might speculate that the major contribution to the ~90° Mn^{2+}–F^-–Cr^{3+} interaction would be the direct overlap of half-filled t_{2g} orbitals located between the two ions, which should result in a medium-strength antiferromagnetic interaction. Surprisingly, this interaction is ferromagnetic, although quite weak. Equally surprising is the fact that the ~135° Mn^{2+}–F^-–Cr^{3+} and Mn^{2+}–F^-–V^{3+} interactions are antiferromagnetic, since 135° interactions are usually approximately the same as 180° interactions. We found that ~180° interactions in $KMnCrF_6$[14] and $KMnVF_6$[24] are ferromagnetic, which is explained very nicely by the Goodenough–Kanamori rules.[25,26]

The ~90° interactions of Mn^{2+} with Cr^{3+} or V^{3+} are not consistent with predictions based on the direct overlap of half-filled t_{2g} orbitals or of a half-filled t_{2g} orbital with an empty t_{2g} orbital, respectively. The most obvious correlation mechanism would involve the half-filled e_g orbitals of Mn^{2+} and the half-filled or empty t_{2g} orbitals of Cr^{3+} or V^{3+}, respectively. This mechanism, however, is not consistent with the Goodenough–Kanamori rules, as the sign is incorrect in both cases. One possibility of resolving this question is to gather more information. The most obvious systems that should be studied are the trirutile compounds $LiNiVF_6$, $LiNiCrF_6$, and $LiNiFeF_6$, all of which have been reported to exist.[3,7] On the basis of results from $LiMnVF_6$, $LiMnCrF_6$, and $NaMnCrF_6$, the compounds $LiNiVF_6$, $LiNiCrF_6$, and $LiNiFeF_6$ should have strong nearest-neighbor interactions that are negative, positive, and positive, respectively. A study of these three compounds is in progress in our laboratory.

Conclusions

The trirutile compound $LiMnVF_6$ is ionically ordered such that all nearest- and second-nearest-neighboring paramagnetic ions to an Mn^{2+} ion are V^{3+}, and vice versa. The correct space group for $LiMnVF_6$, therefore, is not $P4_2/mnm$, but the structure is of lower symmetry, perhaps $P4_2nm$. A second condition that persists in $LiMnVF_6$, as well as LiV_2F_6, is $|J_1| >> |J_2|$. This condition leads to two linear regions in a χ^{-1} vs. T plot, and all evidence supports the conclusion that magnetic coupling first forms dimers between nearest neighbors, followed at lower temperatures by cooperative, three-dimensional, long-range ordering. Finally, the ~90° Mn^{2+}–F^-–V^{3+} interaction is antiferromagnetic with $J_1/k \approx -26$ K and the ~135° Mn^{2+}–F^-–V^{3+} interaction is antiferromagnetic with $J_2/k \approx -0.83$ K.

Acknowledgment. The authors gratefully acknowledge the National Science foundation (Grant DMR 79-00313) for financial support, and the University of Mississippi for cost sharing. We wish to thank Charles J. O'Connor for sharing his knowledge of magnetochemistry with us. Appreciation is expressed to the University of Mississippi Computer Center for providing data reduction time.

Registry No. $LiMnVF_6$, 55608-61-2.

Supplementary Material Available: A table of measured magnetic susceptibilities of $LiMnVF_6$ vs. T from 4.2 to 300 K (1 page). Ordering information is given on any current masthead page.

---

[24] Unpublished data on $KMnVF_6$.

[25] Goodenough, J. B. "Magnetism and the Chemical Bond"; Interscience: New York, 1963; pp 165-185.

[26] Kanamori, J. *Phys. Chem. Solids* **1959**, *10*, 87.

Contribution from the Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-4630 Bochum, Federal Republic of Germany, and the Anorganisch-chemisches Institut der Universität, D-6900 Heidelberg, Federal Republic of Germany

Preparation and Electrochemical Investigation of Monomeric Complexes of Molybdenum(0–VI) with the Ligand 1,4,7-Trimethyl-1,4,7-triazacyclononane (L). Crystal Structure of $[Mo^{IV}LBr_3](PF_6)$

GABRIELE BACKES-DAHMANN,[†] WILLY HERRMANN,[†] KARL WIEGHARDT,*[†] and JOHANNES WEISS[‡]

Received April 12, 1984

The oxidation of $LMo(CO)_3$, where L represents the facially coordinating triamine 1,4,7-trimethyl-1,4,7-triazacyclononane ($C_9H_{21}N_3$), by various oxidants such as Br_2, I_2, and nitric acid affords a variety of mononuclear complexes of molybdenum in the oxidation states II–VI: $[LMo^{II}(CO)_3X]^+$ (X = Br, I), $[LMo^{III}X_3]$ (X = Cl, Br, I, NCS), $[LMo^{IV}Br_3]^+$, $[LMo^{V}OX_2]^+$ (X = Cl, Br, I), and $[LMoO_2Br]^+$. The electrochemistry of $LMoX_3$ species in acetonitrile has been investigated. Reversible one-electron oxidation–reduction of $[LMo^{III}X_3]$ complexes has been found. Formal redox potentials measured in acetonitrile vs. the ferrocenium/ferrocene (Fc^+/Fc) couple are as follows: X = Cl, +0.395 V; X = Br, +0.50 V; X = I, +0.525 V. $[LMo(SCN)_3]$ exhibits two reversible one-electron-transfer processes at +0.53 and −2.00 V. The latter process corresponds to the couple Mo(III/II). $[LMo(CO)_3]$ in the absence of coordinating anions is found to be reversibly oxidized in acetonitrile; the formal redox potential of the couple $[LMo(CO)_3]^+/[LMo(CO)_3]$ is −0.245 V vs. Fc^+/Fc. $[LMo^{V}OX_2]^+$ species are reversibly reduced in acetonitrile to the $[LMo^{IV}OX_2]^0$ complexes ($E_{1/2} = -0.52$ V for X = Cl and −0.40 V for X = Br vs. Fc^+/Fc). The redox potential of the couple $[LMoO_2Br]^{+/0}$ has also been measured to be −0.695 V vs. Fc^+/Fc in acetonitrile. The crystal structure of $[LMoBr_3](PF_6)$ has been determined. The compound crystallizes in the orthorhombic space group *Pbcm* with $a = 7.642$ (2) Å, $b = 15.232$ (4) Å, $c = 16.275$ (2) Å, $V = 1890$ Å^3, $\rho_{calcd} = 2.29$ g cm^{-3} for $Z = 4$, and molecular weight 651.9. The structure was solved by conventional techniques using 1048 unique reflections resulting in a final R factor of 0.076. The structure consists of pseudooctahedral $[LMoBr_3]^+$ cations and discrete PF_6^- anions.

Introduction

The structural chemistry of complexes of molybdenum(V), -(IV), and -(III) with simple O,N donor ligands in aqueous solution is dominated by dimeric and oligomeric oxo- and/or hydroxo-bridged species, containing for instance structural units such as $Mo^{V}_2O_4^{2+}$, $Mo^{IV}_3O_4^{4+}$, and $Mo^{III}_2(OH)_2^{4+}$.[1] The propensity to oligomerize is thought to be due to the formation of relatively strong metal–metal bonds. Thus, well-characterized stable monomeric complexes of molybdenum(III) and -(IV) with simple O,N donor ligands are still rather scarce. We have been investigating the ligating properties of the small macrocycle 1,4,7-triazacyclononane with some early transition metals in high and low oxidation states. With use of this ligand a series of dinuclear species of molybdenum(V) and -(III) containing metal–metal bonds have been characterized by X-ray crystallography[2,3] where

---

[†] Ruhr-Universität Bochum.

[‡] Universität Heidelberg.

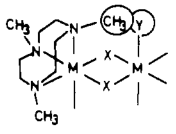
[1] Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

[2] Wieghardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 491.

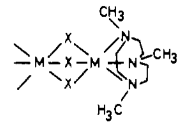
[3] Wieghardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 94.

0020-1669/85/1324-0485$01.50/0

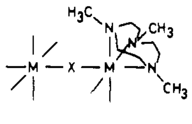
two octahedra are connected via a common edge. The permethylated derivative of the above macrocycle, 1,4,7-trimethyl-1,4,7-triazacyclononane, exhibits the interesting property that for steric reasons this edge-sharing fusion of two octahedra is not possible:



steric hindrance between CH_3 and Y



no steric hindrance



no steric hindrance

Only face-sharing octahedra or moieties with a common corner of two octahedra may be formed without steric hindrance[4]—or alternatively monomeric species are formed. In this paper we describe the preparation and characterization of a series of monomeric complexes of molybdenum(0–VI) containing the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (L). The preparation and characterization of dinuclear species will be reported in a subsequent paper.

Experimental Section

Preparation of Complexes. All compounds gave satisfactory elemental analyses (C, H, N, halides, Mo), which are available as supplementary material. The ligand 1,4,7′-trimethyl-1,4,7-triazacyclononane has been prepared as described previously.[4] The perchlorate salts are potentially hazardous; they may explode upon heating. Only small quantities were prepared.

$[LMo(CO)_3]$. A solution of $Mo(CO)_6$ (3.1 g) and 12 mmol of 1,4,7-trimethyl-1,4,7-triazacyclononane (L) in dry dimethylformamide (DMF) was refluxed for 8 h under an argon atmosphere. Yellow microcrystals were formed, which were filtered off after cooling to 5 °C, washed with ether, and air-dried. The yields were ca. 70% with respect to $Mo(CO)_6$.

$[LMo(CO)_3Br]X$ ($X = Br_3^-$, ClO_4^-, PF_6^-). $LMo(CO)_3$ (0.7 g) was dissolved in 40 mL of $CHCl_3$, and a solution of bromine (1.6 g) in 10 mL of $CHCl_3$ was added. The solution was refluxed for 1.5 h. After the mixture was cooled, an orange-brown precipitate was filtered off, rapidly washed with small amounts of cold $CHCl_3$ and ether, and air-dried; yield 1 g of $[LMo(CO)_3Br]Br_3$. The PF_6^- or ClO_4^- (*Caution*: explosive) salts were obtained from hot solutions of $[LMo(CO)Br]Br_3$ in 0.1 M HBr by adding saturated aqueous solutions of $NaPF_6$ and $NaClO_4$, respectively.

$[LMo(CO)_3I]I_3$. The above procedure using iodine as oxidant instead of bromine was used to prepare red-brown $[LMo(CO)_3I]I_3$. This material decomposes slowly within 2 weeks in the solid state.

$[LMoCl_3]$. $LMo(CO)_3$ (0.36 g) was suspended in 20 mL of CCl_4 under an argon atmosphere, and 4 mL of $SOCl_2$ was added dropwise with stirring. The suspension was refluxed for 4.5 h, after which time the yellow precipitate was filtered off, washed with CCl_4 and ether, and air-dried; yield 85%. The complex is soluble in DMF, Me_2SO, and acetonitrile without decomposition and was recrystallized from dilute hydrochloric acid. The material is stable in air for many weeks. The same product was obtained when $LMo(CO)_3$ was reacted with concentrated HCl at 25 °C for 24 h.

$[LMoBr_3]$. To $LMo(CO)_3$ (0.9 g) in 40 mL of $CHCl_3$ was added a solution of bromine (0.8 g) in 10 mL of $CHCl_3$, and the mixture was refluxed for 22 h. After cooling of the solution the yellow precipitate was filtered off, washed with ethanol and ether and air-dried; yield 0.9 g. An identical product was obtained by reacting $LMo(CO)_3$ with concentrated HBr at 25 °C (48 h). The $LMoBr_3$ complex is stable in air; it is soluble in acetonitrile, DMF, and Me_2SO without decomposition. The compound was recrystallized from hot, dilute HBr. $LMoBr_3$ is not soluble in water and not air-sensitive.

$[LMoI_3]$. A suspension of 0.36 g of $LMo(CO)_3$ in 25 mL of concentrated HI was refluxed for 4.5 h. Upon cooling and addition of 20 mL of water orange crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried; yield 0.45 g. The material is soluble in CH_3CN, DMF, and Me_2SO, and not in water. The complex is stable in air and does not decompose in the solid state for weeks.

$[LMo(NCS)_3]$. $[LMo(CO)_3Br]Br_3$ (0.35 g) in 30 mL of argon-scrubbed water and 0.97 g of NaSCN were refluxed for 2 h under an argon atmosphere. The suspension was cooled, and a red-orange precipitate was filtered off, washed with ethanol and ether, and air-dried; yield 0.15 g. The complex is air stable and soluble in organic solvents (DMF, Me_2SO, CH_3CN) and insoluble in water.

$[LMoBr_3]X$ ($X = PF_6^-$, ClO_4^-). A 0.25-g amount of $MoLBr_3$ was dissolved in 15 mL of concentrated HNO_3 at 22 °C. A deep red solution was obtained immediately, from which, upon addition of saturated aqueous solutions of $NaPF_6$ and $NaClO_4$, analytically pure red crystals precipitated after standing for 24 h in the refrigerator. The crystals were filtered off and air-dried; yield 0.1 g. The compounds are soluble in CH_3CN and Me_2SO. In ethanol the original red color fades and yellow $MoLBr_3$ is obtained.

$[LMoOCl_2]PF_6$. A 0.38-g amount of $MoLCl_3$ was dissolved in 15 mL of concentrated HNO_3 at 25 °C. To the now yellow solution 5 mL of water was added dropwise, which initiated a color change to green. The solution was stirred for 4 h at 25 °C, after which time 5 mL of a saturated aqueous solution of $NaPF_6$ was added. After 24 h in the refrigerator green crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried. $[LMoOCl_2]ClO_4$ and $[LMoOCl_2]Br_3$ were prepared analogously with use of saturated solutions of $NaClO_4$ and NaBr (*Caution*! Br_2 is formed). The three salts are soluble in CH_3CN, DMF, CH_2Cl_2, and acetone and produce green solutions. In cold water they are only moderately soluble but in hot water they are very soluble without decomposition or hydrolysis.

$[LMoOBr_2]PF_6$. $MoLBr_3$ (0.3 g) was dissolved in 20 mL of 7 M HNO_3. The resulting red color changes slowly to green. After 14 h at 25 °C a saturated, aqueous solution of $NaPF_6$ was added to initiate the precipitation of a green solid material, which was filtered off, washed with ethanol and ether, and air-dried. $[LMoOBr_2](ClO_4)$ and $[LMoOBr_2]Br_3$ were prepared from such solutions with use of $NaClO_4$ and NaBr, respectively. Solubility and stability are as described for $[LMoOCl_2]X$.

$[LMoOI_2]PF_6$. $MoLI_3$ (0.32 g) suspended in 20 mL of 6 M HNO_3. This suspension was heated to 60 °C for 10 min, yielding a deep green, clear solution. Addition of a saturated, aqueous solution of $NaPF_6$ yielded a green precipitate, which was filtered off, washed with ether, and air-dried: yield 0.2 g. The complex is soluble in CH_3CN, CH_2Cl_2, or acetone.

$[LMoO_2Br]Br_3$. $[MoL(CO)_3Br]Br_3$ (0.67 g) was dissolved in 35 mL of concentrated HNO_3 (*Caution*! Br_2). The orange solution was stirred for 1 h at 25 °C. Then 5 mL of a saturated solution of NaBr was added (*Caution*! Br_2). A yellow solid precipitated, which was filtered off, washed with ethanol and ether, and air-dried; yield 0.3 g. From aqueous solutions of this complex the perchlorate or hexafluorophosphate salt was obtained by adding $NaClO_4$ and $NaPF_6$, respectively. The salts are soluble in CH_3CN, CH_2Cl_2, and H_2O without decomposition.

X-ray Structural Determination of $[MoLBr_3](PF_6)$. A crystal of $[MoLBr_3](PF_6)$ (0.4 × 0.4 × 0.1 mm) was attached to the end of a glass fiber and mounted on a Syntex R3 four-circle diffractometer. The unit cell parameters were obtained at 22 °C by least-squares refinements of the respective angular setting of 32 reflections (Table II). Intensity data were corrected for Lorentz and polarization effects; an empirical correction of absorption effects has been carried out.[5] The scattering factors for neutral atoms were corrected for both the real and imaginary components of anomalous dispersion. The function minimized during least-squares refinements was $(\sum||F_o| - |F_c||)^2$. The structure was solved via three-dimensional Patterson synthesis and subsequent Fourier syntheses, which yielded the positions of all non-hydrogen atoms. The PF_6^- anions were found to be statistically disordered. The structure was refined smoothly with use of a model for this disorder that included two distinct orientations of the PF_6 octahedron for each of the six fluorine ligands with an occupancy of 0.5. Positions of the hydrogen atoms were calculated (based upon d(C–H) of 0.97 Å and regular tetrahedral geometry about the carbon atoms). Attempts to refine the structure in the acentric space group C_{2v}^5 failed; the refinements did not converge to an acceptable R value. Tables of anisotropic thermal parameters, observed and calculated structure factors, and calculated positional parameters of hydrogen atoms are given as supplementary material. Atomic parameters are given in Table III.

Electrochemical Measurements. All electrochemical measurements were performed with Princeton Applied Research equipment, which included the Model 173/175/179. The electrochemical cell (Metrohm) used for cyclic voltammetry employed a planar platinum electrode (0.071 cm^2) as the working electrode, a platinum pin as the counter electrode, and a Ag/AgCl reference electrode. The reference electrode was filled with a saturated solution of lithium chloride in absolute ethanol, which was connected to the sample solution via a liquid junction. The supporting electrolyte was in all cases a 0.1 M solution of tetra-*n*-butylammonium hexafluorophosphate in acetonitrile. Purification of the solvent was achieved according to a published procedure.[15] [N(*n*-

---

(4) Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 3086.

(5) Computations were carried out on a Nova (General Data) computer using the SHELXTL program package (Revision 3.0, July 1981) by G. M. Sheldrick, University of Göttingen.

Table I. UV-Visible Spectra[a] (λ, nm (ε, L mol^{-1} cm^{-1})), IR Data (cm^{-1}), and Magnetic Moments (μ_{eff}, μ_B)

complex	color	UV-vis	IR	μ_{eff} (298 K)
[LMo(CO)$_3$]	yellow		ν(CO): 1880 (vs), 1750 (s, sh)	diamag
[LMo(CO)$_3$Br]$^+$	orange		ν(CO): 2015 (vs), 1945 (s), 1925 (s)	diamag
[LMoCl$_3$]	yellow	315 (410), 355 (246), 421 (130) 684 (16)[b]		3.78
[LMoBr$_3$]	orange-yellow	245 (1 × 10^3), 279 (1.3 × 10^3), 426 (324) 698 (19)[b]		3.69
[LMoI$_3$]	orange	332 (2.6 × 10^3), 385 (5.8 × 10^3), 469 (132) 732 (66)		3.9
[LMo(NCS)$_3$]	orange-red	349 (7.12 × 10^3)[b]		3.4
[LMoBr$_3$]ClO$_4$	red	269 (3.1 × 10^3), 360 (3.1 × 10^3), 490 (1.2 × 10^3)		2.2
[LMoOCl$_2$]PF$_6$	green	357 (1.4 × 10^3), 656 (11)	ν(Mo=O): 970 (vs)	1.87
[LMoOBr$_2$]PF$_6$	green	429 (170), 674 (10)	ν(Mo=O): 965 (vs)	1.9
[LMoOI$_2$]PF$_6$	green	361 (2.8 × 10^3), 469 (7.7 × 10^2), 663 (1.4 × 10^3)	ν(Mo=O): 960 (vs)	1.85
[LMoO$_2$Br]PF$_6$	yellow		ν(Mo=O): 930 (vs), 900 (vs)	diamag

[a] Measured in acetonitrile unless noted otherwise. Abbreviations: vs = very strong, s = strong, sh = shoulder. [b] Measured in DMF.

Table II. Summary of Crystal Data and Data Collection Parameters of [MoLBr$_3$]PF$_6$ at 22 °C

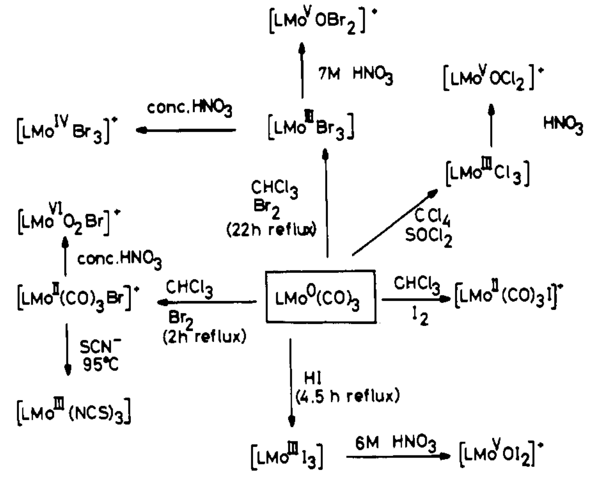
formula	[C$_9$H$_{21}$N$_3$MoBr$_3$](PF$_6$)
fw	651.9
cryst syst	orthorhombic
space group	*Pbcm*-D_{2h}^{11}
a, Å	7.642 (2)
b, Å	15.232 (4)
c, Å	16.275 (1)
V, Å^3	1890
Z	4
d_{calcd}, g cm^{-3}	2.29
μ(Mo Kα), cm^{-1}	70.98
diffractometer	Syntex R3
radiation	Mo Kα (λ = 0.71069 Å)
monochromator	graphite
scan method	ϑ-2ϑ (3 < 2ϑ < 55°)
no. of unique data	1048 ($I \geqslant 2.5\sigma(I)$)
no. of variables refined	118
std reflcns	2 every 150 reflcns, no decay obsd
octants	+*h*,+*k*,+*l*
R_1	0.075
R_2	0.066
weighting factor *w*	$1/\sigma(F)^2$

Table III. Atom Coordinates (×10^4)

atom	*x*	*y*	*z*
Mo	−6.4 (3)	−129 (1)	2500
Br1	1182 (3)	792 (2)	3594 (1)
Br2	2187 (5)	−1197 (2)	2500
N1	−1706 (17)	−917 (9)	1632 (8)
N2	−2622 (26)	590 (13)	2500
C1	−3118 (34)	−353 (19)	1309 (16)
C2	−3631 (34)	351 (13)	3261 (19)
C3	−2307 (28)	−1747 (11)	2075 (14)
C4	−776 (27)	−1296 (14)	921 (11)
C5	−2422 (34)	1612 (15)	2500
P1	5962 (9)	2500	0
F1	5408 (19)	2621 (10)	930 (6)
F2	4102 (17)	2812 (9)	−276 (9)
F3	5272 (19)	1523 (7)	46 (10)
F4	7807 (15)	2162 (8)	306 (8)
F5	6658 (19)	3459 (7)	−15 (10)
F6	6520 (20)	2355 (11)	−907 (7)

Bu)$_4$]PF$_6$ (Fluka) 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 with stirring to yield ~10^{-3} M concentrations of the respective complexes. Cyclic voltammograms were recorded at scan rates from 5 to 250 mV s^{-1} in order to obtain criteria for electrochemical and electrode kinetic reversibility of the systems.[16] Then an equimolar amount of ferrocene was added as internal standard. The formal redox potentials are given vs. the reference electrode system ferrocenium/ferrocene (Fc$^+$/Fc) in volts.[17,18] Coulometric analyses were performed under an argon atmosphere with use of a platinum-net electrode at controlled potentials. Solutions of the supporting electrolyte were preelectrolyzed, and after addition of the sample the electrolyses were controlled via current–time curves.

Scheme I



Instrumentation. The magnetic susceptibilities of powdered samples were measured by using the Faraday method between 95 and 298 K, and diamagnetic corrections were applied with use of published tables.

Mass spectra were recorded on a Finnigan MAT CH-5 instrument with direct inlet, 70 eV, and an ion source temperature of 250 °C.

Electronic spectra of complexes dissolved in acetonitrile were recorded on a Unicam SP8-100 spectrophotometer.

Results and Discussion

Synthesis of Complexes. Scheme I summarizes the synthetic routes to various monomeric complexes of molybdenum in the oxidation states II–VI using the readily accessible LMo(CO)$_3$ as starting material. Controlled oxidation by bromine or iodine of this complex leads to cationic species [LMo^{II}(CO)$_3$X]$^+$ (X = Br, I). These cations are probably seven-coordinate with a 4:3 piano-stool configuration as has been previously reported for the analogous [([9]aneN$_3$)Mo(CO)$_3$Br](ClO$_4$)·H$_2$O, where the tridentate ligand 1,4,7-triazacyclononane occupies three and the carbonyl and bromide ligands four coordination sites.[6] The ^{95}Mo NMR signal of [LMo(CO)$_3$Br](PF$_6$), which was measured at room temperature in acetonitrile, occurs at +174 ppm (line width 300 Hz).[26] The [LMo(CO)$_3$Br]$^+$ complex is the most deshielded Mo(II) complex known to date. The analogous CpMo(CO)$_3$X complexes have chemical shifts from −836 to −1248 ppm.[27]

Prolonged reaction times in the absence of water leads to complete removal of carbonyl ligands, and molybdenum(III) complexes LMoX$_3$ (X = Cl, Br, I) are obtained. The thiocyanato analogue is formed by reaction of [LMo(CO)$_3$Br]Br$_3$ with NCS$^-$.

---

(6) Wieghardt, K.; Chaudhuri, P.; Tsai, Y.; Krüger, C. *Inorg. Chem.* **1984**, *23*, 427.

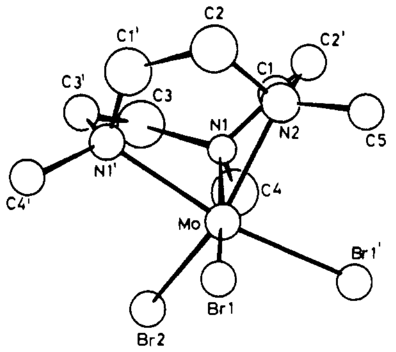


Figure 1. Perspective view of the cation $[MoLBr_3]^+$ showing atom labels used in the tables.

These molybdenum(III) complexes are not air sensitive in the solid state or in solution. They are soluble in organic solvents such as dimethylformamide, dimethyl sulfoxide, dichloromethane, ethanol, etc., but only sparingly in water. The monomeric nature of these complexes is bolstered by the fact that excellent mass spectra were obtained exhibiting molecular ion peaks of $[MoLX_3]^+$ (X = Cl, *m/e* 374; Br, *m/e* 508; I, *m/e* 650) with the expected isotopic pattern. $LMo(CO)_3$ also gives a molecular ion peak at *m/e* 353.

Oxidation of $LMoX_3$ (X = Cl, Br, I) with concentrated nitric acid generates monomeric oxo complexes of molybdenum(V) of the type $[LMo^VOX_2]^+$ (X = Cl, Br, I). Oxidation of $[LMo(CO)_3Br]^+$ with nitric acid yields $[LMoO_2Br]^+$, a molybdenum(VI) species. The oxo–molybdenum(V) complexes show strong absorptions in the infrared region at ~965 cm^{-1}, which are assigned to the ν(Mo=O) stretching frequency. $[LMoO_2Br]^+$ exhibits two such bands at 900 and 930 cm^{-1} indicative of a *cis*-dioxomolybdenum(VI) moiety. Since perchlorate and hexafluorophospate salts are obtained, an octahedral environment of the molybdenum(V) and -(VI) centers is proposed.

Interestingly, during the oxidation of $LMoBr_3$ by nitric acid an immediate rapid color change to deep red and then slowly to green is observed. From such solutions it has been possible to isolate a red hexafluorophosphate salt of $[LMoBr_3](PF_6)$, a molybdenum(IV) complex, and at a later stage of the reaction green $[LMoOBr_2](PF_6)$ has been precipitated, a molybdenum(V) species. $[LMoBr_3]^+$ is a strong oxidant, as is shown from its quite positive redox potential. Mild reductants such as ethanol quantitatively produce $[MoLBr_3]$. The chemistry described here is very similar to reactions of $[HB(3,5\text{-}Me_2pz)_3Mo(CO)_3]^-$ and $[HB(3,5\text{-}Me_2pz)_3MoCl_3]^-$, which also yield monomeric complexes of Mo(IV) and Mo(V)[7,8] $(HB(3,5\text{-}Me_2pz)_3^-$ is the facially coordinating tridentate ligand hydrotris(3,5-dimethyl-1-pyrazolyl)borate). The observed magnetic moments of the various complexes (Table I) are in good agreement with the monomeric nature of the respective species and the assigned oxidation state. Thus all molybdenum(V) complexes are paramagnetic with magnetic moments $\mu_{eff}(298\text{ K}) \approx 1.9\ \mu_B$, which is characteristic for oxo–molybdenum(V) complexes with a d^1 configuration.[1] Similarly, the magnetic moments of paramagnetic $LMoX_3$ ($\mu_{eff}(298\text{ K}) \approx 3.6\ \mu_B$) are typical for monomeric molybdenum(III) species with a d^3 configuration. $\mu_{eff}(298\text{ K})$ for $LMoBr_3(ClO_4)$ was found to be 2.2 μ_B, which is well in the range of 1.9–2.8 μ_B observed for six-coordinate halo and pseudohalo complexes of molybdenum(IV). Carbonyl complexes of molybdenum(0) and -(II) reported here are diamagnetic; they adhere to the EAN rule. $[LMoO_2Br](PF_6)$ is also diamagnetic (d^0).

Details of the electronic spectra are given in Table I. Solution spectra of $[LMoOX_2]^+$ in acetonitrile exhibit absorption maxima in the visible region (~660 and ~460 nm) of low intensities. This behavior has been found for many $[MoOX_5]^{2-}$ species (X = halogen) and is characteristic for oxo–molybdenum(V) complexes.[1] In the $LMoX_3$ complexes the symmetry of the MoN_3X_3 skeleton is less than octahedral (C_{3v}). In agreement with previously reported spectra for $MoCl_3(NC(CH_2)_2CH_3)_3$ three transitions are observed for $LMoX_3$ species (~700, ~420, and ~350 nm).[9,10]

Table IV. Bond Distances (Å) and Angles (deg)[a] of $[LMoBr_3]^+$

Mo-Br1	2.458 (3)	Mo-N1	2.237 (13)
Mo-Br2	2.365 (4)	Mo-N2	2.236 (20)
N1-C1	1.474 (30)	N2-C2	1.50 (3)
N1-C3	1.53 (2)	N2-C5	1.56 (3)
N1-C4	1.474 (23)	C1-C2	1.34 (4)
Br2-Mo-Br1	96.5 (1)	N1-Mo-Br2	92.1 (4)
N1-Mo-Br1	168.5 (4)	N2-Mo-Br2	165.8 (5)
N2-Mo-Br1	93.3 (4)	Br1'-Mo-Br2	96.5 (1)
Br1'-Mo-Br1	92.9 (1)	N1'-Mo-Br2	92.1 (4)
N1'-Mo-Br1	93.7 (3)	N2-Mo-N1	77.0 (5)
Br1'-Mo-N2	93.3 (4)	Br1'-Mo-N1	93.7 (3)
N1'-Mo-N2	77.0 (5)	N1'-Mo-N1	78.3 (7)
Br1'-Mo-N1'	168.5 (5)		

[a] Values for the MoN_3Br_3 octahedron are given only.

Table V

complex[a]	av Mo-N, Å	av Mo-Br, Å	oxidn no. of Mo	ref
$[L'_2Mo(CO)_3Br]^+$	2.26	2.68	II	6
$[L'_2Mo(\mu\text{-}OH)_2]^{2+}$	2.22		III	3
$[L'_2Mo(\mu\text{-}OH)_2(\mu\text{-}OAc)]^{3+}$	2.22		III	3
$[MoBr_3(C_6H_7N)_3]$	2.21	2.57	III	11-13
$[LMoBr_3]^+$	2.24	2.43	IV	this work
$[L'_2Mo(\mu\text{-}O)_2O_2]^{2+}$	2.22		V	2

[a] L' = 1,4,7-triazacyclononane; L = 1,4,7-trimethyl-1,4,7-triazacyclononane.

Crystal Structure of $[MoLBr_3](PF_6)$. The molecular geometry and the atomic labeling scheme for the cation $[MoLBr_3]^+$ are shown in Figure 1. Bond distances and bond angles are listed in Table IV. The structure consists of discrete $[MoLBr_3]^+$ cations and well-separated PF_6^- anions. The molybdenum(IV) center is in a pseudooctahedral environment of the facially bound cyclic triamine and three bromo ligands. The cation possesses a crystallographically imposed mirror plane; atoms Mo, Br2, N2, and C5 lie on this plane. Mo–Br distances of 2.458 (3) Å for Mo–Br1 and Mo–Br1' and 2.365 (4) Å for Mo–Br2 are found, which is considerably shorter than the 2.676 (1) Å found in the seven-coordinate cation $[Mo([9]aneN_3)(CO)_3Br](ClO_4)\cdot H_2O$, where the molybdenum center has a formal oxidation state of II.[6] They are also shorter than distances reported for molybdenum(III)–bromo complexes $MoBr_3X_3$ (average 2.57 (1) Å),[11-13] which agrees well with the increased oxidation number of IV. In $MoBr_4(PPh(CH_3)_2)_3$—a seven-coordinate complex of Mo(IV)—two Mo–Br bond distances of 2.560 (5) and 2.425 (7) Å have been reported.[14] Due to the steric constraints of the cyclic triamine the Mo–N bond distances do not vary extensively as a function of the respective oxidation state of the molybdenum centers (Table V).

It is noted that the carbon atoms of the five-membered rings, Mo–N–C–C–N, exhibit unusually large anisotropic temperature factors. Due to the crystallographically imposed mirror plane the respective conformations of the three five-membered rings are

---

[7] Trofimenko, S. *Inorg. Chem.* **1971**, *10*, 504.

[8] Lincoln, S. S.; Koch, S. A. *J. Am. Chem. Soc.* **1982**, *104*, 288.

[9] Westland, A. D.; Murüthi, N. *Inorg. Chem.* **1972**, *11*, 2971.

[10] Morita, T. S.; Sasaki, Y.; Saito, K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2678.

[11] Brenčic, J. V.; Leban, I.; Slokar, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B26*, 698.

[12] Brenčic, J. V.; Leban, I. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1292.

[13] Brenčic, J. V.; Leban, I. *Z. Anorg. Allg. Chem.* **1978**, *445*, 251.

[14] Drew, M. G. B.; Wilkins, J. D.; Wolters, A. P. *J. Chem. Soc., Chem. Commun.* **1972**, 1278.

[15] Walter, M.; Ramaley, L. *Anal. Chem.* **1973**, *45*, 165.

[16] Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

[17] Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1982**, *54*, 1527.

[18] Gagnê, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2855.

Table VI. Summary of Electrochemical Data at 25 °C

couple	complex	E^f vs. Fc$^+$/Fc, V[a]	ΔE_p, mV[b]	$i_{p,b}/i_{p,f}$[c]	cf, μA V$^{-1/2}$ s$^{1/2}$ mmol^{-1} L[d]
Mo(I/0)	$[LMo(CO)_3]^{+/0}$	−0.245	68	*f*	66
		−0.180[e]			136
Mo(II)	$[LMo(CO)_3Br]^+$	*g*			
Mo(IV/III)	$[LMoCl_3]^{+/0}$	+0.395	65	0.8	66
	$[LMoBr_3]^{+/0}$	+0.50	72	0.9	89
	$[LMoI_3]^{+/0}$	+0.525	65	*f*	67
	$[LMo(NCS)_3]^{+/0}$	+0.53	68	0.8	83
Mo(III/II)	$[LMo(NCS)_3]^{0/-}$	−2.00	68	1.1	79
Mo(V/IV)	$[LMoOCl_2]^{+/0}$	−0.52	65	1.0	72
	$[LMoOBr_2]^{+/0}$	−0.40	70	0.9	69
Mo(VI/V)	$[LMoO_2Br]^{+/0}$	−0.695	70	0.9	58

[a] Formal redox potentials in volts vs. the reference system ferrocenium (Fc$^+$)/ferrocene (Fc); $E^f_{Fc^+/Fc} = +0.535$ V vs. Ag/AgCl. [b] Peak potential difference at a scan rate of 50 mV s^{-1}. [c] Peak current ratio. [d] Peak current function of the oxidation: $i_{p,ox}v^{-1/2}c_0^{*-1}$. [e] Peak potential of the oxidation with 0.1 M $[N(t\text{-}Bu)_4]Br$ in acetonitrile as supporting electrolyte. [f] Dependent on scan rate. [g] Electrochemically inactive in the potential range +1.8 to −2.0 V (vs. Ag/AgCl).

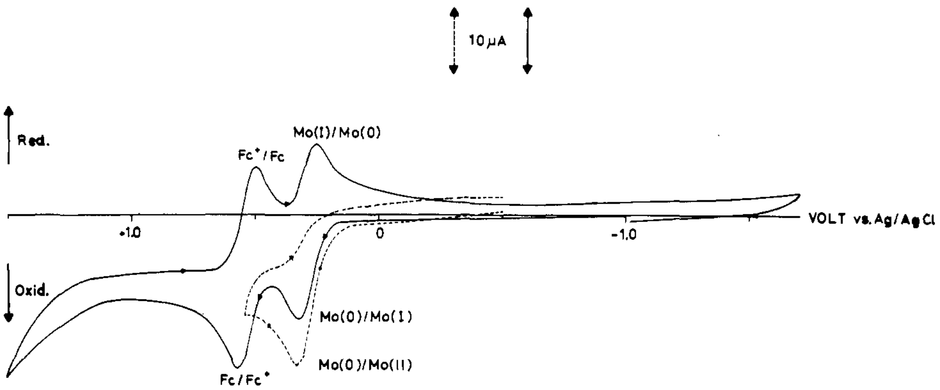


Figure 2. Cyclic voltammograms of $[LMo(CO)_3]$ in acetonitrile at 25 °C: (solid line) $[Mo^0] = 1.3 \times 10^{-3}$ M, 0.1 M $[TBA]PF_6$, and ferrocene as internal standard (1×10^{-3} M) at a scan rate of 50 mV s^{-1}; (broken line) $[Mo^0] = 1 \times 10^{-3}$ M with [TBA]Br (0.1 M) as supporting electrolyte.

(λλλ), (δδδ), and one ring with no such conformation at all, Mo–N1′–C3′–C3–N1. This represents a very unusual situation since in all structures determined by X-ray diffraction with cyclic triamines 1,4,7-triazacyclononane and 1,4,7-trimethyl-1,4,7-triazacyclononane in the facial coordination mode the conformations of all *three* rings were found to be either (λλλ) or (δδδ).[2-4,6] It is conceivable that in the above structure a statistical distribution of cations with these conformations mimics the unusual situation found in the present structure, which effects the artificially large anisotropic thermal parameters of the ring-carbon atoms.

Electrochemistry. Electrochemical data of complexes are summarized in Table VI. The cyclic voltammogram of $LMo(CO)_3$ exhibits one oxidation and one reduction peak in the potential range between −1.70 and +1.50 V vs. Ag/AgCl (Figure 2) in the absence of coordinating anions (supporting electrolyte $[N(n\text{-}Bu)_4]PF_6$). The peak potential difference of 68 mV indicates reversible behavior of the one-electron-transfer process since an identical value is observed for the couple ferrocenium/ferrocene. The formal redox potential for the couple $[LMo(CO)_3]^+/[LMo(CO)_3]$ is −0.245 V vs. Fc$^+$/Fc. The peak current function of the oxidation is independent of scan rate, and the value of 66 μA V$^{-1/2}$ s$^{1/2}$ mmol^{-1} L is in good agreement with those of all reversible one-electron-transfer reactions reported here (Table VI) (cf. 72 ± 8 μA V$^{-1/2}$ s$^{1/2}$ mmol^{-1} L). The peak current function of the reduction is slightly dependent on the scan rate, indicating slow decomposition of the Mo(I) species.

In the presence of bromide ions (supporting electrolyte $[N(n\text{-}Bu)_4]Br$) only one oxidation peak at −0.18 V vs. Fc$^+$/Fc is observed with a peak current function of 136 μA V$^{-1/2}$ s$^{1/2}$ mmol^{-1} L, which is about twice the value observed for reversible one-electron processes. This indicates an irreversible two-electron oxidation of $[LMo(CO)_3]$ and formation of $[LMo(CO)_3Br]^+$. This species has also been prepared chemically via bromine oxidation of $[LMo(CO)_3]$. This complex was found to be electrochemically inactive in the potential range employed. Thus the electrochemistry is represented by eq 1 and 2.

$$[LMo(CO)_3] \underset{+e^-}{\overset{-e^-/[TBA]PF_6}{\rightleftharpoons}} [LMo(CO)_3]^+ \qquad (1)$$

$$[LMo(CO)_3] + Br^- \xrightarrow{-2e^-/[TBA]Br} [LMo(CO)_3Br]^+ \qquad (2)$$

Similar results have been reported for the electrochemistry of complexes of the type $L^1Mo(CO)_3$, where L^1 represents tridentate macrocycles with P,N,S,As donor atoms. The reversibility of Mo(O)/Mo(I) electron-transfer reactions in CH_2Cl_2 disappeared also in the presence of coordinating ligands.[19] Trofimenko[20] has postulated two electrochemical processes for $[HB(pyz)_3Mo(CO)_3]^-$ ($HB(pyz)_3^-$ = hydrotripyrazolylborate, a facially coordinating tridentate ligand) without giving details concerning number of transferred electrons or reversibility. This system is interesting since the ligand is very similar to ours. The two-electron reduction of seven-coordinate complexes $[Mo(CO)_3(L^2)_2X_2]$ ($L^2 = PPh_3$; X = Cl$^-$, Br$^-$, I$^-$) has also been reported,[21] but the intermediate Mo(I) species were not detected.

Cyclic voltammograms of $[MoLX_3]$ complexes (X = Cl$^-$, Br$^-$, I$^-$) show one reversible electron-transfer process in the potential range between −1.5 and +1.5 V vs. Ag/AgCl. From the observed peak potential difference (65–70 mV) and coulometric oxidations of $Mo^{III}LX_3$ at an electrode potential of +1.5 V vs. Ag/AgCl (1.0 ± 0.05 electron/molecule) it is concluded that one-electron-transfer reactions according to eq 3 occur. Plots of the anodic peak current

$$[Mo^{IV}LX_3]^+ + e^- \rightleftharpoons [Mo^{III}LX_3] \qquad X = Cl, Br, I \qquad (3)$$

for the processes $[LMoX_3]^0 \rightarrow [LMoX_3]^+$ vs. the half-power of the scan rate (V$^{1/2}$ s$^{-1/2}$) are linear in all cases (Figure 3b), which

---

(19) Fox, M. A.; Campbell, K. A.; Kyba, E. P. *Inorg. Chem.* **1981**, *20*, 4163.
(20) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588.
(21) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1978**, *17*, 105.

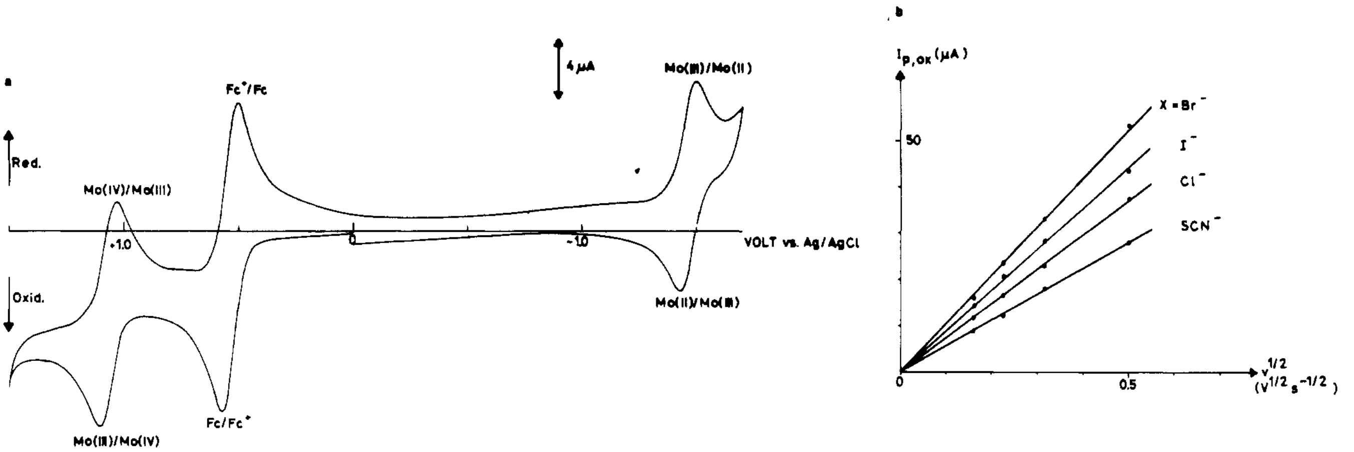


Figure 3. (a) Cyclic voltammogram of $[LMo(NCS)_3]$ (0.7×10^{-3} M) in acetonitrile with $[TBA]PF_6$ (0.1 M) as supporting electrolyte at a scan rate of 50 mV s^{-1} and ferrocene (0.6×10^{-3} M) as internal standard. (b) Anodic peak current of $[LMoX_3]^0 \rightarrow [LMoX_3]^+$ as a function of the scan rate.

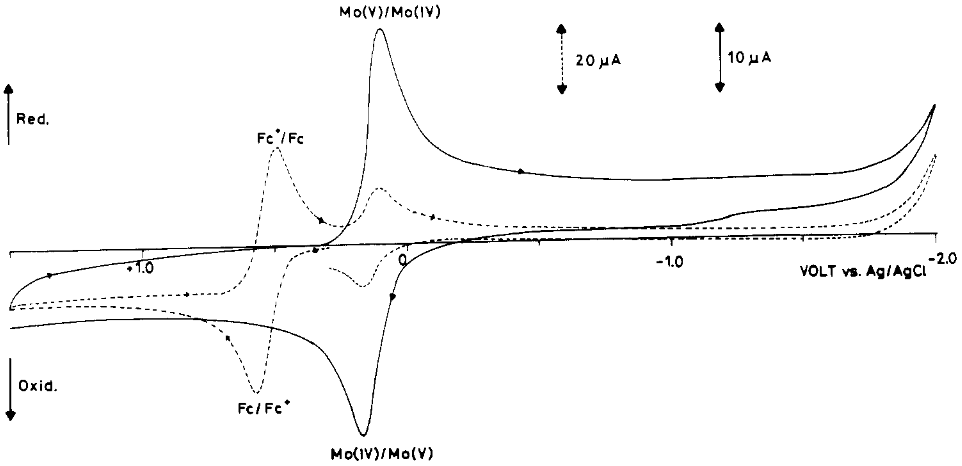


Figure 4. Cyclic voltammogram of $[LMoOBr_2]PF_6$ (1×10^{-3} M) with (broken line) and without (solid line) ferrocene as internal standard in acetonitrile and 0.1 M $[TBA]PF_6$ as supporting electrolyte (scan rates 50 and 250 mV s^{-1}, respectively).

indicate diffusion-controlled electron transfer at the electrode.[16]

During the electroanalytical oxidation of $MoLX_3$ species a color change of the solutions from yellow to red-brown is observed. The electronic spectrum of the oxidized solution of $[MoLBr_3]$ was found to be identical with that recorded for a genuine sample of $[MoLBr_3](PF_6)$. A solution containing the cation $[MoLCl_3]^+$ also exhibits three absorption maxima (226, 310, and 435 nm). The cation $[MoLI_3]^+$ decomposes slowly on the time scale of a cyclic voltammetric experiment as was deduced from a small dependence of the peak current ratio on the scan rate.

The cyclic voltammogram of $[MoL(SCN)_3]$ in acetonitrile (Figure 3a) exhibits two reversible one-electron-transfer reactions in the potential range between −1.7 and +1.5 V vs. Ag/AgCl, which are assigned to the couples Mo(IV)/Mo(III) and Mo(III)/Mo(II) according to eq 4.

$$[LMo^{IV}(NCS)_3]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [LMo^{III}(NCS)_3]^0 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [LMo^{II}(NCS)_3]^- \quad (4)$$

Thus all Mo(III) complexes of the type $[MoLX_3]$ (X = Cl, Br, I, SCN) are reversibly oxidized electrochemically to the corresponding Mo(IV) species, $[MoLX_3]^+$. The redox potentials for these Mo(IV)/Mo(III) couples are quite positive and span the relatively small range from +0.395 V ($X = Cl^-$) to +0.53 V ($X = SCN^-$) vs. the Fc^+/Fc couple. The order of increasing positive redox potentials as a function of X^- is found to be $SCN^- \approx I^- > Br^- > Cl^-$. Thus the small chloride ligand stabilizes the +IV oxidation state of the molybdenum centers to a larger extent than do the sterically more demanding ligands iodide or thiocyanide. The nonbonding interactions between the X^- ligands are reduced in the +III oxidation state of molybdenum since the Mo–X bond lengths are longer; they increase in the +IV oxidation state, where shorter Mo–X distances are observed. Therefore, small ligands stabilize Mo(IV) centers as compared to the case for their Mo(III) analogues and vice versa.

As a general result of this and other studies[8,22] on the electrochemistry of Mo(III) complexes of the type $[MoLX_3]$, where X represents Cl, Br, and I and L is a tridentate nitrogen donor ligand, the surprisingly large stability of these molybdenum(III) complexes toward redox reactions emerges. Millar et al. have in their paper[8] ascribed this property to a π-acceptor function of the tripyrazolylborate ligand. It is therefore interesting to note that our complexes with the 1,4,7-trimethyl-1,4,7-triazacyclononane ligand are also very stable toward oxidation and reduction although the ligands cannot be regarded as π-acceptors. The $[Mo^{IV}LX_3]^+$ species are strong one-electron oxidants, and no disproportionation reactions have been observed. Only in the case of $[LMo^{III}(NCS)_3]$ is a reduction to the anionic species $[Mo^{II}L(NCS)_3]^-$ observed at a very negative potential in the potential range investigated. Contrary to the situation for the halide ligands the NCS^- ligand may function as a π-acceptor stabilizing the Mo(II) species. $[MoCl_3(py)_3]$ and $[Mo^{III}Cl_3HB(3,5\text{-}Me_2pz)_3]^-$ are also known to be reversibley reduced to the corresponding Mo(II) species.[8,22] In both instances the nonhalide ligands are good π-acceptor ligands.

The two monomeric complexes $[Mo^VLOX_2]^+$ dissolved in acetonitrile (X = Cl, Br) are reduced electrochemically to the corresponding neutral Mo(IV) complexes, $[Mo^{IV}LOX_2]$. The cyclic voltammogram of $[MoLOBr_2]^+$ is shown in Figure 4. One reversible one-electron-transfer reaction is observed in the potential range between +1.5 and −2.0 V vs. Ag/AgCl, which is adequately

---

[22] Millar, M.; Du Bois, D. W.; Iwamoto, R. T.; Kleinberg, J. *Inorg. Chem.* **1969**, *8*, 815.

described by eq 5. It is interesting to note that in acetonitrile

$$[\mathrm{LMoOX_2}]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{LMoOX_2}] \qquad X = \mathrm{Cl, Br} \qquad (5)$$

as solvent further oxidation to Mo(VI) or reduction to Mo(III) is not observed. This behavior has been observed previously.[23-25]

The cyclic voltammogram of $[\mathrm{LMoO_2Br}]\mathrm{PF_6}$ in acetonitrile exhibits one reversible electron transfer, which is assigned to the couple $[\mathrm{LMoO_2Br}]^+/[\mathrm{LMoO_2Br}]^0$. Excess of bromide ions of the supporting electrolyte affects the peak current ratio, $I_p(\mathrm{ox})/I_p(\mathrm{red})$ at scan rates smaller than 0.05 V s^{-1}. This indicates slow decomposition of the reduced species (most probably loss of Br^-) according to eq 6.

$$[\mathrm{LMoO_2Br}]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{LMoO_2Br}]^0 \rightleftharpoons \mathrm{Br}^- + \text{products} \qquad (6)$$

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie. We wish to thank Professor J. H. Enemark and Dr. M. Minelli (University of Arizona) for measuring the ^{95}Mo NMR spectrum.

Supplementary Material Available: Listings of thermal parameters, positional parameters of hydrogen atoms, observed and calculated structure factors, and elemental analyses of complexes (10 pages). Ordering information is given on any current masthead page.

---

(23) Isbell, A. F.; Sawyer, D. T. *Inorg. Chem.* **1971**, *10*, 2499.

(24) Taylor, R. D.; Street, J. P.; Minelli, M.; Spence, J. T. *Inorg. Chem.* **1978**, *17*, 3207.

(25) Spence, J. T.; Minelli, M.; Kroneck, P. *J. Am. Chem. Soc.* **1980**, *102*, 4538.

(26) Experimental details have been reported elsewhere: Minelli, M.; Enemark, J. H.; Wieghardt, K.; Hahn, M. *Inorg. Chem.* **1983**, *22*, 3952.

(27) LeGall, J. Y.; Kubicki, M. M.; Petillon, F. Y. *J. Organomet. Chem.* **1981**, *221*, 287.

Contribution from Exxon Research and Engineering Company,
Annandale, New Jersey 08801

Steric Effects in $[\mathrm{CpMoS}(\mu\text{-S})]_2$ Dimers Studied by Interactive Molecular Graphics

J. M. NEWSAM* and T. R. HALBERT

Received April 24, 1984

Interactive molecular graphics (IMG) has been applied to modeling steric effects in the sulfido-bridged molybdenum dimers, $[(\mathrm{C_5H_{5-n}Me_n})\mathrm{MoS}(\mu\text{-S})]_2$ (n = 0 and 5). This technique, which is already well established in other areas, proves to be a convenient means of probing steric effects in such organometallic complexes. It is shown that the intramolecular van der Waals energies of the syn isomers of these cyclopentadienyl derivatives are higher than those of the corresponding anti isomers for configurations that have been previously indicated to be electronically the most favorable.

Introduction

Systematic studies of the synthesis, structure, and reactivity of molybdenum(V) coordination complexes with sulfur-containing ligands are important in the search for an understanding of the active sites in molybdoenzymes[1] and in heterogeneous hydrotreating catalysts.[2] Among the more widely studied classes of such complexes is that containing the dinuclear $[\mathrm{MoS}(\mu\text{-S})]_2^{2+}$ core. A variety of well-characterized examples are known, in which the ligands L (L′) that complete the coordination about each molybdenum are a pair of monodentate S ligands, a chelating S,S or N,S ligand, or a cyclopentadienyl group.[3-12] Full structural details for a number of these complexes have been obtained by single-crystal X-ray diffraction. In each case, the molecular structure corresponds to one of the two geometric isomers shown in Figure 1, designated syn and anti. The "closed" form shown in Figure 1 has been suggested as a third possible isomer, but it has not yet been observed experimentally. The syn isomer is the more common, having been found for L = L′ = diethyldithiocarbamate,[4,5] dibutyldithiocarbamate,[6] tetrasulfide ($\mathrm{S_4}^{2-}$),[8] disulfide ($\mathrm{S_2}^{2-}$),[7] and 1,2-ethanedithiolate[9,10] and for L = disulfide and L′ = tetrasulfide.[8,11] The anti configuration was observed for L = 1,2-ethanedithiolate,[9,10] methylcyclopentadienyl,[12] and pentamethylcyclopentadienyl.[12] Only the 1,2-ethanedithiolate complex has been characterized in both configurations. The anti isomer was prepared in low yield (3%) from a complex reaction involving $\mathrm{MoCl_3}$, NaHS, NaOMe, and 1,2-ethanedithiol. The syn isomer was isolated (6% yield) from a mixture of the same reagents having a slightly different composition. Three higher yielding procedures that have been developed for synthesis of the complex[13] invariably result in the syn isomer. This is in keeping with the molecular orbital calculations of Lichtenberger et al.[16] that predicted relative stabilities in the order syn > closed > anti.

Given these relative stabilities, it is then somewhat intriguing that the cyclopentadienyl complexes have only been characterized

---

(1) Coughlan, M. P., Ed. "Molybdenum and Molybdenum-Containing Enzymes"; Pergamon Press: New York, 1980.

(2) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. "Chemistry of Catalytic Processes"; McGraw-Hill: New York, 1979; pp 390–445.

(3) Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Wherland, S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5102.

(4) Muller, A.; Bhattacharyya, R. G.; Mohan, N.; Pfefferkorn, B. *Z. Anorg. Allg. Chem.* **1979**, *454*, 118–124.

(5) Huneke, J. T.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3698.

(6) Spivack, B.; Dori, Z.; Stiefel, E. I. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 501.

(7) Pan, W.-H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459.

(8) Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baezinger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321–3332.

(9) Bunzey, G.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 682.

(10) Bunzey, G.; Enemark, J. H.; Howie, J. K.; Sawyer, D. T. *J. Am. Chem. Soc.* **1977**, *99*, 4168.

(11) Clegg, W.; Christou, G.; Garner, C. D.; Sheldrick, G. M. *Inorg. Chem.* **1981**, *20*, 1562.

(12) Rakowski Dubois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064–3071.

(13) $\mathrm{Mo_2S_4}(1,2\text{-ethanedithiolate})_2^{2-}$ has been prepared from the reaction of 1,2-ethanedithiol with $(\mathrm{NH_4})_2\mathrm{MoS_4}$,[14] with $(\mathrm{TEA})_2\mathrm{Mo_2S_8}$,[15] and with $(\mathrm{NH_4})_2\mathrm{Mo_2S_{12}}$.[3] In each case, yields of better than 50% could be obtained.

(14) Pan, W.-H.; Leonowicz, M. E.; Stiefel, E. I., unpublished work.

(15) Halbert, T. R., unpublished work.

(16) Chandler, T.; Lichtenberger, D. L.; Enemark, J. H. *Inorg. Chem.* **1981**, *20*, 75–77.

(17) Gelder, J. I.; Enemark, J. H. *Inorg. Chem.* **1976**, *15*, 1839–1843.