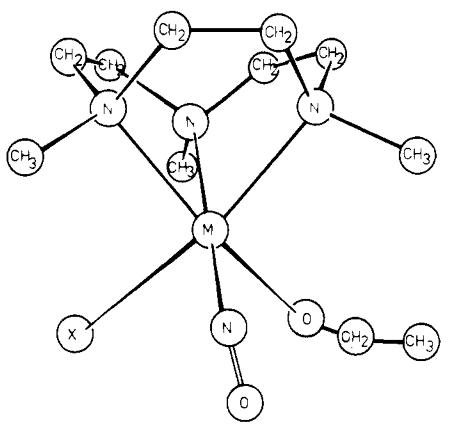
**Chart I**



M = Mo, X = Cl
W, X = Br

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 $\pi$-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.

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# 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

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*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]

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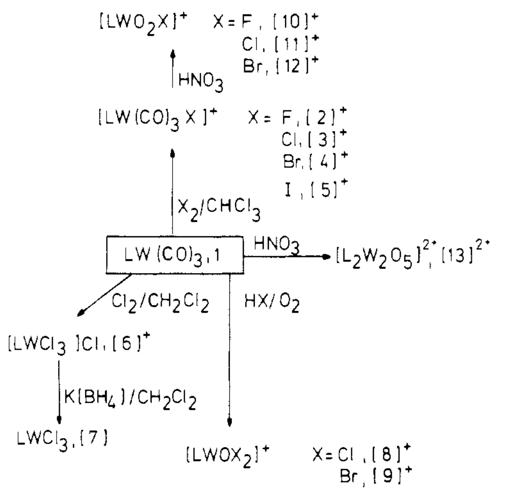
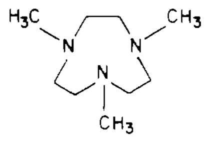
Scheme I



This has prompted an increased activity of inorganic chemists in developing the chemistry of tungsten[9] in its higher oxidation states (III–VI) with special emphasis on *cis*-dioxotungsten(VI) and oxotungsten(V) complexes in view of their structural similarity to analogous molybdenum species in enzymes. Tungsten is therefore thought to develop into a useful probe for the active site of molybdenum enzymes. Available evidence supports this view that in the above-mentioned enzymes monomeric oxomolybdenum complexes in the oxidation states IV, V, and VI are involved.[2–6] Preparative, electrochemical and EPR studies on monomeric tungsten(VI)–dioxo[10] and tungsten(V)–oxo complexes[10–14] have revealed remarkable similarities to their molybdenum analogues.[16] On the other hand, the standard potentials of analogous Mo and W redox couples differ by 0.4–0.8 V, the tungsten couples being the more cathodic. This effect has been invoked to explain the catalytic inactivity of tungsten-substituted molybdenum enzymes. For this reason oxotungsten(IV) complexes are very rare,[15] and as we will show in this paper, oxodihalotungsten(IV) complexes with a tridentate N-donor are very strong reductants, in contrast to their Mo(IV) analogues.

Well-characterized, monomeric, octahedral complexes of tungsten(III) are very rare; examples are $WX_3(py)_3$ (X = Cl, Br),[17] $[(pic)_2H][WBr_4(pic)_2]$ (pic = 4-methylpyridine)[18] and $[[HB(3,5\text{-}Me_2pz)_3]WCl_3]^-$ ($HB(3,5\text{-}Me_2pz)_3$ = hydridotris(3,5-dimethylpyrazolyl)borate).[19] The propensity of tungsten(III) to form strong metal–metal bonds and/or its oxidative instability preclude the preparation of monomeric species from simple reaction paths. The complexes above have been prepared by chemical reduction of the more readily accessible, monomeric tungsten(IV) species.

We have recently prepared the simple tridentate, cyclic triamine *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L) and have dem-



L

onstrated that this ligand prevents for steric reasons the formation of dimeric, octahedral complexes that are bridged by two atoms or ions, X (edge-sharing octahedra), a structure type that dominates the coordination chemistry of molybdenum[1] and —less pronounced—of tungsten[9] in their higher oxidation states. We have developed a strategy to synthesize monomeric molybdenum complexes in the oxidation states 0–VI using $LMo(CO)_3$ as starting material. Halogenation,[21] nitrosylation,[22] and oxidative decarbonylation[21] reactions have led to a great variety of monomeric complexes of molybdenum(II), -(III), -(IV), -(V), and -(VI). In this paper we describe the analogous chemistry of $LW(CO)_3$. New complexes prepared are summarized in Scheme I. Interestingly, oxidative decarbonylation reactions of $([9]\text{aneN}_3)W(CO)_3$, where $[9]\text{aneN}_3$ is unmethylated 1,4,7-triazacyclononane, afford also a variety of tungsten(III), -(IV), and -(V) complexes, most of which are dimeric or trimeric species containing metal–metal bonds.[23]

## Experimental Section

**Preparation of Complexes.** All new compounds gave satisfactory elemental analyses (C, H, N, halide, W); the data are available as supplementary material. The ligand *N,N′,N″*-trimethyl-1,4,7-triazacyclononane (L) and the complex $LW(CO)_3$ (**1**) have been prepared as described previously.[20,22]

**$[LW(CO)_3F]PF_6$ ([2]$PF_6$).** A solution of **1** (0.22 g, 0.5 mmol) in 40% HF (20 mL) was stirred in an open vessel in the presence of air for 2 h at room temperature. A saturated aqueous solution of $NaPF_6$ (5 mL) was added to initiate the precipitation of yellow microcrystals, which were filtered off, washed with ethanol and ether, and air-dried (yield 0.2 g).

**$[LW(CO)_3Cl]PF_6$ ([3]$PF_6$). Method 1.** A solution of **1** (0.22 g, 0.5 mmol) in concentrated HCl (10 mL) was refluxed in the presence of air for 2 h. To the cooled, green solution was added 5 mL of a saturated solution of $NaPF_6$. After the mixture was allowed to stand for 24 h at 0 °C, a greenish yellow precipitate was filtered off, washed with ethanol and ether, and air-dried. Recrystallization was from dilute HCl.

**Method 2.** Chlorine gas was slowly bubbled for 5 min through a solution of **1** (0.22 g, 0.5 mmol) in deoxygenated $CH_2Cl_2$ (20 mL). Addition of a saturated solution of $NaPF_6$ (5 mL) initiated the precipitation of [**3**]$PF_6$ (yield 0.2 g). The perchlorate salt, [**3**]$(ClO_4)$, was obtained by using a saturated solution of $NaClO_4$. The chloride salt, [**3**]Cl, was obtained from reduced volumes of the above mother liquor.

**$[LW(CO)_3Br]PF_6$ ([4]$PF_6$).** To a slurry of **1** (0.44 g, 1 mmol) in $CHCl_3$ (20 mL) was added a solution of bromine (0.8 g, 5 mmol) in $CCl_4$ (5 mL). After the mixture was refluxed for 5 h, the orange precipitate, [**4**]$(Br_3)$, was filtered off and converted to the $PF_6^-$ salt. [**4**]$(Br_3)$ (0.38 g, 0.5 mmol) was dissolved with gentle warming in 0.2 M HBr (30 mL), and a saturated solution of $NaPF_6$ (5 mL) was added. After 24 h at 0 °C orange crystals were filtered off, washed with ethanol and ether, and air-dried (yield 0.38 g).

**$[LW(CO)_3I](I_3)$ ([5]$(I_3)$).** A slurry of **1** (0.22 g, 0.5 mmol) in concentrated HI (25 mL) was stirred in the presence of air for 4 h. After addition of water (10 mL), this solution was stirred for a further 22 h. The orange-brown precipitate was filtered off, washed with ether, and air-dried. Recrystallization from a MeCN/water mixture (1:2) yielded 0.2 g of [**5**]$(I_3)$.

**$[LWCl_3]Cl$ ([6]Cl).** Chlorine gas was bubbled through a slurry of **1** (0.44 g, 1 mmol) in deoxygenated $CH_2Cl_2$ (30 mL) with stirring at room temperature for 25 min. A clear deep red solution was obtained, from which red crystals precipitated after the volume was reduced to one-half. These were filtered off, washed with ether, and dried under argon (yield 0.4 g).

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**$LWCl_3$ (7).** A slurry of [6]Cl (0.25 g, 0.5 mmol) in deoxygenated $CH_2Cl_2$ (20 mL) and an aqueous solution (5 mL) of $KBH_4$ (0.3 g) were vigorously stirred for 30 min. The color of the suspension changed to yellow-green. After the mixture was allowed to stand for 24 h at 0 °C, the yellow-green precipitate was filtered off, washed with ethanol and ether, and air-dried (yield 0.17 g).

**$[LWOCl_2]PF_6$ (Blue) ([8]$PF_6$).** [6]Cl (0.25 g, 0.5 mmol) was dissolved in water (30 mL) and warmed to 40 °C for 20 min until a clear blue solution was obtained, to which a saturated solution of $NaPF_6$ (5 mL) was added dropwise, initiating the precipitation of blue crystals, which were filtered off, washed with ethanol and ether, and air-dried (yield 0.18 g). Blue [8]($ClO_4$) was obtained analogously by using a saturated solution of $NaClO_4$. Both salts are soluble in water, acetone, and MeCN affording *blue* solutions.

**$[LWOCl_2]PF_6$ (Green) ([8]$PF_6$).** A solution of **1** (0.44 g, 1 mmol) in 10 M HCl (20 mL) was refluxed in the presence of air for 2 days. To the dark green solution was added a saturated solution of $NaPF_6$ (5 mL). The green precipitate was filtered off, washed with ethanol and ether, and air-dried. This material dissolved in dilute HBr or in a MeCN/water mixture (1:1), yielding stable green solutions from which green crystals of [8]$PF_6$ or [8]($ClO_4$) were obtained upon addition of $NaPF_6$ or $NaClO_4$.

**$[LWOBr_2]PF_6$ (Green) ([9]$PF_6$).** A solution of **1** (0.44 g, 1 mmol) in 48% HBr (15 mL) and water (5 mL) was refluxed in the presence of air for 48 h. To the cooled, green solution was added a saturated solution of $NaPF_6$ (5 mL), precipitating a green solid, which was filtered off, washed with ethanol and ether, and air-dried. Recrystallization from 0.1 M HBr yielded 0.34 g of [9]$PF_6$.

**$[LWOBr_2]PF_6$ (Blue) ([9]$PF_6$).** The above green [9]$PF_6$ (0.2 g, 0.3 mmol) was dissolved in an MeCN/water mixture (2:1) (30 mL) and was allowed to stand in an open vessel for 2 days, during which time blue crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried (yield 0.14 g).

**$[LWO_2F]Br$ ([10]Br).** To a slurry of [2]$PF_6$ (0.3 g, 0.5 mmol) in water (10 mL) was added concentrated $HNO_3$ dropwise with stirring at 22 °C until a clear yellow solution was obtained. A saturated, aqueous solution of NaBr (5 mL) was added whereupon a yellow solid precipitated, which was filtered off, washed with ethanol and ether, and air-dried (yield: 0.2 g).

**$[LWO_2Cl]PF_6$ ([11]$PF_6$).** A solution of [6]Cl (0.25 g, 0.5 mmol) in concentrated $HNO_3$ (10 mL) was stirred at room temperature for 2 h. Upon addition of a saturated aqueous solution of NaBr (5 mL) (*caution*! $Br_2$ effervescence!), a yellow precipitate of [11]($Br_3$) formed, which was filtered off and converted to the $PF_6$ salt. [11]($Br_3$) (0.33 g, 0.5 mmol) was dissolved in 0.1 M HCl (25 mL), and a saturated solution of $NaPF_6$ (5 mL) was added. After the mixture was allowed to stand at 0 °C for 24 h, a yellow solid was filtered off, washed with ethanol and ether, and air-dried (yield 0.27 g).

**$[LWO_2Br](ClO_4)$ ([12]($ClO_4$)).** A solution of [4]($Br_3$) (0.38 g, 0.5 mmol) in concentrated $HNO_3$ (15 mL) (*caution*! $Br_2$ effervescence) was stirred at room temperature for 4 h in the presence of air. Addition of a saturated NaBr solution (5 mL) initiated the precipitation of a yellow solid, [12]($Br_3$), which was converted to the perchlorate salt. [12]($Br_3$) (0.35 g, 0.5 mmol) was dissolved in 0.1 M HBr (25 mL), and a saturated $NaClO_4$ solution (5 mL) was added. After the mixture was allowed to stand for 24 h at 0 °C, a pale yellow precipitate was filtered off, washed with ethanol and ether, and air-dried (yield 0.29 g).

**$[L_2W_2O_5](Br_3)_2$ ([13]$(Br_3)_2$).** A solution of **1** (0.22 g, 0.5 mmol) in 5 M $HNO_3$ (25 mL) was stirred at 50 °C for 6 h and a further 12 h at room temperature. Addition of an aqueous, saturated solution of NaBr (5 mL) initiated the precipitation of a yellow solid, [13]$(Br_3)_2$, which was filtered off, washed with ethanol and ether, and air-dried (yield 0.14 g).

**$[L_2W_2O_5](PF_6)_2$ ([13]$(PF_6)_2$). Method 1.** To a clear yellow solution of [13]$(Br_3)_2$ (0.4 g, 0.33 mmol) in water (40 mL) was added a saturated solution of $NaPF_6$ (5 mL). After the mixture was allowed to stand for 24 h at 0 °C, a colorless precipitate was filtered off, washed with ethanol and ether, and air-dried (yield 0.35 g).

**Method 2.** A slurry of **1** (0.22 g, 0.5 mmol) in 1 M $CH_3SO_3H$ (20 mL) was stirred for 22 h in an open vessel in the presence of air at room temperature. To the clear, yellow solution was added solid $NaPF_6$ (0.3 g), initiating the precipitation of a colorless solid, which was filtered off, washed with ethanol and ether, and air-dried (yield 0.14 g).

**Instrumentation.** The apparatus used for electrochemical measurements has been described previously.[21] Cyclic voltammograms were measured in DMF at a planar Pt-button electrode (0.071 $cm^2$) as the working electrode, a platinum pin as the counter electrode, and an Ag/AgCl reference electrode. The supporting electrolyte was in all cases a 0.1 M solution of tetra-*n*-butylammonium hexafluorophosphate ([TBA]$PF_6$), which was recrystallized twice from acetone/ethanol and dried in vacuo at 70 °C for several hours. At the beginning of each experiment a cyclic voltammogram of the solution containing only the supporting electrolyte was measured under an argon atmosphere. To this solution were added solid samples, and these were dissolved to yield $\sim 10^{-3}$ M concentrations of the respective complexes. Then a nearly equimolar amount of ferrocene was added as internal standard. Formal redox potentials are given vs. the reference electrode system ferrocenium/ferrocene ($Fc^+/Fc$) in volts.

The magnetic susceptibilities of powdered samples were measured by using the Faraday method between 98 and 298 K, and diamagnetic corrections were applied with use of published tables.

Electronic spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer (200–1500 nm).

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

## Results and Discussion

The air-stable, monomeric *fac*-tricarbonyl complex **1** is a useful starting material for nitrosylation, halogenation, and oxidative decarbonylation reactions. The latter two aspects of this chemistry are now described. The successful preparation of monomeric complexes of molybdenum and tungsten in their higher oxidation states III–VI is in essence due to two properties of the cyclic triamine *N,N′,N″*-trimethyl-1,4,7-triazacyclononane:

(1) This ligand occupies facially three coordination sites of an octahedron. This leads to a kinetically very stable situation since simple reaction paths for ligand dissociation are not readily available. In addition, a macrocyclic effect of three tertiary amine nitrogens may also contribute to an enhanced thermodynamic stability as compared to that of open-chain amine analogues.

(2) The presence of three *N*-methyl groups enforces a steric situation, which precludes the formation of dimeric complexes with edge sharing to two octahedra.

Oxidation of **1** in concentrated hydrogen halide acids, HX, by oxygen yields diamagnetic, cationic, seven-coordinate complexes of the type $[LW(CO)_3X]^+$ (X = F ([2]$^+$), Cl ([3]$^+$), Br ([4]$^+$), I ([5]$^+$)). [3]$^+$ has also been obtained by chlorination of **1** in $CCl_4$; [4]$^+$ and [5]$^+$ were obtained by using $Br_2$ and $I_2$ in chloroform, respectively. They were isolated as air- and moisture-stable hexafluorophosphate salts, which are soluble in MeCN, DMF, or dilute HX acids without decomposition. These tungsten complexes are relatively strong oxidants, and the reaction of [4]$PF_6$ in an aqueous solution of $Na_2S$ produces quantitatively **1**. In analogy to the known structure of $[([9]aneN_3)Mo(CO)_3Br](ClO_4)\cdot H_2O$ a 4:3 piano-stool configuration[24] is proposed for these complexes. In the infrared spectra three strong $\nu$(CO) stretching frequencies are observed (Table I), respectively, the wavenumbers of which increse in the order F < Cl < Br < I.

Interestingly, in the analogous series of molybdenum complexes,[25] $[LMo(CO)_3X]^+$ (X = Cl, Br, I) a reverse order is observed, which would appear to be the natural order, considering the decreasing electronegativity of X and concomitant increasing $\pi$-back-donation of metal to carbonyl.

Exhaustive chlorination of **1** in $CH_2Cl_2$ yields a deep red solution, from which red crystals of [6]Cl were obtained, which are stable in the solid state for months. In the presence of air, very slowly a color change to green is observed due to the formation of green $[LWOCl_2]Cl$ ([8]Cl). [6]Cl reacts in oxygen-containing water spontaneously to yield [8]$^+$. Even in deoxygenated DMF or MeCN, [6]Cl is only stable for a few hours. The reaction of [6]Cl with nitric acid affords [11]$^+$, a tungsten(VI) species.

The magnetic moment of [6]Cl is slightly temperature dependent; the effective magnetic moment varies from 1.7 $\mu_B$ at 93 K to 1.96 $\mu_B$ at 293 K. This behavior has been reported for other monomeric, octahedral complexes of W(IV)[26] ($\mu_{eff}$ of W(IV) complexes range from 1.5–2.8 $\mu_B$ at 298 K).[26,27] The electronic spectrum of [6]Cl in $CH_2Cl_2$ exhibits an absorption maximum at 525 nm (Table I).

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**Table I.** Selected Infrared Data, Electronic Spectral Data, and Effective Magnetic Moments of Complexes

| complex | IR, cm$^{-1}$ $\nu$(CO) | IR, cm$^{-1}$ $\nu$(W=O) | electronic spectrum[a] $\lambda_{max}$, nm ($\epsilon$, L mol$^{-1}$ cm$^{-1}$) | color | $\mu_{eff}$(298 K), $\mu_B$ |
|---|---|---|---|---|---|
| [**2**]$PF_6$ | 1985, 1895, 1855 | | | yellow-green | diamagnetic |
| [**3**]$PF_6$ | 1990, 1910, 1865 | | | orange | diamagnetic |
| [**4**]($ClO_4$) | 2000, 1930, 1895 | | | orange | diamagnetic |
| [**5**]$PF_6$ | 2010, 1950, 1895 | | | orange-brown | diamagnetic |
| [**6**]Cl | | | 525 (210)[b] | red | 1.96 |
| **7** | | | 350 (250), 453 (100), 690 (10) | yellow-green | 4.0 |
| [**8**]$PF_6$ | | 980 | 286 (1500), 715 (20) | blue | 2.0 |
| [**8**]$PF_6$ | | 965 | 420 (1200), 695 (40) | green | 1.9 |
| [**9**]$PF_6$ | | 970 | 360 (1200), 639 (35) | blue | 1.9 |
| [**9**]$PF_6$ | | 960 | 356 (1300), 633 (36) | green | 1.9 |
| [**10**]Br | | 920, 960 | | yellow | diamagnetic |
| [**11**]$PF_6$ | | 915, 955 | | yellow | diamagnetic |
| [**12**]($ClO_4$) | | 905, 945 | | yellow | diamagnetic |
| [**13**]$(PF_6)_2$ | | 960, 915<br>800[c] | | colorless | diamagnetic |

[a] Solution spectra, measured in MeCN. [b] In $CH_2Cl_2$. [c] $\nu$(W–O–W).

Reduction of [**6**]Cl in $CH_2Cl_2$ with an aqueous solution of $K[BH_4]$ affords a yellow-green, paramagnetic solid, **7**, which is stable in the presence of air for weeks. It is soluble in DMF and MeCN and insoluble in water. Oxygen causes a rapid color change of such solutions from yellow to red to green indicating the formation of [**6**]$^+$ and finally [**8**]$^+$. The magnetic moment of **7** is again slightly temperature-dependent; $\mu_{eff}$ is 3.0 $\mu_B$ at 93 K and 4.0 $\mu_B$ at 293 K.[17a] These values are substantially greater than those observed for dimeric, chloro-bridged tungsten(III) complexes (e.g. $\mu_{eff}$ of $W_2Cl_9^{3-}$ is 0.4 $\mu_B$ per dimer at 298 K[28]) and are in agreement with a $d^3$ configuration of monomeric tungsten(III) in an octahedral environment. In the mass spectrum of **7** the correct molecular ion peak is observed (*m/z* 462), although with a rather low intensity. The electronic spectrum of **7** exhibits three d–d absorptions in the visible region at 350, 453, and 690 nm. The magnetic, spectroscopic, and chemical properties of [**6**]$^+$ and **7** closely parallel those of $[HB(3,5\text{-}Me_2pz)_3]WCl_3$ and $[[HB(3,5\text{-}Me_2pz)_3]WCl_3]^-$.[19]

Oxidative decarbonylation reactions of **1** in concentrated hydrochloric and hydrobromic acid with oxygen afford green solutions, from which upon addition of $NaPF_6$ *green* crystals of [**8**]$PF_6$ and [**9**]$PF_6$ were obtained, respectively. In the infrared spectrum of both species a strong $\nu$(W=O) stretching frequency is observed at 965 and 960 cm$^{-1}$, respectively; the effective magnetic moments of 1.9 $\mu_B$ are indicative of a $d^1$ configuration of W(V) in both cases. Both salts dissolve readily in DMF, MeCN, acetone, and dilute HX acids (X = Cl, Br) with a green color. In solution and in the solid state they are stable toward oxygen and do not hydrolyze in aqueous solution.

Interestingly and rather unexpectedly, it is also possible to obtain *blue* crystals of [**8**]$PF_6$ and [**9**]$PF_6$. Blue [**8**]$PF_6$ is formed in an aqueous solution of [**6**]Cl in the presence of air and addition of $NaPF_6$, whereas blue [**9**]$PF_6$ was obtained when green [**9**]$PF_6$ was recrystallized from an acetonitrile/water mixture (1:1). The effective moments of the blue forms indicate an unchanged $d^1$ configuration. The blue and green species gave identical elemental analyses (supplementary material). In the infrared spectrum $\nu$(W=O) is observed at 980 cm$^{-1}$ for blue [**8**]$PF_6$ and at 970 cm$^{-1}$ for blue [**9**]$PF_6$. Thus a small shift of $\nu$(W=O) to higher wavenumbers is detected in going from the green to blue forms. It is not quite clear what causes the green ↔ blue transformation, but as a tentative rule we found that in the presence of water the blue forms prevail, whereas in $H_2O$-free DMF or MeCN green species appear to be formed. The electronic spectra of green and blue isomers of [**8**]$^+$ and [**9**]$^+$ in solution are also slightly but not dramatically different (Table I). It is noted that in $H_2O$-free MeCN the blue *and* green crystalline isomers dissolve to give stable blue and green solutions, respectively. Addition of water to such a green solution affects a color change to blue. These blue ↔ green interconversions in solution and in the solid state have been detected by Chatt et al. in 1972 for neutral Mo(IV)–oxo complexes, e.g. $MoOCl_2(PPhMe_2)_3$,[29] and recently by Wilkinson et al. for $MoOCl_2(PMe_3)_3$.[30] The first pair of isomers has been characterized by X-ray crystallography.[29] Recently blue and green isomers of $[MoO(CN)_5]^{3-}$ and of $[MoO(CN)_4(H_2O)]^{2-}$ have also been characterized.[31] Furthermore, in a series of nitrosyl alkoxy complexes of Mo(II) this effect has been found but not yet characterized by X-ray crystallography.[22,32] In essence, the only difference between the blue and green forms are relatively short Mo=O bond distances in the blue and somewhat longer Mo=O lengths in the green isomers, not considering small deviations of bond angles. Chatt has coined the term "distortional isomerism" for this effect.[29b] The present tungsten complexes [**8**]$^+$ and [**9**]$^+$ may also belong to this category because the $\nu$(W=O) frequencies are significantly different in the blue and green forms. This is to the best of our knowledge the first example of distortional isomerism of tungsten(V) complexes.[36]

The oxidation of $[LW(CO)_3X]^+$ (X = F, Cl, Br) with nitric acid leads to completely decarbonylated, yellow complexes of tungsten(VI), $[LWO_2X]^+$ (X = F ([**10**]$^+$), Cl ([**11**]$^+$), Br ([**12**]$^+$)). [**11**]$^+$ has also been obtained from **7** with nitric acid. These complexes are very stable in the solid state as hexafluorophosphate or perchlorate salts. In aqueous solution they slowly hydrolyze, affording the colorless dimer $[L_2W_2O_5]^{2+}$ ([**13**]$^{2+}$) (see below). They are diamagnetic species containing a *cis*-dioxotungsten(VI) moiety, which gives rise to two strong $\nu$(W=O) stretching frequencies at 900 and 950 cm$^{-1}$ (Table I).

Complexes containing the oxo-bridged $[M_2O_5]^{2+}$ entity are quite common in the chemistry of Mo(VI),[1] but rather surprisingly, this structure type has not been described for tungsten(VI). We have recently characterized the first example, $[L'_2W_2O_5]^{2+}$ (L' =

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**Table II.** Electrochemical Data of Complexes at 25 °C in DMF ([TBA]$PF_6$ Supporting Electrolyte)

| couple | $E^f$,[a] V | $\Delta E_p$,[b] mV | cf,[c] $\mu A\ V^{-1/2}\ s^{1/2}\ mmol^{-1}\ L$ | $I_p^b{:}I_p^f$ |
|---|---|---|---|---|
| [**1**]$^+$/**1** | −0.34 (−0.245) | 76 | 50[d] | 0.9 |
| [**4**]$^+$/**1** | −0.27[f] (−0.18) | irreversible | 95[d] | |
| [**6**]$^+$/**7** | −0.44 (+0.395) | 65 | 35[d] | 0.9 |
| [**8**]$^+$ (blue)/**8** | −1.14 (−0.52) | 65 | 47[e] | 1.0 |
| [**8**]$^+$ (green)/**8** | −1.15 | 75 | 40[e] | 0.98 |
| [**9**]$^+$/**9** | −0.98 | 70 | 32[e] | 0.9 |
| [**11**]$^+$/**11** | −1.44 | 70 | 32[d] | 1.0 |
| [**13**]$^{2+}$/[**13**]$^+$ | −1.43 (−0.77) | 75 | 32[e] | 0.9 |

[a] Formal redox potential, $(E_p^{ox} + E_p^{red})/2$, vs. ferrocenium ($Fc^+$)/ferrocene (Fc) as internal standard; values in parentheses are the redox potentials of the corresponding molybdenum complexes from ref 21. [b] At scan rate 50 mV $s^{-1}$. [c] Peak current function. [d] Oxidation peak. [e] Reduction peak. [f] Supporting electrolyte [TBA]Br.

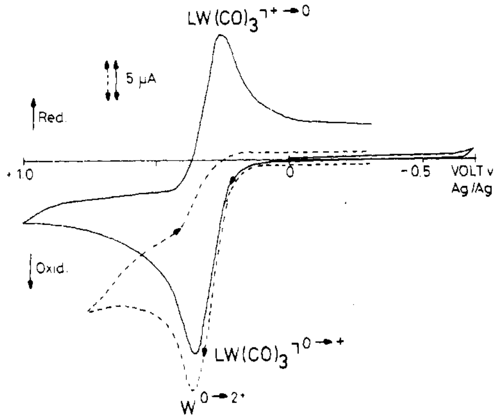

**Figure 1.** Cyclic voltammogram of **1** in DMF at 25 °C with 0.1 M [TBA]$PF_6$ (—) and 0.1 M [TBA]Br (- -) supporting electrolyte (Pt-button electrode, scan rate 50 mV $s^{-1}$).

1,4,7-triazacyclononane).[23] A salt of [**13**]$^{2+}$ has been obtained from oxidative decarbonylation of **1** with 5 M $HNO_3$ upon addition of NaBr ([**13**]$(Br_3)_2$), which was converted to [**13**]$(PF_6)_2$. In the infrared spectrum $\nu_{as}$(W=O), $\nu_s$(W=O) and $\nu$(W—O—W) stretching frequencies are observed at 960, 915, and 800 $cm^{-1}$, respectively. $[L_2Mo_2O_5](Br_3)_2$ has been characterized by X-ray crystallography.[33] We propose a similar structure for the tungsten(VI) analogue [13]$^{2+}$, containing a linear W-O-W moiety and two *cis*-dioxotungsten(VI) groups. [**13**]$(PF_6)_2$ is soluble in DMF, in MeCN, and only a little in water, from which it is readily recrystallized.

**Electrochemistry.** Electrochemical data are summarized in Table II. The cyclic voltammogram of **1** in DMF using [TBA]$PF_6$ and [TBA]Br as supporting electrolyte is shown in Figure 1. In the absence of coordinating anions one reversible one-electron-transfer process occurs at a Pt-electrode in the potential range −1.7 to +1.5 V vs. Ag/AgCl as judged from the diagnostic criteria. Repetitive scans do not indicate a chemical reaction (decomposition) of the 17e species, $[LW^I(CO)_3]^+$, under these conditions. In the presence of bromide ions only an irreversible two-electron-oxidation peak is observed, which corresponds to the formation of redox-inactive $[LW(CO)_3Br]^+$. Thus the electrochemistry of **1** may be described adequately by eq 1 and 2. Similar behavior has been reported for a series of *cis*-tri-

$$LW^0(CO)_3 \underset{E^f = -0.34\ V\ vs.\ Fc^+/Fc}{\overset{DMF,\ [TBA]PF_6}{\rightleftharpoons}} [LW^I(CO)_3]^+ + e^- \quad (1)$$

$$LW^0(CO)_3 + Br^- \xrightarrow[E_{ox} = -0.27\ V\ vs.\ Fc^+/Fc]{DMF,\ [TBA]Br} [LW^{II}(CO)_3Br]^+ + 2e^- \quad (2)$$

carbonylmolybdenum(0) complexes containing tridentate N, P, As, or S donor ligands.[34] Interestingly, the redox potential of the corresponding $[LMo(CO)_3]^+/LMo(CO)_3$ couple[21] is more anodic by only 95 mV, contrasting the behavior of many other analogous complexes of molybdenum and tungsten, where an anodic shift of ~700 mV is frequently observed (see below).

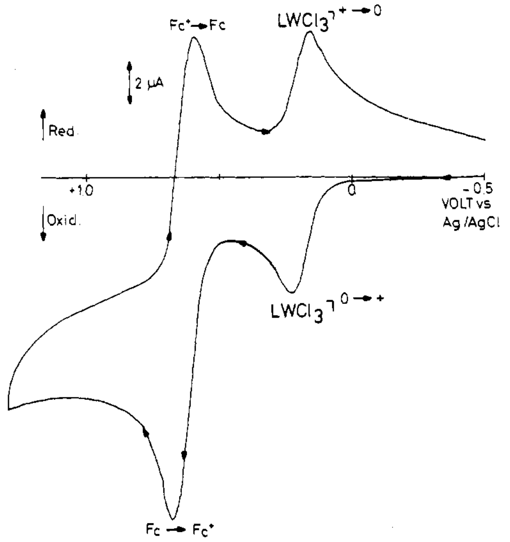

**Figure 2.** Cyclic voltammogram of **7** in DMF at 25 °C (0.1 M [TBA]$PF_6$, ferrocene internal standard, scan rate 50 mV $s^{-1}$)

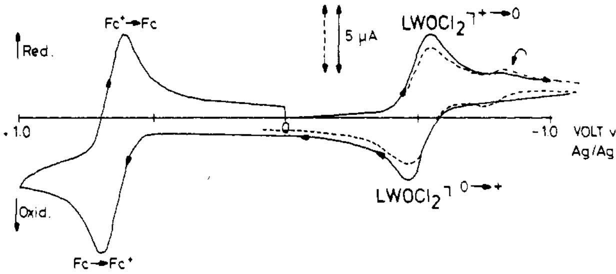

**Figure 3.** Cyclic voltammogram of blue (–) and green (- -) forms of [**8**]$PF_6$ in DMF at 25 °C (0.1 M [TBA]$PF_6$ supporting electrolyte, ferrocene internal standard, scan rate 100 mV $s^{-1}$). The arrow indicates a small impurity of $[LWO_2Cl]^+$.

Figure 2 displays the cyclic voltammogram of the monomeric tungsten(III) species **7**. In the potential range −1.7 to +1.5 V vs. Ag/AgCl in 0.1 M [TBA]$PF_6$ DMF solution a reversible one-electron-transfer reaction is observed according to eq 3. An

$$e^- + [LW^{IV}Cl_3]^+ \underset{E^f = -0.44\ V\ vs.\ Fc^+/Fc}{\rightleftharpoons} LW^{III}Cl_3 \quad (3)$$

identical cyclic voltammogram has been obtained with [**6**]Cl as starting complex, and from a coulometric measurement a one-electron transfer has been confirmed. The corresponding $[LMoCl_3]Cl$ complex exhibits similar behavior,[21] but the redox potential is shifted anodically by 835 mV, indicating a substantial stabilization of the +III oxidation state of molybdenum as compared to tungsten(III). **7** is a strong reductant that reacts with oxygen to give [**6**]$^+$, whereas $[LMoCl_3]^+$ is easily reduced by mild reductants such as alcohols. These observations parallel those by Millar and Koch[19] for $[HB(3,5\text{-}Me_2pz)_3]MCl_3$ (M = Mo, W; $[HB(3.5\text{-}Me_2pz)_3]$ = hydriotris(3,5-dimethyl-1-pyrazolyl)borate). These authors ascribed this unusual redox behavior at least in part to the interaction of Mo $d_\pi$ orbitals with ligand $\pi^*$ orbitals. Since ligand L does not have $\pi$-acceptor capabilities–it is a simple $\sigma$-donor–the observed trends of relative stabilities of monomeric

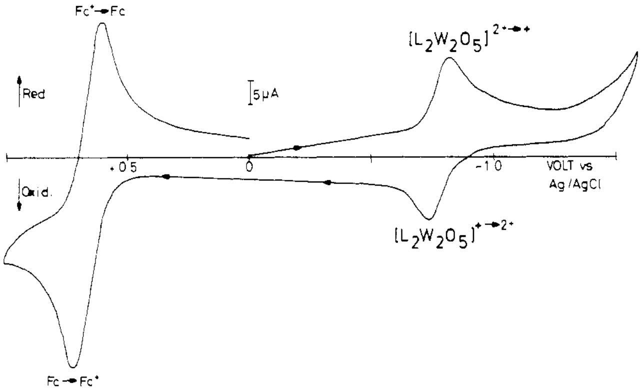

**Figure 4.** Cyclic voltammogram of $[\mathbf{13}](PF_6)_2$ in DMF at 25 °C (0.1 M $[TBA]PF_6$, ferrocene internal standard, scan rate 50 mV $s^{-1}$)

molybdenum(III,IV) and tungsten(III,IV) complexes may be an inherent feature of the metal centers regardless of their specific ligand environment.

Cyclic voltammograms of blue and green forms of $[\mathbf{8}]PF_6$ in DMF (Figure 3) and of green $[\mathbf{9}]PF_6$ exhibit one reversible one-electron-transfer reaction in the potential range +1.0 to −1.8 V vs. Ag/AgCl according to eq 4. Thus the reduction of $[\mathbf{8}]^+$

$$[LW^{V}OX_2]^+ + e^- \rightleftarrows LW^{IV}OX_2 \qquad X = Cl, Br \tag{4}$$

and $[\mathbf{9}]^+$ to form the corresponding oxotungsten(IV) species is accomplished electrochemically. We have not been able to prepare these complexes chemically; e.g., the reduction of $[\mathbf{8}]PF_6$ in 0.1 M HCl with $K[BH_4]$ yields $LWCl_3$ as the only isolable product. Interestingly, the blue and green forms of $[\mathbf{8}]PF_6$ have within experimental error identical redox potentials (Table II). The oxotungsten(IV) species are strong reductants. The redox potentials of the corresponding oxomolybdenum(V/IV) complexes are again shifted anodically by 620 mV for the chloro and 580 mV for the bromo complex. This indicates that oxomolybdenum(IV) complexes are more readily accessible than their tungsten analogues.[10] This may have implications for the bioinorganic relevance of molybdenum(IV) vs. tungsten(IV) complexes in enzymatic oxygen atom transfer reactions suggested for xanthine oxidase or nitrate reductase.

Spence, et al. have recently investigated the electrochemical properties of a series of oxotungsten(V) complexes displaying similar but less reversible one-electron-transfer reactions at much more negative redox potentials than those of their molybdenum analogues.[10,16] Interestingly, electrochemical oxidation of oxotungten(VI) has not been observed previously. The chemical oxidation of $[\mathbf{8}]^+$ and $[\mathbf{9}]^+$ with nitric acid yields $[LWO_2X]^+$ species.

$[LWO_2Cl]^+$ ($[\mathbf{11}]^+$) exhibits a reversible one-electron reduction at $E^f = -1.44$ V vs. $Fc^+/Fc$ according to eq 5. This is a relatively

$$[LW^{VI}O_2Cl]^+ + e^- \rightleftarrows LW^{V}O_2Cl \tag{5}$$

rare instance in which a *cis*-dioxotungsten(VI) species is reduced reversibly to the corresponding tungsten(V) complex. In many instances only an irreversible reduction of the $[WO_2]^{2+}$ moiety has been observed.[10]

In the cyclic voltammogram of binuclear $[\mathbf{13}]^{2+}$, one reversible one-electron-transfer reaction is observed (Figure 4) at a rather negative redox potential of −1.43 V vs. $Fc^+/Fc$. A coulometric measurement at −1.0 V vs. Ag/AgCl yielded 1.0 ± 0.1 e/dimer. During the electrolysis the colorless solution of $[\mathbf{13}]^{2+}$ ($1 \times 10^{-3}$ M) changed to deep blue. The chemical reduction of $[\mathbf{13}](PF_6)_2$ in aqueous solution with zinc amalgam also produced an intensely blue color of the tungsten(VI/V) mixed-valence species, which is very oxygen-sensitive.

$$[L_2W^{VI}{}_2O_5]^{2+} + e^- \rightleftarrows [L_2W^{VI}W^{V}O_5]^+ \tag{6}$$

The corresponding molybdenum dimer $[L_2Mo_2O_5](PF_6)_2$ has been shown to be reversibly reduced by two successive one-electron-transfer reactions, eq 7, in aprotic media (DMF).[33] The redox

$$[L_2Mo_2O_5]^{2+} + e^- \underset{E^f{}_1 = -0.77\ V}{\rightleftharpoons} [L_2Mo_2O_5]^+ + e^- \underset{E^f{}_2 = -1.88\ V\ vs.\ Fc^+/Fc}{\rightleftharpoons} [L_2Mo_2O_4]^0 \tag{7}$$

potential of the couple $[L_2W_2O_5]^{2+}/[L_2W_2O_5]^+$ is cathodically shifted by 660 mV as compared to that of its molybdenum analogue. The second reduction producing the tungsten(V) dimer is probably outside the potential range available (+1.5 to −1.8 V vs. Ag/AgCl), assuming a similar cathodic shift of this redox potential. In contrast to the molybdenum chemistry, mixed-valence species of tungsten(VI/V) are known, e.g. tetrameric $[W_4O_8Cl_8(H_2O)_4]^{2-}$ has been characterized by X-ray crystallography.[35]

## Concluding Remarks

We have shown that halogenation and oxidative decarbonylation reactions of the *cis*-tricarbonyltungsten(0) complex **1** containing the kinetically and thermodynamically stabilizing tridentate macrocycle *N,N′,N″*-trimethyl-1,4,7-triazacyclononane lead to a variety of monomeric complexes of tungsten in the oxidation states II–VI in good yields. The electrochemical properties of *cis*-dioxohalotungsten(VI) and oxodihalotungsten(V) show that reversible one-electron-transfer reactions occur, although at much more negative redox potentials than those of their molybdenum analogues (0.5–0.8-V cathodic shift). This is thought to account for the observed lack of activity of some molybdenum-containing enzymes in which tungsten has been incorporated. Paramagnetic, monomeric tungsten(III) and -(IV) complexes have also been obtained via this route, $LWCl_3$ and $[LWCl_3]^+$. The chemistry of these tungsten complexes parallels nearly all aspects of studies on analogous complexes containing hydridotripyrazolylborate type ligands. It is therefore concluded that stabilities and electrochemical properties of these complexes are not primarily determined by π-acceptor properties of the pyrazolyl groups but rather by kinetic and thermodynamic factors introduced by facially coordinating, tridentate N-donor ligands.

**Acknowledgment.** Financial support for this work from the Fonds der Chemischen Industrie is gratefully acknowledged.

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