REDUCTIVE NITROSYLATION OF V_2O_5 AND MoO_3 WITH HYDROXYLAMINE IN THE PRESENCE OF 1,4,7-TRIAZACYCLONONANE

Christina HAUSER[1], Thomas WEYHERMÜLLER[2] and Karl WIEGHARDT[3,*]

Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34–36, D-45470 Mülheim an der Ruhr, Germany; e-mail: [1] chauser@cmm.vcsd.edu, [2] weyherm@mpi-muelheim.mpg.de, [3] wieghardt@mpi-muelheim.mpg.de

Received September 13, 2000
Accepted December 10, 2000

Dedicated to the memory of the late Professor Antonín A. Vlček.

From the reaction mixture of an alkaline aqueous solution of V_2O_5, 1,4,7-triazacyclononane (tacn) and hydroxylamine, orange, diamagnetic crystals of $[V(tacn)(NO)_2(NH_3)]I$ were obtained upon addition of NaI. Air-stable $[V(tacn)(NO)_2(N_3)]$ has also been isolated and characterized by X-ray crystallography. In a similar reaction using MoO_3 as starting material, yellow crystals of $[MoCl(tacn)(NO)(H_2NO)]ClO_4$ were isolated and characterized by X-ray crystallography. A less reducing reagent, *N*-methylhydroxylamine, produces in the above reaction mixture colorless crystals of $[Mo^{VI}(tacn)(O)_2(MeNHO)]ClO_4$; its structure has also been determined. A mechanism for the formation of $\{M(NO)_2\}^6$ complexes (M = Mo, V) from high-valent oxometallates and hydroxylamine is proposed.

Keywords: Reductive nitrosylation; *cis*-Dinitrosylvanadium; Nitrosylmolybdenum; X-Ray structures; Hydroxylamine; Vanadium oxide; Molybdenum oxide; Oxometallates.

The generation of nitrosylvanadium complexes, $\{V(NO)\}^4$ according to the Enemark and Feltham nomenclature[1], *via* reductive nitrosylation[2] of VO_4^{3-} (or V_2O_5 in aqueous KOH) with hydroxylamine as shown in Eq. (*1*), is a convenient and well explored route to such species[3–7].

$$V^VO_3^- + H_2NOH + [\text{chelating ligand}]^{n-} \rightarrow$$

$$\rightarrow [V(NO)(\text{chelating ligand})]^{(n-2)-} + 3\ H_2O + 3\ H^+ \qquad (1)$$

Even the reverse reaction has been demonstrated in acidic solution[5,8]. In this reaction, hydroxylamine is formally oxidized by 4 electrons yielding

doi: 10.1135/cccc20010125

NO^+ with concomitant reduction of the metal ion V^V to V^I. Note that in this case, no ammonia is formed. The same reaction occurs with MoO_3 or MoO_4^{3-}, where $\{Mo(NO)\}^4$ complexes are generated[2]. In both cases the ratio oxometallate : hydroxylamine : $\{M(NO)\}^4$ is 1 : 1 : 1.

On the other hand, the first reported[9] nitrosylation by hydroxylamine involves the formal disproportionation of H_2NOH with formation of a nitrosyl complex and one equivalent of NH_3. The ratio starting complex : H_2NOH : nitrosyl complex : NH_3 is 1 : 2 : 1 : 1 as in Eq. (*2*) in the absence of oxygen.

$$[Ni^{II}(CN)_4]^{2-} + 2\ H_2NOH \rightarrow [Ni^0(CN)_3(NO)]^{2-} + NH_3 + HCN + H_2O \qquad (2)$$

Vepřek-Šiška and Luňák have subsequently shown in two elegant kinetic studies[10,11] that, in fact, two different mechanisms are operative in the formation of $[Ni(CN)_3(NO)]^{2-}$: reaction (*2*) under anaerobic conditions and reaction (*3*) in the presence of air. Here the ratio starting complex : H_2NOH : oxygen : nitrosyl complex is 1 : 1 : 0.5 : 1.

$$[Ni(CN)_4]^{2-} + H_2NOH + 1/2\ O_2 + OH^- \rightarrow [Ni(CN)_3(NO)]^{2-} + CN^- + 2\ H_2O \qquad (3)$$

In this instance, no ammonia is formed but an external oxidant O_2 is needed. Note the differing stoichiometries of reactions (*2*) and (*3*).

It is also established that diamagnetic dinitrosylmolybdenum complexes, $\{Mo(NO)_2\}^6$, are accessible[12] from the reaction of molybdate with H_2NOH: $[Mo(NO)_2X_4]^{2-}$ (X = NCS^-, CN^-) and $[Mo(NO)_2X_2L]^0$ (X = NCS^-; L = 1,10-phenanthroline, 2,2′-bipyridine) have been reported.

Only one report describes the formation of *paramagnetic* dinitrosylvanadium complexes prepared *via* reductive nitrosylation of VO_4^{3-} with NH_2OH and CN^- in an alkaline aqueous medium, obviously in the presence of air[13]: $[V^0(NO)_2(CN)_4]^{2-}$ and $[V^0(NO)_2(CN)_2(L–L)]$ have been characterized, where L–L is either 1,10-phenanthroline or 2,2′-bipyridine. Surprisingly, both species are of the $\{V(NO)_2\}^5$ type. They have not been characterized by X-ray crystallography. The former one displays two ν(NO) frequencies at 1 650 and 1 520, and the latter at 1 680 and 1 540 cm^{-1}.

In an attempt to generate *diamagnetic* $\{V(NO)_2\}^6$ complexes *via* reductive nitrosylation of VO_4^{3-} with H_2NOH, we added the macrocyclic triamine 1,4,7-triazacyclononane (tacn) as co-ligand. We have synthesized the diamagnetic, air-stable $\{V(NO)_2\}^6$ species, $[V(tacn)(NO)_2(NH_3)]I$ (**1**) and

[V(tacn)$(NO)_2(N_3)$] (**2**), *via* reductive nitrosylation with H_2NOH in the absence or presence of air. We also investigated this type of nitrosylation reaction with MoO_4^{2-} and H_2NOH or a less reducing agent, *N*-methylhydroxylamine, in the presence of the above amine tacn, and isolated the $\{Mo(NO)\}^4$ species [MoCl(tacn)(NO)(H_2NO)]ClO_4 (**3**) or [Mo(tacn)$(O)_2$(MeNHO)]ClO_4 (**4**), respectively.

EXPERIMENTAL

The ligand 1,4,7-triazacyclononane has been synthesized by published methods[14].

Syntheses of Complexes

[V(tacn)$(NO)_2(NH_3)$]I (**1**). V_2O_5 (0.90 g, 5.0 mmol) and KOH (1.8 g, 32 mmol) were dissolved in water (20 ml). To the filtered, colorless solution was added 1,4,7-triazacyclononane (1.28 g, 10 mmol). After heating to 70 °C for 30 min, the solution was cooled to 20 °C and hydroxylammonium chloride (1.4 g, 20 mmol) was added whereupon the color changed to deep green and NH_3 evolved. Upon addition of NaI (≈2 g) and cooling to 4–5 °C, orange microcystals of **1** precipitated within a few hours. Yield 1.5 g (40% based on V_2O_5). FAB$^+$ MS, *m/z*: 257 ([V(tacn)$(NO_2)_2(NH_3)$]$^+$), 240 ([V(tacn)$(NO)_2$]$^+$). ^{1}H NMR (DMSO-d_6): δ 2.68–2.98 (m, 12 H, -CH_2-CH_2-); 3.31 (s, 3 H, NH(NH_3)); 4.82 (s, 2 H, NH(tacn)); 5.55 (1 H, NH(tacn)). For $C_6H_{18}N_6O_2V$ (257.2) calculated: 18.8% C, 4.7% H, 21.9% N; found: 18.6% C, 4.9% H, 21.6% N.

[V(tacn)$(NO)_2(N_3)$] (**2**). To a solution of **1** (0.35 g, 0.9 mmol) in water (20 ml) NaN_3 (0.6 g, 9 mmol) was added. The solution was warmed up to 30 °C and stirred for 10 min. Upon cooling to 4–5 °C, brown microcrystals of **2** precipitated. Recrystallization from a CH_3CN–C_2H_5OH mixture (1 : 1) yielded single crystals of **2** suitable for X-ray crystallography. Yield 0.12 g (47%). For $C_6H_{15}N_8O_2V$ (282.2) calculated: 25.5% C, 5.4% H, 39.7% N; found: 25.4% C, 5.3% H, 39.6% N.

[MoCl(tacn)(NO)(H_2NO)]ClO_4 (**3**). To a solution of NaOH (0.67 g, 16.8 mmol) and MoO_3 (0.30 g, 2.1 mmol) in water (20 ml) at 60 °C a solution of $(NH_3OH)Cl$ (2.8 g, 40 mmol) in H_2O (10 ml) was added dropwise with stirring. The pH of the resulting yellow solution was adjusted to ≈7 by addition of 1.0 M aqueous NaOH. 1,4,7-Triazacyclononane (0.26 g, 2.0 mmol) was added. After stirring at 85 °C for 1 h, pH of the cooled solution was lowered to ≈1 by careful addition (dropwise) of concentrated $HClO_4$ and 3 g of $NaClO_4 \cdot H_2O$. This initiated the formation of a colorless precipitate that was filtered off and discarded. From the yellow-orange filtrate yellow microcrystals of **3** were formed within 24 h. Single crystals suitable for X-ray crystallography were obtained from a saturated aqueous solution of **3** by slow evaporation of the solvent. Yield 0.52 g (59% based on MoO_3). FAB$^+$ MS, *m/z*: 324 ([Mo(tacn)(NO)(Cl)(H_2NO)]$^+$). ^{1}H NMR (DMSO-d_6): δ 2.58–2.79 and 2.89–3.61 (two multiplets, 12 H, -CH_2-CH_2-); 4.19 (s, 1 H, NH(tacn)); 7.33 (s, 1 H, NH(tacn)); 7.79 (s, 1 H, NH(tacn)); 8.01 (d, *J* = 5.88, 1 H, NH (hydroxylamine)); 9.39 (d, *J* = 5.88, 1 H, NH (hydroxylamine)). For $C_6H_{17}Cl_2MoN_5O_6$ (422.1) calculated: 17.1% C, 4.1% H, 16.6% N; found: 17.1% C, 4.4% H, 16.9% N.

[Mo(tacn)$(O)_2$(MeNHO)]ClO_4 (**4**). To a suspension of [Mo^{VI}(tacn)$(O)_2$(OH)]ClO_4 (0.35 g, 0.9 mmol) in water (20 ml) *N*-methylhydroxylammonium chloride (0.10 g, 1.2 mmol) was

added. pH of this solution was adjusted to ≈7 by dropwise addition of 1.0 M NaOH with stirring for 1 h until a clear colorless solution was obtained. $NaClO_4 \cdot H_2O$ (3.0 g) was added which initiated the precipitation of colorless **4**. Recrystallization from a saturated aqueous solution of **4** by slow evaporation of the solvent produced colorless crystals suitable for X-ray crystallography. Yield 0.20 g (56%). ^1H NMR (DMSO-d_6): δ 2.74 (d, *J* = 3.6, 3 H, CH_3); 2.73–3.10 (m, 12 H, $-CH_2-CH_2-$); 5.64 (s, 2 H, NH(tacn)); 6.54 (s, 1 H, NH(tacn)); 8.50 (q, *J* = 4.3, 1 H, NH (hydroxylamine)). For $C_7H_{19}ClMoN_4O_7$ (402.7): 20.9% C, 4.8% H, 13.9% N; found: 20.3% C, 4.7% H, 13.8% N.

The starting material[15], $[Mo(tacn)(O)_2(OH)]ClO_4$, has been prepared as follows[16,17]: $[Mo(tacn)(O)_3]$ (0.5 g, 1.8 mmol) was dissolved in water (20 ml) to which 1.0 M NaOH (7 ml) was added. After heating to 80 °C for a few minutes, concentrated $HClO_4$ (1 ml) was carefully added to the cooled (20 °C) solution. Upon addition of 3 g of $NaClO_4 \cdot H_2O$, a colorless precipitate formed which was collected by filtration and washed with cold ethanol–diethyl ether. Yield 0.4 g (56%). For $C_6H_{16}ClMoN_3O_7$ (373.6): 19.29% C, 4.32% H, 11.25% N; found: 19.3% C, 4.1% H, 11.3% N.

X-Ray Crystallographic Data Collection and Refinement of the Structures

Single crystals of brown $[V(tacn)(NO)_2(N_3)]$, pale yellow $[MoCl(tacn)(NO)(H_2NO)]ClO_4$, and a colorless specimen of $[Mo(tacn)(O)_2(MeNHO)]ClO_4$ were mounted in sealed glass capillaries. Graphite monochromatized MoKα radiation (λ = 0.71073 Å) was used. Crystallographic data of the compounds and diffractometer types used are listed in Table I. Cell constants for $[V(tacn)(NO)_2(N_3)]$ and $[Mo(tacn)(O)_2(MeNHO)]ClO_4$ were obtained from a least-square fit of the setting angles of several thousand strong reflections. Twentyfive carefully centred reflections were used for the cell determination of $[MoCl(tacn)(NO)(H_2NO)]ClO_4$. Intensity data were corrected for Lorentz and polarization effects. Crystal faces of a thin platelet shaped crystal of $[Mo(tacn)(O)_2(MeHNO)]ClO_4$ were determined and the face-indexed correction routine embedded in ShelXTL (ref.[18]) was used to account for absorption giving a maximum and minimum transmission coefficient of 0.93 and 0.50. The Siemens ShelXTL software package[18] was used for solution, refinement and artwork of the structures; neutral atom scattering factors of the program were used. All structures were solved and refined by direct methods and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically except oxygen atoms of the perchlorate anion in $[MoCl(tacn)(NO)(H_2NO)]ClO_4$; this anion was found to be severely disordered. A split atom model with three different orientations was used and occupation factors of 0.5, 0.25, and 0.25 were chosen for the parts; only the major part was anisotropically refined. The Cl–O and O–O distances of the anion were restrained to be equal within errors using the SADI instruction in ShelXL. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-148249 (**2**), CCDC-148250 (**3**), and CCDC-148251 (**4**). Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

TABLE I
Crystallographic data for [V(tacn)$(NO)_2(N_3)$], [Mo(tacn)(NO)(H_2NO)Cl]ClO_4, and [Mo(tacn)$(O)_2$(MeNHO)]ClO_4

Parameter	**2**	**3**	**4**
Empirical formula	$C_6H_{15}N_8O_2V$	$C_6H_{17}Cl_2MoN_5O_6$	$C_7H_{19}ClMoN_4O_7$
M_w	282.20	422.09	402.65
Space group	$P2_1/c$	*Pbca*	*Pbca*
a, Å	7.2770(12)	13.052(4)	12.127(2)
b, Å	7.8736(12)	15.400(2)	12.258(2)
c, Å	20.047(2)	14.903(6)	19.413(3)
β, °	94.15(2)	90	90
V, Å^3	1 145.6(3)	2 996(2)	2 885.8(8)
Z	4	8	8
T, K	100(2)	293(2)	293(2)
Crystal size, mm^3	0.16 × 0.07 × 0.04	0.39 × 0.32 × 0.18	0.72 × 0.66 × 0.6
ρ_{calcd}, g cm^{-3}	1.636	1.872	1.854
μ(MoKα), cm^{-1}	8.73	12.63	11.30
Diffractometer used	Nonius KappaCCD	Nonius CAD4	Nonius KappaCCD
Reflections collected/R_{int}	7 329/0.130	2 636	15 326/0.088
Unique reflections/[$I > 2\sigma(I)$]	2 012/1 442	2 636/1 953	2 919/2 600
No. of parameters	154	214	184
maximum and minimum residual density, e Å^{-3}	+0.37/–0.35	+0.94/–0.59	+0.78/–1.02
$R1^a[I > 2\sigma(I)]/2\theta_{max}$, °	0.045/50.00	0.051/49.98	0.041/52.66
$wR2^b[I > 2\sigma(I)]$	0.091	0.136	0.111

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$, where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$.

RESULTS

Syntheses and Characterization of Complexes

The reaction of an alkaline aqueous solution of divanadium pentoxide, V_2O_5, excess KOH and the macrocyclic 1,4,7-triazacyclononane with an excess of hydroxylammonium chloride, $(H_3NOH)Cl$, produced, in the presence or absence of dioxygen, a deep green solution. Addition of NaI to this solution generated diamagnetic, orange red microcrystals of $[V(tacn)(NO)_2(NH_3)]I$ (**1**) in ≈40% yield based on V_2O_5. Gaseous ammonia is formed during the reaction.

The fast atom bombardment mass spectrum of **1** displays two prominent peaks at m/z = 257 and 240 which correspond to the cations $[V(tacn)(NO)_2(NH_3)]^+$ and $[V(tacn)(NO)_2]^+$. In the IR spectrum of **1**, three strong ν(NO) frequencies are observed at 1 678 cm^{-1} (ν_s(NO)) and 1 559, 1 537 cm^{-1} (ν_{as}(NO)), resembling closely the spectrum of $[V(en)_2(NO)_2]Br$ (ref.[19]) (en = ethylenediamine), where the ν_s(NO) and ν_{as}(NO) are reported at 1 687 and 1 538 cm^{-1}, respectively. The splitting of the ν_s(NO) band in the case of **1** is probably due to differing site symmetry of the cations in the solid state structure of **1**. It is well known that the ratio of the intensities of ν_{as}(NO) and ν_s(NO) depends[20] on the ON–M–NO bond angle δ. Since both ν_s(NO) and ν_{as}(NO) have the same intensity, the bond angle is expected to be ≈90°. Compound **1** contains the *cis*-$[V(NO)_2]^+$ moiety or, in the Enemark–Feltham notation, a *cis*-$\{V(NO)_2\}^6$.

The electronic spectrum of **1** recorded in aqueous solution displays absorption maxima at 350 nm (sh, ε = 600 l mol^{-1} cm^{-1}), 402 (485), 475 ($1.22 \cdot 10^3$), 788 (50). A very similar spectrum has been reported for $[V(NO)_2(CO)(\eta^5\text{-}C_p)]$ with maxima at 415, 490, and 710 nm (ref.[21]). This indicates that an identical *cis*-$\{V(NO)_2\}^6$ chromophore is present in both species.

The ammonia ligand in **1** is quite labile and can readily be substituted by water in aqueous solution, producing $[V(tacn)(NO)_2(H_2O)]^+$. In the presence of the coordinating, monodentate azide ligand, the neutral complex $[V(tacn)(NO)_2(N_3)]$ (**2**) has been obtained as brown microcrystals. The IR spectrum of **2** exhibits a strong $\nu_{as}(N_3)$ band at 2 060 cm^{-1} and the ν_s(NO) and ν_{as}(NO) bands of equal intensity at 1 667 and 1 533 cm^{-1}, respectively. The electronic spectrum of **2** in CH_3CN displays maxima at 217 nm (ε = $2.05 \cdot 10^4$ l mol^{-1} cm^{-1}), 290 sh ($2.0 \cdot 10^3$), 337 (770), 401 (595), 481 ($1.11 \cdot 10^3$), 850 (40).

We have also recorded the ^{51}V NMR spectra of **1** in water and **2** in CH_3CN. The spectrum of **1** displays two resonances at δ –500 and –371 ppm (external standard $VOCl_3$, δ 0), where the former loses intensity with time and the latter slowly grows. We assign the former to the $[V(tacn)(NO)_2(NH_3)]^+$ and the latter to its hydrolyzed form $[V(tacn)(NO)_2(H_2O)]^+$. Rehder[19] and Herberhold *et al.*[21] have previously established the ^{51}V chemical shift range for a number of dinitrosylvanadium complexes of the type $\{V(NO)_2\}^6$ to be from –1 300 to +300 ppm. The spectrum of **2** dissolved in CH_3CN exhibits a single resonance at δ –405 ppm.

The reaction of an alkaline aqueous solution of MoO_3, NaOH, and excess hydroxylammonium chloride produces a pale yellow solution from which, upon addition of polydentate ligands, nitrosylmolybdenum complexes of the type $\{Mo(NO)\}^4$ can be readily isolated[22–24]. Thus, upon addition of 1,4,7-triazacyclononane to such a solution and heating to 80 °C for 1 h, it has been possible to isolate yellow microcrystals of $[MoCl(tacn)(NO)(H_2NO)]ClO_4$ (**3**) after adjustment of pH of the solution to 1 with concentrated $HClO_4$ and $NaClO_4$. In the IR spectrum the ν(NO) band is observed at 1 651 cm^{-1}.

The ^{1}H NMR spectrum (DMSO-d_6) of **3** clearly shows the presence of a coordinated η^2-H_2NO^- ligand. Two doublets at δ 8.01 and 9.39 (J = 5.88 Hz) are observed. The stoichiometry of the reaction is as shown in Eq. (*4*). Note that in this case no NH_3 is produced.

$$\begin{aligned} &MoO_4^{2-} + 2\,[H_3NOH]Cl + tacn + 2\,H^+ \rightarrow \\ &\rightarrow [MoCl(tacn)(NO)(H_2NO)]^+ + 4\,H_2O + Cl^- \end{aligned} \qquad (4)$$

The formation of the $\{Mo(NO)\}^4$ species can be suppressed by using *N*-methylhydroxylammonium chloride as a reagent. $(CH_3NH_2OH)Cl$ is a considerably less strong reductant than $(H_3NOH)Cl$. The reaction of $[Mo^{VI}(tacn)(O)_3]$ dissolved in alkaline aqueous solution with concentrated $HClO_4$ (added dropwise) and addition of $NaClO_4$ produce the colorless mononuclear species $[Mo^{VI}(tacn)(O)_2(OH)]ClO_4$. In the IR spectrum, a sharp ν(OH) band is observed at 3 505 cm^{-1} and two ν(N–H) bands at 3 223 and 3 085 cm^{-1}, respectively. In addition, the *cis*-$Mo(O)_2$ unit gives rise to two ν(Mo=O) bands, ν_{as} and ν_s, at 934 and 906 cm^{-1}, respectively. This species reacts with $(CH_3)HNOH$ in water at pH 6–7, yielding colorless crystals of $[Mo^{VI}(tacn)(O)_2(MeNHO)]ClO_4$ (**4**). A similar complex, containing two η^2-coordinated *N*-methylhydroxylamido ligands, was prepared previously from the reaction of MoO_4^{2-} with MeNHO, namely $[Mo^{VI}(O)_2(MeNHO)_2]$ (ref.[23]).

Crystal Structures

Details of the crystal structure determinations are given in Table I. Table II summarizes important bond distances and angles.

Figure 1 shows the structure of a neutral molecule $[V(tacn)(NO)_2(N_3)]$ in crystals of **2**. Surprisingly, this structure is the first crystallographically characterized dinitrosylvanadium complex. The vanadium ion is in a distorted octahedral environment, comprising three secondary amine nitrogens of the macrocycle 1,4,7-triazacyclononane in *cis*-position to each other, two nitrogen donors of two *cis*-positioned nitrosyl ligands, and a nitrogen of the azido ligand in the sixth position. The three five-membered chelate rings, V–N–C–C–N, of the coordinated macrocycle adopt λλλ or δδδ conformation; both enantiomeric forms are present in equal amounts in the centrosymmetric space group $P2_1/c$. The *cis*-$[V(NO)_2]$ unit displays two short, but within the 3σ limit, equidistant V–N bonds at 1.742 Å, indicating considerable double bond character; the ON–V–NO bond angle at 88.5° is close to 90° expected from IR spectroscopy. The average N–O distance of 1.200(3) Å is also short and indicative of a double bond. Both nitrosyls are nearly linearly bound (α(V–N–O): 177.6(2) and 171.4(2)°). The two nitrosyls

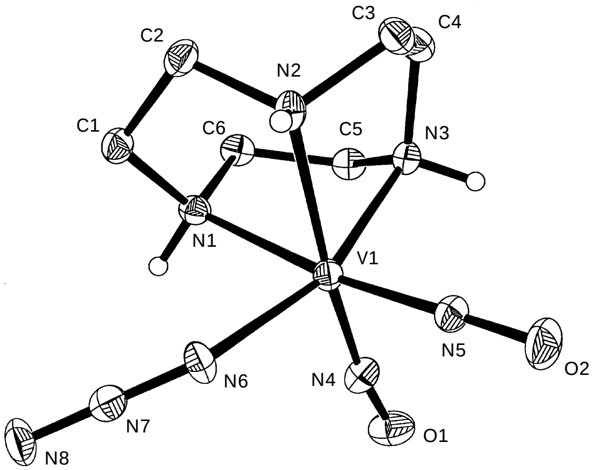


FIG. 1
ORTEP drawing of the neutral complex in crystals of **2** at the 40% probability level. H-Atoms are omitted

TABLE II
Selected bond lengths (in Å) and angles (in °)

	Complex **2**		
V1–N1	2.192(2)	V1–N2	2.142(2)
V1–N3	2.194(2)	V1–N4	1.746(2)
V1–N5	1.737(2)	V1–N6	2.092(2)
N4–O1	1.193(3)	N5–O2	1.207(3)
N6–N7	1.174(3)	N7–N8	1.152(3)
N6–V1–N4	95.4(1)	N4–V1–N5	88.5(1)
N6–V1–N5	101.5(1)	N7–N6–V1	132.0(2)
V1–N5–O2	171.4(2)	V1–N4–O1	177.6(2)
N8–N7–N6	177.8(2)		
	Complex **3**		
Mo1–Cl1	2.440(2)	Mo1–O1	2.042(5)
Mo1–N1	2.118(6)	Mo1–N2	2.183(2)
Mo1–N3	2.263(6)	Mo1–N4	2.197(6)
Mo1–N5	1.764(6)	N5–O2	1.193(8)
O1–N1	1.396(8)		
N1–Mo1–O1	39.2(2)	Mo1–N5–O2	174.4(6)
Mo1–N1–O1	67.5(3)		
Mo1–O1–N1	73.4(3)		
	Complex **4**		
Mo1–O1	1.724(2)	Mo1–O2	1.733(3)
Mo1–O7	1.963(2)	Mo1–N7	2.159(3)
Mo1–N2	2.240(3)	Mo1–N3	2.303(3)
Mo1–N1	2.335(3)	O7–N7	1.415(4)
N7–C7	1.462(5)		
O1–Mo1–O2	111.4(1)	O7–N7–Mo1	62.6(2)
Mo1–N7–O7	77.6(2)	C7–N7–O7	113.7(4)
O7–Mo1–N7	39.8(1)	C7–N7–Mo1	124.7(3)

exert a moderately strong *trans* influence on the two V–N_{amine} bonds in *trans* position. Thus V–N1 and V–N3 at 2.192(2) and 2.194(2) Å are longer by 0.05 Å than the V–N2 bond at 2.142(2) Å.

Figure 2 displays the structure of the monocation $[Mo(tacn)(NO)(Cl)(H_2NO)]^+$ in crystals of **3**. The molybdenum ion is heptacoordinate, comprising five nitrogens, a chloro ligand and an oxygen. The resulting coordination polyhedron is best described as pentagonal bipyramidal where the nitrosyl and one amine nitrogen occupy the apical positions and the chlorine, η^2-H_2NO^- and two remaining amine nitrogens are in the pentagonal plane. The side-on coordinated H_2NO^- anion displays an N–O bond distance of 1.396(7) Å typical of a single bond. As in many other nitrosyl complexes of the $\{Mo(NO\}^4$ type, the Mo–NO unit is nearly linear (α = 174.4(5)°); the Mo–N_{NO} bond at 1.764(5) Å is short and displays a double bond character. The nitrosyl N–O bond at 1.193(7) Å is also short (double bond).

Figure 3 shows the structure of the monocation $[Mo^{VI}(tacn)(O)_2(MeNHO)]^+$ in crystals of **4**. The molybdenum(VI) ion is also heptacoordinate comprising three amine nitrogens, a side-on coordinated η^2-$MeNHO^-$ anion and two terminal oxo groups in *cis* position to each other. In this case, the resulting coordination polyhedron is described as derived from an octahedron where the sixth coordination site is occupied by a didentate, *N*,*O*-coordinated *N*-methylhydroxylamido ligand. Overall the structure is

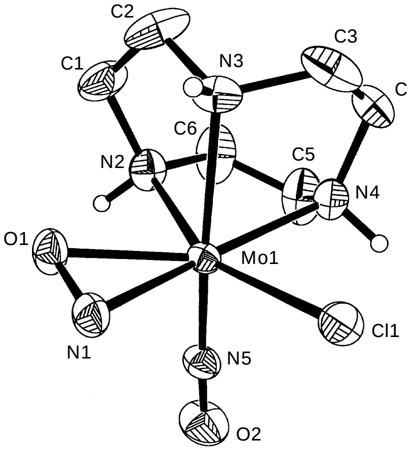


FIG. 2
ORTEP drawing of the monocation in crystals of **3** at the 40% probability level. H-Atoms are omitted

quite similar to that of the six-coordinate complex $[Mo(O)_2(MeNHO)_2]$ reported previously[23].

DISCUSSION

Taking the new synthetic results together with previous work cited in the references we can propose reasonable mechanistic pathways for the different nitrosylation reactions of oxometallates of vanadium(V) and molybdenum(VI) yielding mono- and dinitrosyl complexes of the type $\{M(NO)\}^4$, $\{M(NO)_2\}^6$, and $\{M(NO)_2\}^5$. They are schematically depicted in Scheme 1 (charges omitted).

In the first step, an oxo group (or another labile ligand) of the high-valent metal centre in VO_4^{3-} or MoO_4^{2-} is substituted by a side-on *N,O*-coordinated H_2NO^- ligand. Such (hydroxylamido)V^V and Mo^{VI} complexes were isolated in the past and structurally characterized[2]. It has also been shown that more than one oxo group may be replaced. Such complexes are stable if *N*-monoalkyl- or *N,N*-dialkylhydroxylamines are employed because they are less easily oxidized than the parent hydroxylamine.

The η^2-coordinated hydroxylamido(1–) ligands are weak acids that readily deprotonate with formation of η^2-coordinated HNO^{2-} ligands in aqueous solution (especially in the presence of a base). Two such species have been structurally characterized: [Mo(NO)(terpy)(CN)(HNO)] (ref.[25])

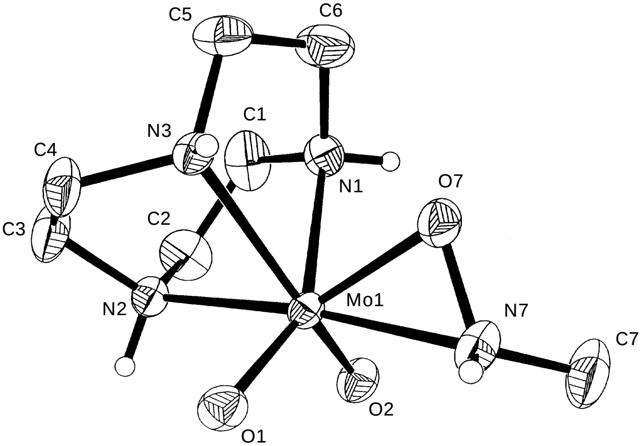
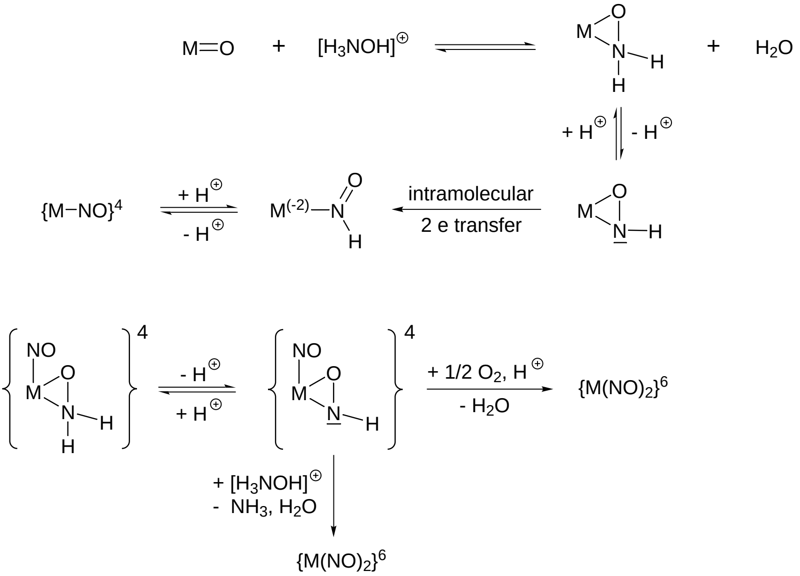


FIG. 3
ORTEP drawing of the monocation in crystals of **4** at the 40% probability level. H-Atoms are omitted

and [Mo(O)(dipic)(ONPh)(hmpt)] (ref.[26]), where hmpt is hexamethylphosphoric triamide and dipic is the dipicolinato dianion.



SCHEME 1

Then the high-valent moiety M(η^2-HNO) (M = V^V, Mo^{VI}) is proposed to undergo an intramolecular two-electron transfer, generating a species containing a two-electron reduced metal ion and an *N*-coordinated HN=O molecule (hyponitrous acid) which is the two-electron-oxidized form of HNO^{2-}. Such a species has also been structurally characterized[27] in $[OsCl_2(CO)(HNO)(PPh_3)_2]$. Simple deprotonation yields then the mononitrosyl complexes $\{M(NO)\}^4$. Thus the overall stoichiometry can be formulated as in Eq. (*5*) in agreement with experiments.

$$MO_4^{n-} + (H_3NOH)^+ \rightarrow \{M(NO)\}^4 + 4\ H_2O \qquad (5)$$

The formation of the dinitrosylmetal complexes $\{M(NO)_2\}^6$ is more complicated because the metal ion in the precursor $\{M(NO)(H_2NO)\}^4$ is in most cases not a strong enough oxidant to bring about the required intramolecular two-electron oxidation of the η^2-coordinated hydroxylamido(2–) ligand. Instead, an external oxidant is now required to perform the oxidative transformation of HNO^{2-} to η^1-coordinated HNO. This oxidant can either be dioxygen or an excess molecule of hydroxylamine. The stoichiometry and products are different in both cases. If dioxygen is the external oxidant (Eq. (*6*)) no ammonia is formed.

$$\{M(NO)\}^4 + H_2NOH + 1/2\ O_2 \rightarrow \{M(NO)_2\}^6 + H_2O \qquad (6)$$

Taking Eqs (*5*) and (*6*) together, we arrive at an overall stoichiometry as in Eq. (*7*).

$$MO_4^{n-} + 2\ H_3NOH^+ + 1/2\ O_2 + 2\ H^+ \rightarrow \{M(NO)_2\}^6 + 5\ H_2O \qquad (7)$$

On the other hand, if hydroxylamine is present in large excess, it may act as a two-electron oxidant. The reduction products are now ammonia and water (Eqs (*8*) and (*9*)).

$$\{M(NO)\}^4 + 2\ H_2NOH \rightarrow \{M(NO)_2\}^6 + NH_3 + H_2O \qquad (8)$$

or

$$MO_4^{n-} + 3\ H_3NOH^+ + H^+ \rightarrow \{M(NO)_2\}^6 + NH_3 + 5\ H_2O \qquad (9)$$

Note that the ratio $\{M(NO)_2\}^6 : NH_3$ is 1 : 1, as observed, but the ratio $MoO_4^{n-} : H_2NOH$ is 1 : 3 in contrast to the aerobic reaction where this ratio is only 1 : 2.

Thus the mechanistic Scheme 1 provides an excellent rationale for the nitrosylation reaction of oxometallates with hydroxylamine.

REFERENCES

1. Enemark J. H., Feltham R. D.: *Coord. Chem. Rev.* **1974**, *13*, 339.
2. Wieghardt K.: *Advances in Inorganic and Bioinorganic Mechanism* (A. G. Sykes, Ed.), Vol. 3, p. 213. Academic Press, London 1984.
3. a) Hartkamp H.: *Z. Anal. Chem.* **1964**, *202*, 13; b) Beneš R., Novák J.: *Collect. Czech. Chem. Commun.* **1971**, *36*, 180; c) Beneš R., Novák J., Šulcek Z.: *Collect. Czech. Chem. Commun.* **1972**, *37*, 1118.
4. Wieghardt K., Quilitzsch U.: *Z. Anorg. Allg. Chem.* **1979**, *457*, 75.
5. Wieghardt K., Quilitzsch U.: *Z. Naturforsch., B* **1981**, *36*, 683.
6. Wieghardt K., Quilitzsch U., Nuber B., Weiss J.: *Angew. Chem.* **1978**, *90*, 381.
7. Sarkar S., Müller A.: *Z. Naturforsch., B* **1978**, *33*, 1053.

8. Wieghardt K., Kleine-Boymann M., Swiridoff W., Nuber B., Weiss J.: *J. Chem. Soc., Dalton Trans*. **1985**, 2493.
9. Nast R., Nyul K., Grziwok E.: *Z. Anorg. Allg. Chem*. **1952**, *267*, 306.
10. Vepřek-Šiška J., Luňák S.: *Collect. Czech. Chem. Commun*. **1972**, *37*, 3846.
11. Vepřek-Šiška J., Luňák S.: *Collect. Czech. Chem. Commun*. **1974**, *39*, 41.
12. Bhattacharyya R., Bhattacharjee G. P.: *J. Chem. Soc., Dalton Trans*. **1983**, 1593.
13. Bhattacharyya R., Roy P. S., Dasmahapatra A. K.: *J. Organomet. Chem*. **1984**, *267*, 293.
14. Wieghardt K., Schmidt W., Nuber B., Weiss J.: *Chem. Ber*. **1979**, *112*, 2220.
15. Schreiber P., Wieghardt K., Nuber B., Weiss J.: *Z. Anorg. Allg. Chem*. **1990**, *587*, 174.
16. Herrmann W., Wieghardt K.: *Polyhedron* **1986**, *5*, 513.
17. Schreiber P., Wieghardt K., Nuber B., Weiss J.: *Z. Naturforsch., B: Chem. Sci*. **1990**, *45*, 619.
18. *ShelXTL V.5*. Siemens Analytical X-Ray Instruments, Inc. 1994.
19. Rehder D., Näumann F.: *Z. Naturforsch., B* **1984**, *39*, 1654.
20. Richter-Addo G. B., Legzdins P.: *Metal Nitrosyls*, p. 66. Oxford University Press, New York, Oxford 1992.
21. Herberhold M., Kremnitz W., Trampisch H., Hitam R. B., Rest A. J., Taylor D. J.: *J. Chem. Soc., Dalton Trans* **1982**, 1261.
22. Wieghardt K., Backes-Dahmann G., Swiridoff W., Weiss J.: *Inorg. Chem*. **1983**, *22*, 1221.
23. Wieghardt K., Holzbach W., Weiss J., Nuber B., Prikner B.: *Angew. Chem*. **1979**, *91*, 583.
24. Müller A., Mohan N.: *Z. Anorg. Allg. Chem*. **1981**, *480*, 157.
25. Wieghardt K., Holzbach W., Weiss J.: *Z. Naturforsch., B* **1982**, *37*, 680.
26. Muccigrosso D. A., Jacobsen S. E., Apgar P. A., Mares F.: *J. Am. Chem. Soc*. **1978**, *100*, 7063.
27. Wilson R. D., Ibers J. A.: *Inorg. Chem*. **1979**, *18*, 336.