}(OR)_4(NO)}]^{3-}$ anions need further stabilization, which can be achieved by complexation with inorganic (Na$^+$, Li$^+$, NH$_3$OH$^+$, ...) or organic (ArNH$_3^+$, RC(NH$_2$)$_2^+$)[38] cations. Solutions of **1** in methanol have been kept for several months at room temperature without any decomposition. On the contrary, the ethoxo derivative transforms easily into (n-Bu$_4$N)$_3$[Mo$_6$O$_{18}$(NO)].

Conclusions. The synthesis of nitrosylpolyoxomolybdates demonstrates the feasibility of incorporating the soft π-acceptor nitrosyl ligand into an oxometalate framework. The defect $[\mathrm{Mo_5O_{13}(OMe)_4(NO)}]^{3-}$ species is a convenient starting material for the synthesis of a number of other nitrosyl-containing polyoxometalates. First, as other monovacant polyoxometalates,[46–48] it can act as an inorganic porphyrin-like ligand. The sodium cation is easily displaced by lanthanide cations[23] and by unsaturated organometallic cations.[49] Second, it can act as a source of the Mo$^{\mathrm{II}}$(NO)$^{3+}$ fragment. Recrystallization of **1** in acetonitrile or dichloromethane affords (n-Bu$_4$N)$_3$[Mo$_6$O$_{18}$(NO)].[22,32] Reaction of **1** with (n-Bu$_4$N)$_3$[PM$_{12}$O$_{40}$] in acetonitrile in the presence of *n*-Bu$_4$NOH yields (n-Bu$_4$N)$_4$[PM$_{11}$O$_{39}$Mo(NO)] (M = Mo, W).[50]

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Supplementary Material Available: Tables giving crystal data, anisotropic thermal parameters, bond lengths, and bond angles for compounds 1–4 (19 pages). Ordering information is given on any current masthead page.

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