triplet in the ^1H NMR spectrum for the Me groups of the phosphine ligands at 1.81 ppm, $J = 9.8$ Hz, no resonances for NMe_2 protons; one single resonance was observed in the $^{31}P\{^1H\}$ NMR spectrum at −1.91 ppm).

The volatile components were identified (by ^1H NMR and GC/mass spectroscopy) to contain, other than benzene-d_6 and PMe_2Ph, Me_2NH and $\overline{CH_2CH_2N}H$.[8]

X-ray Structural Determinations. General operating facilities and listings of programs have been described previously.[9] Crystal data for the two compounds studied in this work are given in Table VII.

$W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$. A suitable sample was cleaved under an inert atmosphere from a larger crystal and transferred to the goniostat. A systematic search of a limited hemisphere of reciprocal space revealed no systematic absences or symmetry, leading to the assignment of a triclinic space group.

The structure was solved by a combination of Patterson and Fourier techniques and refined by full-matrix least squares. All hydrogen atoms were located and refined isotropically. Examination of ψ scans revealed only a 4% fluctuation in intensities, so no absorption correction was performed.

A final difference Fourier was featureless, the largest peak (of intensity 1.1 e/Å^3) lying at the site of W(2).

$W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$. A suitable, well-formed small crystal was selected and transferred to the goniostat, where it was cooled to −158 °C and characterized in the usual manner. The crystal was observed to be monoclinic, and the systematic extinctions identified the space group as $P2_1/c$. A total of 3259 reflections having F_o greater than $3\sigma(F_o)$ were used in the least-squares refinement of the structure.

The W atoms were located by means of direct methods, and the remaining atoms were located by Fourier techniques. All hydrogen atoms were located in a difference Fourier map. All non-hydrogen atoms were refined by full-matrix least squares with anisotropic thermal parameters, while the hydrogen atoms were refined by using isotropic thermal parameters. An absorption correction was carried out, and the corrected data were used for the refinements. The final difference map was essentially featureless, the largest peaks being associated with the W atoms.

Acknowledgment. We thank the National Science Foundation and the Wrubel Computing Center for support.

Registry No. $W_2Cl_2(NMe_2)_4(Me_2PCH_2PMe_2)$, 98481-55-1; $Mo_2Cl_2(NMe_2)_4(Me_2PCH_2PMe_2)$, 98481-56-2; $W_2Cl_2(NMe_2)_4(Me_2PCH_2CH_2PMe_2)$, 98481-57-3; $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$, 97285-93-3; $W_2Cl_3(NMe_2)_3(PMe_3)_2$, 98481-58-4; $Mo_2Cl_3(NMe_2)_3(PMe_3)_2$, 98481-59-5; $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$, 98481-60-8; $Mo_2Cl_4(NMe_2)_2(PMe_2Ph)_2$, 98481-61-9; $W_2Cl_2(NMe_2)_4$, 63301-81-5; $Mo_2Cl_2(NMe_2)_4$, 63301-82-6; $W_2(NMe_2)_6$, 54935-70-5; W, 7440-33-7.

Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, anisotropic thermal parameters, complete bond distances and angles excluding those of H atoms, and F_o and F_c and VERSORT drawings showing the atom-numbering scheme (71 pages). Ordering information is given on any current masthead page. The complete structural reports are available from the Indiana University Chemistry Library in microfiche form only at a cost of $2.50 per copy. For $W_2Cl_3(NMe_2)_3(PMe_2Ph)_2$ and $W_2Cl_4(NMe_2)_2(PMe_2Ph)_2$ request IU MSC Report Nos. 83057 and 83104, respectively.

---

(8) "Registry of Mass Spectral Data"; Wiley: New York, 1974; Vol. 1. Bovey, F. A. "NMR Data Tables for Organic Compounds"; Interscience: New York, 1967; Vol. 1.

(9) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

Contribution from the Lehrstuhl für Anorganische Chemie I,
Ruhr-Universität, D-4630 Bochum, Federal Republic of Germany

Preparation, Characterization, and Electrochemistry of Novel, Air-Stable Nitrosyl Complexes of Molybdenum and Tungsten of the Type $\{M\text{–}NO\}^{6,5,4}$ Containing the Ligand *N,N′,N″*-Trimethyl-1,4,7-triazacyclononane

GABRIELE BACKES-DAHMANN and KARL WIEGHARDT*

Received March 12, 1985

The reaction of $LM(CO)_3$ (L = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane; M = Mo (**1a**), W (**1b**)) with nitric acid yields air- and water-stable complexes $[LM(CO)_2NO]PF_6$ (M = Mo ([**2a**]PF_6), W ([**2b**]PF_6)) that contain a $\{M\text{–}NO\}^6$ group. Halogenation reactions of [**2a**]$^+$ and [**2b**]$^+$ afford a series of cationic complexes $[LM(NO)X_2]^+$ with a $\{M\text{–}NO\}^4$ moiety (M = Mo, X = Cl, Br, I; M = W, X = Br, Cl) that were reduced electrochemically and chemically to give paramagnetic, neutral 17e species $[LM(NO)X_2]$ with a $\{M\text{–}NO\}^5$ structure (M = Mo, X = Br, Cl; M = W, X = Br). $[LMo(NO)Cl_2]PF_6$ reacts with ethanol to yield the air- and water-stable species $[LMo(NO)Cl(OEt)]PF_6$, which was obtained as green crystals. Recrystallization of these green crystals from acetonitrile in the presence of a small amount of water gave blue crystals of identical composition. The tungsten analogue $[LW(NO)Br(OEt)]^+$ has also been obtained as a green Br_3^- salt and a blue PF_6^- salt. Cyclic voltammograms of all complexes with the $\{M\text{–}NO\}^4$ structure exhibit a reversible one-electron reduction to yield the corresponding species with $\{M\text{–}NO\}^5$ structure. Formal redox potentials are reported.

Introduction

The chemistry of neutral nitrosyl complexes of the type $[ML''(CO)_2NO]$ where L″ is η^5-$C_5H_5^-$[1,2] or hydridotris(1-pyrazolyl)borate[3] and M is molybdenum and tungsten has been investigated in depth in the past. Halogenation reactions of these complexes have led to an extensive class of compounds $ML''(NO)X_2$ (X = Cl, Br, I);[3-5] mixed alkoxy halogeno complexes have also been obtained, $ML''(NO)X(OR)$.[5] Two aspects of this chemistry have been intriguing: (i) While the η^5-C_5H_5 complexes are in general extremely oxygen- and moisture-sensitive, the corresponding tris(1-pyrazolyl)borate derivatives have been found to be quite stable in air and many of them do not react with water. (ii) Interestingly and rather unexpectedly, even the alkoxy complexes $Mo[HB(3,5\text{-}Me_2pz)_3]X(NO)(OR)$ (X = Cl,Br,I) do not hydrolyze,[5] in contrast with the behavior of many simple alkoxy complexes of molybdenum in various oxidation states.

We have recently investigated the chemistry of the small macrocycle, 1,4,7-triazacyclononane ([9]aneN_3) with chromium, molybdenum, and tungsten in low oxidation states and reported the preparation of air- and moisture-stable carbonyl and cationic

---

(1) Fischer, E. O.; Beckert, O.; Hafner, W.; Stahl, H. O. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1955**, *10B*, 598.

(2) Brunner, H. *J. Organomet. Chem.* **1969**, *16*, 119.

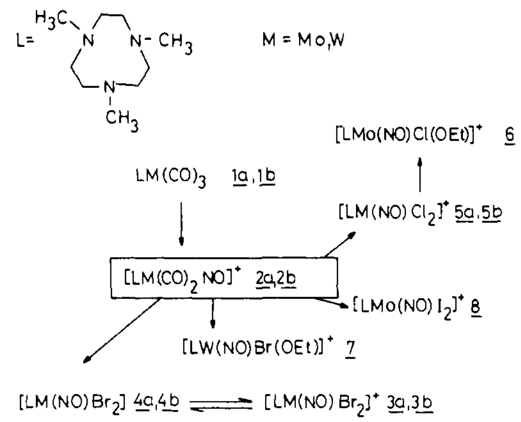
(3) (a) Trofimenko, S. *Inorg. Chem.* **1969**, *8*, 2675. (b) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17. (c) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497.

(4) (a) McCleverty, J. A.; Seddon, D. *J. Chem. Soc., Dalton Trans.* **1972**, 2526. (b) James, T. A.; McCleverty, J. A. *J. Chem. Soc. A* **1971**, 1068, 1596.

(5) McCleverty, J. A.; Seddon, D.; Bailey, N. A.; Walker, N. W. *J. Chem. Soc. Dalton Trans.* **1976**, 898.

0020-1669/85/1324-4044$01.50/0 © 1985 American Chemical Society

Scheme I



nitrosyl complexes, e.g. $[(9]\mathrm{aneN_3})\mathrm{M(NO)(CO)_2}]^+$, via nitrosylation of $[(9]\mathrm{aneN_3})\mathrm{M(CO)_3}$ with nitric acid.[6] In this work we have pointed out the similarities of the cyclic triamine- and hydridotris(1-pyrazolyl)borate-containing complexes. We here report the preparation and spectroscopic characterization of nitrosyl complexes of molybdenum and tungsten with the ligand *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L).[7] This ligand coordinates facially to a metal center in an octahedral environment and is sterically more demanding than 1,4,7-triazacyclononane.

In general, the presence of the methyl groups prevents the formation of dimeric species with two edge-sharing octahedra.[8] Thus we have prepared cationic complexes of the type $\{\mathrm{M{-}NO}\}^6$ according to Enemark's and Feltham's nomenclature,[9] $[\mathrm{LM(NO)(CO)_2}]^+$. Halogenation reactions of these complexes give air-stable $[\mathrm{LM(NO)X_2}]^+$ (X = Cl, Br, I) complexes of the type $\{\mathrm{M{-}NO}\}^4$, which can be reduced chemically or electrochemically to yield paramagnetic, neutral $\mathrm{LM(NO)X_2}$ complexes of the type $\{\mathrm{M{-}NO}\}^5$. Blue and green crystalline samples of the ethoxy complexes $[\mathrm{MoL(NO)Cl(OEt)}]\mathrm{PF_6}$ and $[\mathrm{WL(NO)Br(OEt)}]\mathrm{PF_6}$ have also been prepared. They are air- and moisture-stable complexes. The blue and green forms are believed to represent further examples of distortional isomerism.[10,11] The complexes described in this work are summarized in Scheme I.

Experimental Section

The ligand *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L) was prepared as described previously.[7] The preparation of $\mathrm{LMo(CO)_3}$ (**1a**) from $\mathrm{Mo(CO)_6}$ and L has been described.[6] A table of elemental analyses of all new complexes is available as supplementary material.

$\mathrm{LW(CO)_3}$ (1b). A suspension of $\mathrm{W(CO)_6}$ (3.6 g, 10 mmol) in dimethylformamide (DMF, 100 mL) and an 1 M solution of the ligand *N,N′,N″*-trimethyl-1,4,7-triazacyclononane in benzene (10 mL) were refluxed for 14 h under an argon atmosphere. At the beginning of the experiment a clear yellow solution was obtained from which yellow microcrystals precipitated after 10 h, which were filtered off after the mixture was cooled (0 °C) for 24 h, washed with ethanol and ether, and air-dried. The crystals were recrystallized from acetone or acetonitrile (yield 3.5 g).

$[\mathrm{LMo(CO)_2NO}]\mathrm{PF_6}$ ([2a]$\mathrm{PF_6}$). A suspension of **1a** (0.36 g, 1 mmol) in 0.5 M nitric acid (25 mL) was stirred at room temperature for 5 h. To the clear yellow-orange solution was added a saturated aqueous solution of $\mathrm{NaPF_6}$ (5 mL). Yellow crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried. The crystals were recrystallized from hot methanol (yield 0.3 g).

$[\mathrm{LW(CO)_2NO}]\mathrm{PF_6}$ ([2b]$\mathrm{PF_6}$). [**2b**]$\mathrm{PF_6}$ was prepared in the same manner as [**2a**]$\mathrm{PF_6}$ by using 1 M $\mathrm{HNO_3}$ (30 mL) (yield 0.34 g).

$[\mathrm{LMo(NO)Br_2}]\mathrm{PF_6}$ ([3a]$\mathrm{PF_6}$). Method 1. To a suspension of **1a** (0.36 g, 1 mmol) in 0.1 M HBr was added sodium nitrite (0.2 g, 29 mmol) in small amounts with stirring. The solution was stirred at room temperature for 2.5 h ($\mathrm{Br_2}$ effervescence!) and an orange precipitate of [**3a**]($\mathrm{Br_3}$) was filtered off, which was converted to the hexafluorophosphate salt. [**3a**]($\mathrm{Br_3}$) (0.35 g, 0.5 mmol) was dissolved with gentle warming in an 1:1 mixture of acetone and water (20 mL). After a saturated aqueous solution of $\mathrm{NaPF_6}$ (5 mL) was added and the mixture cooled (0 °C) for 24 h, orange crystals of [**3a**]$\mathrm{PF_6}$ were filtered off (yield 0.25 g).

Method 2. A suspension of [**2a**]$\mathrm{PF_6}$ (0.4 g, 0.8 mmol) in $\mathrm{CCl_4}$ (20 mL) and bromine (0.4 g, 2.6 mmol) was refluxed for 24 h, after which time orange microcrystals of [**3a**]($\mathrm{Br_3}$) were filtered off and converted to the $\mathrm{PF_6}^-$ salt as described above.

$[\mathrm{LW(NO)Br_2}]\mathrm{PF_6}$ ([3b]$\mathrm{PF_6}$). A suspension of **1b** (0.44 g, 1 mmol) in 3 M HBr (20 mL) was stirred at room temperature for 30 min, and $\mathrm{NaNO_2}$ (0.69 g, 10 mmol) was added in small amounts. After the mixture was continuously stirred for 2 h, an orange precipitate of [**3b**]($\mathrm{Br_3}$) had formed, which was filtered off, washed with ethanol and ether, and air-dried. This material was converted to the hexafluorophosphate by dissolving [**3b**]($\mathrm{Br_3}$) (0.39 g, 0.5 mmol) in an acetone/water mixture (3:1) (40 mL) and adding a saturated, aqueous solution of $\mathrm{NaPF_6}$ (5 mL). After the mixture was allowed to stand for 24 h at 22 °C in an open vessel and cooled to 0 °C for a further 24 h, orange crystals were filtered off, washed with ethanol and ether, and air-dried (yield 0.2 g).

$\mathrm{LMo(NO)Br_2}$ (4a). A solution of bromine (0.2 g, 1.3 mmol) in deoxygenated $\mathrm{CHCl_3}$ (10 mL) and [**2a**]$\mathrm{PF_6}$ (0.32 g, 0.65 mmol) was refluxed for 16 h under an argon atmosphere. The green precipitate formed was filtered off, washed rapidly with ethanol and ether, and air-dried. This material was recrystallized from an acetonitrile/water mixture (1:1) to give red-green, dichroic crystals of **4a** (yield 0.15 g).

$\mathrm{LW(NO)Br_2}$ (4b). [**3b**]($\mathrm{Br_3}$) (0.26 g, 0.33 mmol) in deoxygenated *N,N*-dimethylhydrazine was stirred for 4 h under an argon atmosphere at room temperature. After this solution was refluxed for 15 min and cooled to 0 °C for 24 h a red-brown precipitate was filtered off, washed with ethanol and ether, and air-dried (yield 0.1 g).

$[\mathrm{LMo(NO)Cl_2}]\mathrm{PF_6}$ ([5a]$\mathrm{PF_6}$). Method 1. To a suspension of **1a** (0.3 g, 1 mmol) in 5 M HCl (15 mL) was added sodium nitrite (0.1 g, 14.3 mmol) in small amounts with stirring. The solution was stirred for 2.5 h at room temperature, yielding a clear orange solution to which a saturated aqueous solution of $\mathrm{NaPF_6}$ (5 mL) was added. Orange microcrystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried. Recrystallization from an acetonitrile/water mixture (1:1) (yield 0.23 g).

Method 2. [**2a**]$\mathrm{PF_6}$ (0.25 g, 0.5 mmol) suspended in $\mathrm{CHCl_3}$ (20 mL) was treated with chlorine gas for 15 min at room temperature. To the clear yellow-orange solution was added a saturated aqueous solution of $\mathrm{NaPF_6}$. Orange crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried (yield 0.18 g).

$[\mathrm{LW(NO)Cl_2}](\mathrm{PF_6})$ ([5b]$\mathrm{PF_6}$). A suspension of [**2b**]$\mathrm{PF_6}$ (0.3 g, 0.5 mmol) in 3 M HCl (15 mL) was stirred for 2 h at room temperature. Addition of sodium nitrite (0.4 g, 5.8 mmol), stirring for 60 min, and then warming to 50 °C for 30 min yielded a clear yellow solution, which was cooled to 0 °C for 24 h. A yellow precipitate was filtered off, washed with ethanol and ether, and air-dried (yield 0.2 g).

$[\mathrm{LMo(NO)Cl(OEt)}]\mathrm{PF_6}$ ([6]$\mathrm{PF_6}$) (Green). A suspension of [**5a**]$\mathrm{PF_6}$ (0.26 g, 0.5 mmol) in deoxygenated ethanol (20 mL) was refluxed for 4 h under an argon atmosphere. A green solution was obtained that contained a small amount of a greenish blue solid material, which was filtered off and discarded. To the green filtrate was added a saturated aqueous solution of $\mathrm{NaPF_6}$ (5 mL). This solution was allowed to stand at 0°C for 24 h, after which time green crystals were filtered off, washed with ethanol and ether, and air-dried (yield 0.15 g).

$[\mathrm{LMo(NO)Cl(OEt)}]\mathrm{PF_6}$ ([6]$\mathrm{PF_6}$) (Blue). Recrystallization of green [**6**]$\mathrm{PF_6}$ from a acetonitrile/water mixture (1:1) yielded blue [**6**]$\mathrm{PF_6}$. Blue [**6**]$\mathrm{PF_6}$ was also obtained when the above green filtrate was treated with an aqueous solution of $\mathrm{NaPF_6}$ (0.3 g) (15 mL). This solution was allowed to stand at room temperature in an open vessel for 3 days. Blue [**6**]$\mathrm{PF_6}$ precipitated.

$[\mathrm{LW(NO)Br(OEt)}](\mathrm{Br_3})$ ([7]($\mathrm{Br_3}$)) (Green). To a deoxygenated solution of [**2b**]$\mathrm{PF_6}$ (0.4 g, 0.7 mmol) in $\mathrm{CHBr_3}$ (20 mL), which contained 1.5% ethanol as stabilizer, was added a deoxygenated solution of bromine (0.26 g, 1.6 mmol) in $\mathrm{CHBr_3}$ (10 mL) dropwise. This solution was stirred under an argon atmosphere for 15 h at room temperature, affording a clear green solution from which upon addition of ether (50 mL) a green precipitate of [**7**]($\mathrm{Br_3}$) was obtained, which was filtered off, washed with ethanol and ether, and air-dried (yield 0.3 g).

$[\mathrm{LW(NO)Br(OEt)}]X$ ([7]X) (Blue) ($X = \mathrm{PF_6}^-$, $\mathrm{ClO_4}^-$). To a green solution of [**7**]($\mathrm{Br_3}$) (0.37 g, 0.5 mmol) in acetonitrile (10 mL) was added water (5 mL), whereupon the color changed immediately to blue. Ad-

---

[6] Chaudhuri, P.; Wieghardt, K.; Tsay, Y. H.; Krüger, C. *Inorg. Chem.* **1984**, *23*, 427.

[7] Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 3086.

[8] Backes-Dahmann, G.; Herrmann, W.; Wieghardt, K.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 485.

[9] Enemark, J. H.; Feltham, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 5002.

[10] (a) Butcher, A. V.; Chatt, J. *J. Chem. Soc. A* **1970**, 2652. (b) Chatt, J.; Manojlović-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1971**, 655.

[11] Wieghardt, K.; Backes-Dahmann, G.; Holzbach, W.; Swiridoff, W. J.; Weiss, J. *Z. Anorg. Allg. Chem.* **1983**, *499*, 44.

Table I. Spectroscopic and Magnetic Properties of Complexes

		IR, cm^{-1}			
complex[a]	color	ν(CO)	ν(NO)	electronic spectrum[b] λ, nm (ϵ, L mol^{-1} cm^{-1})	μ_{eff}(298 K), μ_B
[**2a**]PF_6	yellow	2010, 1920	1665	not measured	diamagnetic
[**2b**]PF_6	orange	1995, 1900	1655	not measured	diamagnetic
[**3a**]PF_6	orange		1700	425 (391)	diamagnetic
[**3b**]PF_6	orange		1660	352 (1.6 × 10^3)	diamagnetic
4a	red-green[c]		1565	417 (173), 617 (17)	1.83
4b	red-brown		1545	418 (200)	1.82 (93 K)-2.6 (298 K)
[**5a**]PF_6	orange		1695	421 (457), 448 (430)	diamagnetic
[**5b**]PF_6	orange		1640	386 (120)	diamagnetic
[**6**]PF_6	green		1660	440 (450), 651 (32)	diamagnetic
[**6**]PF_6	blue		1665	420 (460), 624 (34)	diamagnetic
[**7**](Br_3)	green		1615	641 (50)	diamagnetic
[**7**](PF_6)	blue		1625	601 (55)	diamagnetic
[**8**](PF_6)	green		1710	298 (3.2 × 10^3), 650 (997)	diamagnetic

[a] **a** denotes the molybdenum, and **b** denotes the tungsten species. [b] Measured in MeCN. [c] Dichroic crystals.

dition of a saturated, aqueous solution of $NaPF_6$ or $NaClO_4$ and cooling to 0 °C for 24 h initiated the precipitation of blue crystals of [**7**]PF_6 or [**7**]ClO_4, respectively, which were filtered off, washed with ethanol and ether, and air-dried (yield 0.22 g). *Caution*! Perchlorates are potentially hazardous; they may explode upon heating.

[LMo(NO)I_2]PF_6 ([8]PF_6). A suspension of [**2a**]PF_6 (0.25 g, 0.5 mmol) in concentrated HI (15 mL) was stirred in the presence of air for 4 h at room temperature. After the water (10 mL) was added to the mixture and it was cooled to 0 °C for 2 h, an orange-brown precipitate formed, which was filtered off, washed with ether, and air-dried. This carbonyl-containing material was suspended in water (10 mL) and concentrated HNO_3 was added dropwise until a clear yellow-green solution was obtained to which $NaPF_6$ solution (5 mL) was added. Green-black crystals formed, which were filtered off (yield 0.12 g).

Instrumentation. The magnetic susceptibilities of powdered samples were measured by the Faraday method (Sartorius microbalance, Bruker B-E 10 C8 research magnet, and Bruker B-VT 1000 automatic temperature control) between 98 and 298 K. Diamagnetic corrections have been applied.

Infrared spectra of solid samples (KBr disks) were recorded on a Beckmann Acculab 10(B) instrument in the range 350–4000 cm^{-1}.

Electronic spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer (200–1500 nm). The apparatus used for electrochemical measurements has been described previously.[8]

Mass-spectra were recorded on a Finnigan MAT CH-5 instrument with a direct inlet (70 eV, 250 °C).

^1H NMR spectra were measured on a Bruker HFX 90 spectrometer with Me_4Si as internal standard.

Results and Discussion

Syntheses of Complexes. The synthesis of **1a** has been described previously.[8] **1b** was obtained similarly from $W(CO)_6$ and the cyclic triamine in dimethylformamide (DMF) as air-stable, bright yellow crystals in good yield. The ν(CO) stretching frequencies observed in the infrared spectrum are consistent with the C_{3v} local symmetry of *fac*-$LW(CO)_3$ (Table I). **1a** and **1b** react with nitric acid at room temperature to yield clear, orange solutions from which upon addition of $NaPF_6$ [**2a**]PF_6 and [**2b**]PF_6 were precipitated as orange crystals containing cationic $[LM(CO)_2NO]^+$ species. These compounds are air-stable both in solution (DMF, MeCN, ethanol, and water) and in the solid state and compare favorably in this respect (except for their solubility in water) with the neutral complexes $[HB(pz)_3]M(CO)_2NO$[3a] and $[HB(3,5\text{-}(CH_3)_2pz)_3]M(CO)_2NO$[3] ($HB(pz)_3^-$ = hydridotris(1-pyrazolyl)borate; $HB(3,5\text{-}(CH_3)_2pz)_3$ = hydridotris(3,5-dimethyl-1-pyrazolyl)borate; M = Mo, W). These complexes are diamagnetic 18e species of the type $\{M\text{-}NO\}^6$ according to Enemark and Feltham,[9] with the metal centers in an octahedral environment of a facility coordinated N-donor ligand, two carbonyls, and a nitrosyl. ν(CO) and ν(NO) stretching frequencies of [**2a**]PF_6 and [**2b**]PF_6 (Table I) are very similar to those observed for the corresponding tris(1-pyrazolyl)borate derivatives.[3]

Complexes [2a]PF_6 and [2b]PF_6 are useful starting materials for halogenation reactions with chlorine or bromine, yielding cationic complexes of the type $[LM(NO)X_2]^+$ (M = Mo, X = Cl ([**5a**]$^+$), Br ([**3a**]$^+$); M = W, X = Cl ([**5b**]$^+$), Br ([**3b**]$^+$)). Complexes [3a]PF_6 and [3b]PF_6 were also obtained when **1a** and **1b** reacted with nitrous acid as nitrosylating agent in HBr ([**5a**]$^+$ and [**5b**]$^+$ were obtained in HCl). The diiodomolybdenum complex [**8**]$^+$, formed in concentrated HI solutions of [**2a**]PF_6 in the presence of air. These complexes are all diamagnetic species of the type $\{M\text{-}NO\}^4$ (16e complexes). The ν(NO) stretching frequencies in the series $[LMo(NO)X_2]PF_6$ decrease in the order I > Br > Cl, and in $[LW(NO)X_2]^+$ (X = Cl, Br) the ν(NO) is also shifted to a higher wavenumber in going from the chloro to the bromo complex. Furthermore, the ν(NO) of molybdenum complexes are observed at greater wavenumbers than those of the corresponding tungsten analogues. Interestingly, ν(NO) values of tripyrazolylborate complexes, $[HB(Me_2pz)_3]M(NO)X_2$ (M = Mo, W; X = Cl, Br, I),[5] as well as of $[(\eta^5\text{-}C_5H_5)M(NO)X_2]_2$ complexes[4a] were found to be insensitive to X, which has been explained by an interplay of steric interactions between X and the tripyrazolylborate ligand and electronic factors, e.g. electronegativity of X.[5] On the other hand, in monomeric $(\eta^5\text{-}C_5H_5)Mo(NO)X_2Y$ complexes (X = Cl, Br, I; Y = pyridine, triphenylphosphine) ν(NO) decreases with increasing electronegativity of X.[4a]

The chemical reduction of [**3b**](Br_3) in *N,N*-dimethylhydrazine affords red-brown **4b**, a paramagnetic, neutral complex of type $\{W\text{-}NO\}^5$, a 17e species. The mass spectrum exhibits the correct molecular ion peak at *m/z* 546. **4b** is stable in air in the solid state for months; it is soluble in DMF or acetone but insoluble in water. In solution **4b** is rapidly oxidized by oxygen to give [**3b**]$^+$. The magnetic moment of **4b** is slightly temperature dependent, ranging from 1.83 μ_B at 98 K to 2.6 μ_B at 298 K. In the infrared spectrum of **4b** the ν(NO) stretching frequency is observed at 1545 cm^{-1}, which represents a significant shift to lower wavenumbers as compared to that of [**3b**]PF_6. This indicates a substantially increased π-back-bonding in **4b**. The 1e reduction of [**3b**]$^+$ to **4b** may also be accomplished electrochemically (see below).

Interestingly, the oxidation of [**2a**]PF_6 in CH_2Cl_2 with bromine under argon also affords a 17e species of the type $\{M\text{-}NO\}^5$, complex **4a**. Solutions of **4a** in MeCN, DMF, or methanol are green, but red solutions are obtained in $MeCN/H_2O$ or methanol/H_2O mixtures. From these solutions **4a** was grown as red-green, dichroic crystals. **4a** is stable both in solution and in the solid state; it does not react with oxygen. From magnetic measurements a temperature-independent (98–298 K) moment of 1.83 μ_B has been deduced indicating one unpaired electron. In the mass spectrum of **4a** a molecular ion peak at *m/z* 457 is in agreement with a monomeric structure of **4a**. A single-crystal diffraction study of **4a** was severely hampered by a statistical disorder of the nitrosyl group but confirmed the monomeric nature of **4a**.[12] In the infrared spectrum of **4a** ν(NO) is observed at 1565 cm^{-1}, which is again significantly shifted to lower wavenumbers as compared

---

(12) **4a** crystallizes in the orthorhombic space group *Pcmn*, with *a* = 7.414 (2) Å, *b* = 12.707 (7) Å, *c* = 16.086 (5) Å, *V* = 1515.5 $Å^3$, and *Z* = 4. The structure was refined to a conventional *R* value of 0.075 for 1461 unique reflections (Nuber, B.; Weiss, J.; Universität Heidelberg, unpublished results).

Table II. Formal Redox Potentials of Complexes at 25 °C

couple	$E_{1/2}$,[a] V	ΔE_p,[b] mV	cf,[c] $\mu A\ V^{-1/2}\ s^{1/2}\ mmol^{-1}\ L$	$I_{p,red}/I_{p,ox}$
$[\mathbf{3a}]^+/\mathbf{4a}$	0.10	65	54	0.93
	−2.38	irr	33	
$[\mathbf{3b}]^+/\mathbf{4b}$[d]	−0.38	75	50	0.94
	−1.28	irr	65	
$[\mathbf{5a}]^+/LMo(NO)Cl_2$	−0.06	65	58	0.94
$[\mathbf{5b}]^+/LW(NO)Cl_2$	−0.535	70	30	0.98
	−1.45	irr	43	
[**6**] (green)/LMo(NO)Cl(OEt)	−0.83	75	46	1.1
$[\mathbf{6}]^+$ (blue)/LMo(NO)Cl(OEt)	−0.88	70	42	1.1
$[\mathbf{7}]^+$ (green)/LW(NO)Br(OEt)	−1.34	75	46	0.85
$[\mathbf{7}]^+$ (blue)/LW(NO)Br(OEt)	−1.33	75	45	0.9

[a] Formal redox potential vs. ferrocenium (Fc^+)/ferrocene (Fc) measured in DMF with 0.1 M $[TBA]PF_6$ as supporting electrolyte. [b] Peak potential difference at scan rate of 50 mV s^{-1}; irr = irreversible. [c] Current function of reduction peak. [d] Measured in acetonitrile.

to that of $[\mathbf{2a}]PF_6$. The electrochemical generation of an unstable $\{Mo\text{–}NO\}^5$ type complex in solution with a hydridotris(3,5-dimethylpyrazolyl)borate ligand has recently been reported.[13] An air-stable cationic $\{Mo\text{-}NO\}^5$ complex $[Mo(HB(3,5\text{-}Me_2pz)_3)(NO)(pyrollide)_2]^+$ has also been prepared and characterized by X-ray crystallography.[14]

The following section describes a substitution reaction of $[\mathbf{5a}]PF_6$. This complex reacts in ethanol under an argon atmosphere to give a *green* solid, $[\mathbf{6}]PF_6$ (green); it contains a coordinated ethoxy group and is stable in the solid state in air for months. In MeCN it is soluble, affording a green solution. Water causes a color change to blue. Upon addition of $NaPF_6$, *blue* crystals of $[\mathbf{6}]PF_6$ precipitate. $[\mathbf{6}]PF_6$ (blue) is also stable in the solid state for months. The blue material yields when redissolved in H_2O-free MeCN a blue solution, from which $[\mathbf{6}]PF_6$ (blue) may be crystallized. In the infrared spectra of the green and blue forms $\nu(NO)$ stretching frequencies at 1660 and 1665 cm^{-1} are observed. In addition a band at 1050 cm^{-1} ($\nu(C\text{–}O)$) is observed in the spectrum of both species. Both species are diamagnetic 16e complexes of the type $\{Mo\text{–}NO\}^4$. The blue and green solution ^1H NMR spectra of $[\mathbf{6}]^+$ (green) and $[\mathbf{6}]^+$ (blue) are identical.

Interestingly, the reaction of $[\mathbf{2b}]PF_6$ with bromine in $CHBr_3$, which contains 1.5% ethanol as stabilizer, under an argon atmosphere yields a green product that analyzes as $[\mathbf{7}](Br_3)$. It is soluble in MeCN with a green color, addition of traces of water initiate immediately a color change to blue. From such solutions blue $[\mathbf{7}]PF_6$ was precipitated upon addition of $NaPF_6$. $[\mathbf{7}]PF_6$ (blue) is soluble in MeCN, affording blue solutions. The electronic spectra of both forms are slightly different (Table I). In the infrared spectrum of $[\mathbf{7}](Br_3)$ (green) and $[\mathbf{7}]PF_6$ (blue) the $\nu(NO)$ stretching frequencies are observed at 1615 and 1625 cm^{-1}, respectively, and a $\nu(C\text{-}O)$ band is seen at 1050 cm^{-1}. Both species are diamagnetic, 16e complexes of the type $\{W\text{-}NO\}^4$.

During the last 20 years a number of molybdenum complexes have been described that were obtained in the solid state as blue and green crystals. Chatt et al. have demonstrated for *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ by X-ray crystallography that the blue and green crystals contain neutral species of essentially identical geometry but with significantly different Mo═O bond lengths.[10,15,16] Wilkinson et al. have recently prepared blue and green forms of $MoOCl_2(PMe_3)_3$.[17] Salts of the complexes $[MoO(CN)_5]^{3-}$ and $[MoO(CN)_4(H_2O)]^{2-}$ have also been obtained as blue and green crystals, respectively. Again the most significant difference was found by X-ray crystallography to be the Mo═O bond lengths.

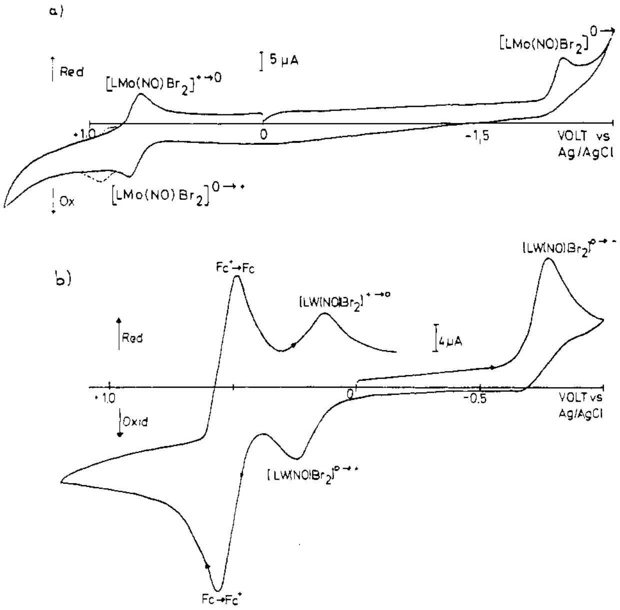


Figure 1. Cyclic voltammograms of (a) $LMo(NO)Br_2$ and (b) $[LW(NO)Br_2]PF_6$ in DMF at 25 °C (0.1 M $[TBA]PF_6$ supporting electrolyte, Pt-button electrode, scan rate 100 mV s^{-1}). The broken line indicates new peaks after several repetitive scans.

This interplay of green ↔ blue species has also been noted for $Mo[HB(Me_2pz)_3(NO)Br(OEt)]$ where a green and a blue crystalline solid have been isolated, but no explanation for this effect has been offered.[5] The latter example is completely analogous to our complexes $[\mathbf{6}]PF_6$ and $[\mathbf{7}]PF_6$. It is conceivable that in these cases distortional isomerism also is encountered (most probably the Mo–OEt bond lengths are different). At present this conclusion is admittedly speculative; we are attempting X-ray diffraction studies of these complexes.

Electrochemistry. Electrochemical data of complexes are summarized in Table II. The cyclic voltammograms of the neutral 17e species **4a** and **4b** exhibit a reversible and an irreversible one-electron-transfer process in the potential range −1.8 to +1.5 V vs. Ag/AgCl, respectively. Identical cyclic voltammograms were obtained when complexes $[\mathbf{3a}]PF_6$ and $[\mathbf{3b}]PF_6$ were dissolved in DMF or MeCN with $[TBA]PF_6$ as supporting electrolyte. Figure 1 displays the cyclic voltammogram of **4a** in DMF. Repetitive scans between +1.5 and −0.4 V vs. Ag/AgCl do not change the positions of the respective reduction and oxidation peaks of the reversible electron-transfer process, whereas after a few scans over the full range +1.5 to −1.8 V, new peaks are generated at quite positive potentials, indicating the formation of new species after the irreversible reduction at very negative potentials. Thus the electrochemistry is described by eq 1. The first reversible

$$\underset{\{M\text{–}NO\}^4}{[LM(NO)Br_2]^+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} \underset{\{M\text{–}NO\}^5}{LM(NO)Br_2} \xrightarrow{+e^-} \underset{\substack{\{M\text{–}NO\}^6 \\ \text{(rapid dec)}}}{[LM(NO)Br_2]^-} \quad (1)$$

---

(13) McCleverty, J. A.; El-Murr, N. *J. Chem. Soc., Chem. Commun.* **1981**, 960.
(14) Obaidi, N. A.; Brown, K. P.; Edwards, A. J.; Hollins, S. A.; Jones, C. J.; McCleverty, J. A.; Neaves, B. D. *J. Chem. Soc., Chem. Commun.* **1984**, 690.
(15) Manojlović-Muir, L.; Muir, K. W.; *J. Chem. Soc., Dalton Trans.* **1972**, 686.
(16) Haymore, B. L.; Goddard, W. A., III; Allison, J. N. In "Abstracts of Papers", International Conference on Coordination Chemistry, Boulder, CO; Cooperative Institute of Research in Environmental Sciences, University of Colorado: Boulder, CO, 1984; p 535.
(17) Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347.

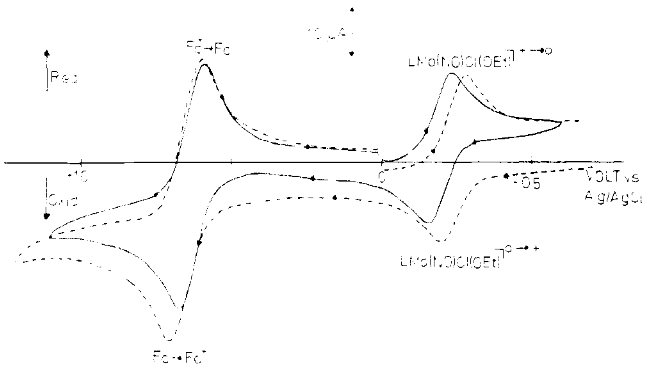


Figure 2. Cyclic voltammogram of green (—) and blue (--) forms of [LMo(NO)Cl(OEt)]PF$_6$ in DMF at 25 °C (0.1 M [TBA]PF$_6$, Pt-button electrode, ferrocene internal standard, scan rate 100 mV s^{-1}).

oxidation–reduction process of **3a** or **4a** has also been achieved chemically (eq 2). The formal reduction potential for the re-

$$\mathrm{LMo(NO)Br_2} \underset{\mathrm{C_2H_5OH}}{\overset{\mathrm{HNO_3}}{\rightleftharpoons}} [\mathrm{LMo(NO)Br_2}]^+ \qquad (2)$$

versible process of the tungsten complex is shifted to a more negative potential by 480 mV as compared to that for the molybdenum analogue. This behavior is considered to be normal for analogous species of tungsten and molybdenum. The remarkably easy one-electron reduction of a 16e molybdenum nitrosyl to yield a {Mo–NO}^{5} species has also been observed for Mo[HB(3,5-Me$_2$pz)$_3$](NO)I$_2$, which again is irreversibly reduced at very negative potentials to the {Mo–NO}^{6} species.[13]

Cyclic voltammograms of [**5a**]PF$_6$ and [**5b**]PF$_6$ in DMF (0.1 M [TBA]PF$_6$ supporting electrolyte) exhibit one reversible one-electron-transfer process (eq 3)

$$\begin{array}{ccc} [\mathrm{LM(NO)Cl_2}]^+ & \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} & \mathrm{LM(NO)Cl_2} \\ \{\mathrm{M{-}NO}\}^4 & & \{\mathrm{M{-}NO}\}^5 \end{array} \qquad (3)$$

$$\mathrm{M = Mo, W}$$

The formal redox potential of [**5b**]PF$_6$ as compared to that of [**5b**]PF$_6$ is again shifted to a more negative potential (475 mV). The chloro complexes [**5a**]PF$_6$ and [**5b**]PF$_6$ are reduced at more negative potentials as compared to their bromo analogues [**3a**]PF$_6$ and [**3b**]PF$_6$ (ΔE = 160 mV). Attempts to reduce [**5a**]PF$_6$ in *N,N*-dimethylhydrazine were met with only partial success. A red-violet solid material was obtained, which was always contaminated with PF$_6^-$ as judged from its infrared spectrum. The ν(NO) stretching frequency was observed at 1575 cm^{-1}, which is significantly lower than in the parent complex [**5a**]PF$_6$. We have not been able to prepare an analytically pure sample.

The cyclic voltammograms of [**6**]PF$_6$ (green) and [**6**]PF$_6$ (blue) in DMF (0.1 M [TBA]PF$_6$) in the potential range −1.7 to +1.5 V vs. Ag/AgCl both show a well-defined reversible one-electron-transfer process (Figure 2), which is described in eq 4.

$$\begin{array}{ccc} [\mathrm{LMo(NO)Cl(OEt)}]^+ & \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} & \mathrm{LMo(NO)Cl(OEt)} \\ \{\mathrm{Mo{-}NO}\}^4 & & \{\mathrm{M{-}NO}\}^5 \end{array} \qquad (4)$$

Interestingly, the formal redox potentials of the blue and green species do not differ greatly (50 mV), but it is noted that substitution of one chloro ligand in [**5a**]PF$_6$ by an ethoxy group, [**6**]PF$_6$ (blue), causes a dramatic shift of 820 mV to more negative potentials. This indicates a substantial stabilization of the {Mo–NO}^{4} oxidation state in [**6**]PF$_6$. McCleverty et al.[5] have reported a short Mo–O bond (1.86 Å) of a coordinated methoxy group in Mo[HB(3,5-Me$_2$pz)$_3$](NO)Cl(OMe) arising from p$_\pi$–d$_\pi$ donation from O to the coordinatively unsaturated Mo atom. This effect may also prevail in the present case and may explain also the pronounced stability of the Mo–ethoxy bond toward hydrolysis, which is rather unusual for Mo–alkoxy bonds.

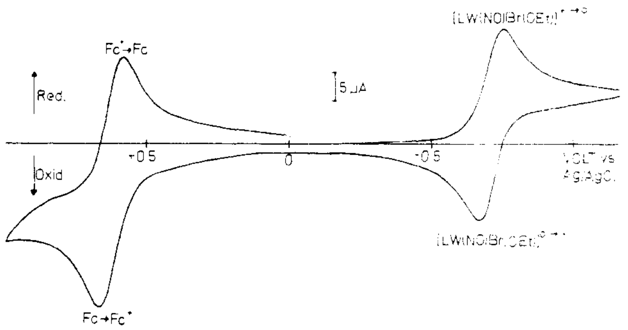


Figure 3. Cyclic voltammogram of blue [LW(NO)Br(OEt)]PF$_6$ in DMF at 25 °C (0.1 M [TBA]PF$_6$, Pt-button electrode, ferrocene internal standard, scan rate 100 mV s^{-1}).

Table III. 90-MHz ^{1}H NMR Spectral Data[a]

complex	δ	assignt
1a	2.8 (m, 12 H)	CH$_2$
	2.97 (s, 9 H)	CH$_3$
[**2a**]PF$_6$	2.75 (s, 3 H)	CH$_3$
	3.10 (s, 12 H)	CH$_2$
	3.20 (s, 6 H)	CH$_3$
[**3a**]PF$_6$	3.15 (s, 3 H)	CH$_3$
	3.20 (m, 12 H)	CH$_2$
	3.32 (s, 6 H)	CH$_3$
[**6**]PF$_6$	1.50 (t, 3 H)	CH$_3$ (J_{HH} = 7.0 Hz)
	2.72 (s, 3 H)	CH$_3$
	3.03 3.12 3.18 (m, 12 H)	CH$_2$
	3.42 (s, 6 H)	CH$_3$
	5.65 (m, 2 H)	CH$_2$
1b	2.8 (m, 12 H)	CH$_2$
	3.1 (s, 9 H)	CH$_3$
[**2b**]PF$_6$	2.85 (s, 3 H)	CH$_3$
	3.18 (s, 12 H)	CH$_2$
	3.30 (s, 6 H)	CH$_3$
[**7**]PF$_6$	1.4 (t, 3 H)	CH$_3$ (J_{HH} = 7.0 Hz)
	2.9 (s, 3 H)	CH$_3$
	3.1 3.2 3.3 (m, 12 H)	CH$_2$
	3.65 (s, 6 H)	CH$_3$
	5.5 (m, 2 H)	CH$_2$

[a] Measured in CD$_3$CN with Me$_4$Si as internal standard at ambient temperature. Key: s = singlet; m = multiplet; t = triplet.

Very similar results have been obtained for blue and green species of [**7**]PF$_6$. The cyclic voltammogram (Figure 3) exhibit one reversible one-electron-transfer reaction in the potential range −1.8 to +1.6 V vs. Ag/AgCl (DMF, 0.1 M [TBA]PF$_6$) according to eq 5. Reductions of [**7**]PF$_6$ occur at very negative potentials

$$\begin{array}{ccc} [\mathrm{LW(NO)Br(OEt)}]^+ & \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} & \mathrm{LW(NO)Br(OEt)} \\ \{\mathrm{W{-}NO}\}^4 & & \{\mathrm{W{-}NO}\}^5 \end{array} \qquad (5)$$

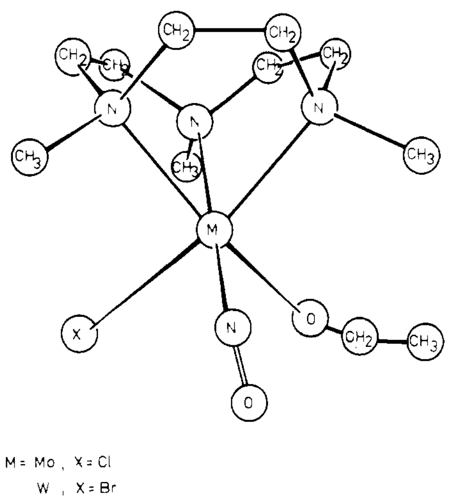
indicating a highly stabilized {W–NO}^{4} oxidation state. The stabilizing effect of the coordinated ethoxy group is again evident when the redox potential of [**3b**]PF$_6$ is compared with that of [**7**]PF$_6$; an anodic shift of 960 mV is observed for the latter.

^{1}H NMR Spectra. The 90-MHz ^{1}H NMR spectra of **1a** and **1b** are consistent with local C_{3v} symmetry (Table III): singlets at 2.97 and 3.1 ppm of nine protons, respectively, indicate three magnetically equivalent methyl groups of the cyclic triamine whereas the 12 methylene protons of the 9-membered ring gave rise to a multiplet, respectively (2.8 ppm).

The resonances due to the methyl protons are a sensitive probe for the overall symmetry of complexes containing facially coordinate *N,N′,N″*-trimethyl-1,4,7-triazacyclononane. Thus in complexes of the type [ML(NO)(CO)$_2$]$^+$, [**2a**]$^+$ and [**2b**]$^+$, only two methyl groups are equivalent and two singlets of overall

Inorg. Chem. **1985**, *24*, 4049–4054 **4049**

Chart I



intensity 9 and relative intensity 2:1 are observed. An unresolved singlet of intensity 12 is due to resonances of the methylene protons. The same pattern emerges for [**3a**]PF_6, but due to the enhanced electronegativity of bromide as compared to carbonyl ligands the corresponding methyl protons are more deshielded.

The solution spectra of blue and green isomers of [**6**]PF_6 and of [**7**]PF_6 are identical. It was expected that due to the fact that three different monodentate ligands are facially coordinated to a molybdenum or tungsten atom, three different signals of the methyl groups of the amine ligand should be observed (Chart I). In fact, only two singlets for these methyl groups are observed, with a relative intensity of 2:1. Interestingly, the protons of the two methyl groups directed between the nitrosyl group and an X^- ligand are in all cases more deshielded than the protons of the third methyl group pointing between two X^- ligand (X = CO, [**2a**]$^+$, [**2b**]$^+$; X = Br [**3a**]) or between one X^- and an ethoxy group ([**6**]$^+$, [**7**]$^+$).

The protons of the ethoxy ligand in [**6**]$^+$ and [**7**]$^+$ gave rise to a triplet (J_{HH} = 7.0 Hz) of the methyl protons and a multiplet (ABX_3 system) of the diastereotopic methylene protons. Since the metal atoms in [6]$^+$ and [7]$^+$ are electron-deficient (16e systems) and are bonded to the strong π-acceptor NO and the electronegative Cl or Br, the group $LM(NO)X^{2+}$ is considered to be strongly electron-withdrawing. Consequently, there should be a net withdrawal of electron density from the ethoxy group. This results in a substantial deshielding of the methylene protons; they resonate at rather low fields ([**6**]$^+$ at 5.65 ppm; [7]$^+$ at 5.5 ppm). Very similar effects have been observed for $Mo[HB(Me_2pz)_3](NO)X(OEt)$ (X = Cl, Br).[5]

Acknowledgment. Financial support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary Material Available: Table of elemental analyses (C, H, N, halide, Mo, W) of all new complexes (1 page). Ordering information is given on any current masthead page.

Contribution from the Lehrstuhl für Anorganische Chemie I,
Ruhr-Universität, D-4630 Bochum, Federal Republic of Germany

Monomeric Complexes of Tungsten(0–VI) Containing the Ligand *N*,*N'*,*N''*-Trimethyl-1,4,7-triazacyclononane and Their Electrochemical Properties. Preparation of $[L_2W_2O_5](PF_6)_2$ and Identification of Its Mixed-Valence Tungsten(VI)/Tungsten(V) Complex

GABRIELE BACKES-DAHMANN and KARL WIEGHARDT*

Received March 25, 1985

Halogenation and oxidative decarboxylation reactions of $LW(CO)_3$ (**1**) afforded a variety of monomeric air- and moisture-stable complexes of tungsten(II–VI). Cationic, seven-coordinate complexes $[LW(CO)_3X]^+$ (X = F, Cl, Br, I) were obtained from reactions of HX solutions of **1** with oxygen or reaction of **1** with X_2 (Br_2, Cl_2) in chloroform. The oxidation of these complexes with nitric acid yielded $[LW^{VI}O_2X]^+$ complexes (X = F, Cl, Br). Prolonged reaction of **1** with Cl_2 in CH_2Cl_2 gave $[LW^{IV}Cl_3]Cl$, and its reduction with $K[BH_4]$ afforded monomeric $LWCl_3$. Both species are paramagnetic. **1** reacted in HX with O_2 at prolonged reaction times to give paramagnetic, stable $[LW^VOX_2]^+$ (X = Cl, Br). Oxidation of **1** with 5 M HNO_3 or slow hydrolysis of $[LWO_2X]^+$ complexes gave the dimeric, oxo-bridged $[L_2W^{VI}_2O_5]^{2+}$ species. $[LW^VOX_2]PF_6$ complexes (X = Cl, Br) were isolated as blue and green crystals, respectively, depending on the reaction conditions (green forms were obtained in water-free MeCN; blue forms were generated in the presence of water). It is proposed that these latter materials represent a further example for distortional isomerism. Cyclic voltammograms were recorded in DMF (0.1 M $[TBA]PF_6$ supporting electrolyte). **1** was reversibly oxidized to produce the 17e species $[1]^+$ (E^f = –0.34 V vs. ferrocenium (Fc^+)/ferrocene (Fc)); a reversible one-electron transfer of $LWCl_3$ to give $[LWCl_3]^+$ was observed (–0.44 V vs. Fc^+/Fc); $[LWOCl_2]^+$ and $[LWOBr_2]^+$ were both reversibly reduced to the corresponding tungsten(IV) species (–1.14, –0.98 V vs. Fc^+/Fc), and even $[LW^{VI}O_2Cl]^+$ was reversibly reduced to LW^VO_2Cl (–1.44 V vs. Fc^+/Fc). $[L_2W_2O_5]^{2+}$ was reversibly reduced to the blue mixed-valence species $[L_2W_2O_5]^+$ (–1.43 V vs. Fc^+/Fc).

Introduction

During the past two decades the chemistry of molybdenum in its various oxidation states has received a great deal of attention[1] as a consequence of its discovery in a series of enzymes such as nitrate reductase, sulfite oxidase, xanthine oxidase, and formate dehydrogenase.[2–4] The structures of the molybdenum coordination spheres have been deduced by spectroscopic methods, in particular by EXAFS and EPR spectroscopy, to an encouraging degree of certainty,[5,6] considering the lack of "hard" evidence from X-ray crystallography. Recently, tungsten has been incorporated into several of these enzymes, producing catalytically inactive species.[7,8]

---

(1) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–223.
(2) Stiefel, E. I. In "Molybdenum and Molybdenum-Containing Enzymes"; Coughlan, M. P., Ed.; Pergamon Press: Elmsford, NY, 1980; p 41.
(3) Spence, J. T.; Minelli, M.; Rice, C. A.; Chasteen, N. C.; Scullane, M. In "Molybdenum Chemistry of Biological Relevance"; Newton, W. E., Otsuka, S., Eds.; Plenum Press: New York and London, 1980, p 263.
(4) Wentworth, R. A. D. *Coord. Chem. Rev.* **1976**, *18*, 1.
(5) Cramer, S. P. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 259–316.
(6) Bray, R. C. In "Molybdenum Chemistry of Biological Significance"; Newton, W. E., Otsuka, S., Eds.; Plenum Press: New York and London, 1980, p 117.
(7) Hewitt, E. J.; Notton, B. A. In "Molybdenum and Molybdenum-Containing Enzymes"; Coughlan, M. P., Ed.; Pergamon Press: Elsmford, NY, 1980; p 273.
(8) Johnson, J. L.; Rajagopalan, K. V. *J. Biol. Chem.* **1976**, *251*, 5505.

0020-1669/85/1324-4049$01.50/0