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Nitrosyl-, Halogeno-, and Oxomolybdenum Complexes with the Ligand 1-Thia-4,7-diazacyclononane (L). Crystal Structures of [LMo(CO)$_2$NO]PF$_6$, [LMo(NO)$_2$Cl]PF$_6$, LMoCl$_3$, and [L$_2$Mo$_2$O$_4$]ZnCl$_4$·H$_2$O

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The reaction of LM(CO)$_3$ (L = 1-thia-4,7-diazacyclononane; M = Mo, W) with nitrous acid (NaNO$_2$/HCl) yields the cationic nitrosyl complexes LM(CO)$_2$NO$^+$ and LM(NO)$_2$Cl$^+$, the ClO$_4^-$ or PF$_6^-$ salts of which were isolated as crystalline solids. The oxidation of LMo(CO)$_3$ by various oxidants such as Br$_2$, O$_2$, or HClO$_4$ affords mono- and dinuclear complexes with molybdenum in the oxidation states II, III, and V: [LMo^{II}(CO)$_3$Br]PF$_6$, LMo^{III}Cl$_3$, [L$_2$Mo$^{V}_2$O$_3$Cl$_2$](ClO$_4$)$_2$, and [*syn*-L$_2$Mo$^{V}_2$O$_4$](ClO$_4$)$_2$. The crystal structures of [LMo(CO)$_2$NO]PF$_6$ (**1**), [LMo(NO)$_2$Cl]PF$_6$ (**2**), LMoCl$_3$ (**3**), and [L$_2$Mo$_2$O$_4$]ZnCl$_4$·H$_2$O (**4**) have been determined. **1** and **2** contain hexacoordinated molybdenum centers with facial coordination of L. The NO groups are bound trans to the secondary amino groups of L. The Mo–NO distances are 1.874 (3) Å in **1** and 1.819 (7) and 1.824 (7) Å in **2**; the Mo–S distances are 2.522 (1) and 2.447 (2) Å, respectively. The thioether groups show π-acidity. **4** contains the bis(μ-oxo)bis[oxo(1-thia-4,7-diazacyclononane)molybdenum(V)] cation with the two Mo═O groups in the syn position. The macrocyclic ligands are rotationally disordered. Crystal data for **1**: monoclinic, space group $P2_1/n$; a = 8.333 (3), b = 21.684 (9), c = 8.609 (3) Å; β = 94.89 (3)°; Z = 4; final R = 0.027 for 2694 observed reflections. Crystal data for **2**: monoclinic, space group $P2_1/c$; a = 8.560 (7), b = 11.483 (8), c = 15.34 (1) Å; β = 91.36 (6)°; Z = 4; final R = 0.056 for 1864 observed reflections. Crystal data for **3**: orthorhombic, space group $Pn2_1a$; a = 12.594 (2), b = 11.041 (2), c = 8.139 (1) Å; Z = 4; final R = 0.017 for 1277 observed reflections. Crystal data for **4**: monoclinic, space group $P2_1/c$; a = 11.516 (5), b = 14.872 (5), c = 14.569 (6) Å; β = 102.02°; Z = 4; final R = 0.040 for 3924 observed reflections.

Introduction

The interest in the properties of complexes of small macrocyclic ligands with pure N or S donor atoms continues. A number of homoleptic, six-coordinate complexes of 1,4,7-trithiacyclononane containing later transition metals in lower oxidation states have recently been synthetized and characterized by X-ray crystallography.[1] The first complexes of the earlier first-row transition metals, of hard acids, have been reported as well.[2] A very interesting aspect is the discovery that both 1,4,7-triazacyclononane and 1,4,7-trithiacyclononane stabilize relatively high oxidation states of transition metals.[3,4]

Various aspects of the chemistry of complexes with the macrocyclic ligand with a mixed N$_2$S donor set, 1-thia-4,7-diazacyclononane, L, have been reported in recent papers.[5-7] Comparisons have been made with the ligands 1,4,7-triazacyclononane and 1,4,7-trithiacyclononane with respect to the ligating properties toward Pd^{2+}, Pt^{2+}, and Pb^{2+}, and with complexes of the open-chain ligand 3-thia-1,7-diazaheptane.[7] Recently the spectroscopic properties of complexes of the ligand 1-oxa-4,7-diazacyclononane, with a mixed ON$_2$ donor set, have been explored as well.[8]

In order to investigate the properties of 1-thia-4,7-diazacyclononane (=L) in more detail, we therefore studied the substitution and oxidative decarbonylation reactions of the readily accessible complex LMo(CO)$_3$ and prepared nitrosyl, halogeno, and oxo complexes of molybdenum in the oxidation states +I to +V with the central atom still attached to the small macrocycle. In this paper, we describe the preparation, characterization, and crystal structures of these complexes. Very extensive results on oxidation and substitution reactions of (1,4,7-triazacyclononane)molybdenum tricarbonyl have been published by Wieghardt and co-workers.[9] Comparison of our results with those of Wieghardt give a detailed picture of the ligating properties of 1-thia-4,7-diazacyclononane, which in contrast to 1,4,7-triazacyclononane may posses some π-acid character.

Experimental Section

1-Thia-4,7-diazacyclononane (L) and LM(CO)$_3$ (M = Mo, W) have been prepared as described previously.[7a] All other starting materials were commercially available. All new compounds gave satisfactory elemental analyses.

[LMo(CO)$_2$NO]PF$_6$. A 0.5-g (1.5-mmol) sample of LMo(CO)$_3$ was added to an aqueous solution of 0.5 g of NaNO$_2$. Within 15 min, 2 mL of 1.2 M HCl was added dropwise. The color of the solution turned to dark brown at first and then slowly to yellow. After filtration, solid NaClO$_4$ was added to precipitate the perchlorate salt. It was filtered off and dissolved in acetonitrile. An ethanolic solution of NaPF$_6$ (2 g in 20 mL of ethanol) was added to obtain yellow crystals of [LMo(CO)$_2$NO]PF$_6$, yield 0.5 g (56%). [LW(CO)$_2$NO]PF$_6$ was prepared by the same method.

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Table I. Crystallographic Data

	$[LMo(CO)_2NO]PF_6$	$[LMo(NO)_2Cl]PF_6$	$LMoCl_3$	$[L_2Mo_2O_4]ZnCl_4 \cdot H_2O$
fw	473.3	482.8	348.5	773.7
a, Å	8.333 (3)	8.560 (7)	12.594 (2)	11.516 (5)
b, Å	21.684 (9)	11.483 (8)	11.041 (2)	14.872 (5)
c, Å	8.609 (3)	15.34 (1)	8.139 (1)	14.569 (6)
β, deg	94.89 (3)	91.36 (6)		102.02
V, Å^3	1549.9	1507.6	1131.6	2440.5
Z	4	4	4	4
space group	$P2_1/n$	$P2_1/c$	$Pn2_1a$	$P2_1/c$
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
T, °C	−135	−135	−135	−135
λ, Å	0.71069	0.71069	0.71069	0.71069
ρ_{obsd}, g/cm^3	1.95	2.05	1.98	2.05
ρ_{calcd}, g/cm^3	2.03	2.12	2.04	2.10
μ, cm^{-1}	11.5	13.4	15.65	21.4
transmissn coeff	0.85–0.75	0.83–0.67	0.68–0.54	0.84–0.58
$R(F_o)$	0.027	0.056	0.017	0.040
$R_w(F_o)$	0.030	0.057	0.020	0.039

$[LMo(NO)_2Cl]PF_6$. A solution of 2 g of $NaNO_2$ in 5 mL of H_2O was added within 15 min to a solution of 0.5 g of $LMo(CO)_3$ in 10 mL of 1 M HCl. The color changed from yellow to green. The solution was stirred for 2 h. To the filtered solution was then added a solution of 3 g of $NaPF_6$ in 5 mL of H_2O. After 12 h, green crystals precipitated. $[LW(NO)_2Br]PF_6$ was prepared by a similar method starting from a solution of $LW(CO)_3$ in HBr.

$[LMo(CO)_3Br]PF_6$. To a solution of 250 mg (0.75 mmol) of $LMo(CO)_3$ in 20 mL of trichloromethane was added a solution of 1 mL of bromine in 10 mL of trichloromethane under argon. After the mixture was heated for 30 min, the solid product was filtered off, washed with cold ethanol, and dissolved in absolute ethanol. Solid $NaPF_6$ was added to precipitate yellow $[LMo(CO)_3Br]PF_6$, yield 240 mg (58%).

$[L_2Mo_2O_4](ClO_4)_2$. A 500-mg (1.5-mmol) sample of $LMo(CO)_3$, dissolved in 10 mL of 0.5 M $HClO_4$, was stirred in air for 24 h. The clear orange solution was slightly heated and filtered. Then, 2 g of $NaClO_4$ were added to precipitate yellow, needle-like crystals of $[L_2Mo_2O_4)](ClO_4)_2$, yield 480 mg (85%). The analogous $[L_2Mo_2O_4](PF_6)_2$ could be prepared as well.

Single crystals suitable for X-ray work were obtained as follows: 5 g of $ZnCl_2$ was added to a solution of 1 g of $[(L_2Mo_2O_4](ClO_4)_2$ (1.34 mmol) in 20 mL of H_2O. This solution was acidified until it turned dark green. Within 15 min 1 M NaOH was carefully added until the color turned back to orange. After 24 h, well-shaped crystals of $[L_2Mo_2O_4]ZnCl_4 \cdot H_2O$ had developed; yield 800 mg (80%).

$[L_2Mo_2O_3Cl_2](ClO_4)_2$. First, 2 M HCl was added to a solution of $[L_2Mo_2O_4](ClO_4)_2$. The solution turned green. $NaClO_4$ was used to precipitate dark green crystals of $[L_2Mo_2O_3Cl_2](ClO_4)_2$.

$LMoCl_3$. To prepare $LMoCl_3$, a solution of 200 mg of $LMo(CO)_3$ in 10 mL of concentrated HCl was aerated until orange crystals precipitated. They were filtered off and washed with ethanol and ether.

Single crystals were mounted in glass capillaries. Diffraction studies were performed at 140 K on a Syntex (Nicolet) $P2_1$ four-circle automated diffractometer with a Mo X-ray (Kα radiation, λ = 0.71069 Å) source equipped with a graphite monochromator and a low-temperature device. The final orientation matrix and unit cell parameters were determined by least-squares treatment of 15 machine-centered reflections having $2\theta > 20°$. The intensities of one check reflection revealed no significant change in intensity during data acquisition. The crystal parameters and further details of the data collection are summarized in Table I. The scan speed ($\theta/2\theta$ mode) varied from 4.88 to 29.3 deg/min; the ratio of background to scan time was 0.75. An empirical absorption correction (ψ scan) was employed throughout.

Structure Solution and Refinement. The structures of $[LMo(CO)_2NO]PF_6$ and $[LMo(NO)_2Cl]PF_6$ were solved by Patterson methods. Direct methods were applied for the remaining compounds. The weighting scheme $1/w = \sigma^2(F_o) + (gF_o)^2$ with $g = 0.015$ was used in all refinements. Final R factors and other data are included in Table I. The final atomic positional parameters are collected in Tables II–V. For $[LMo(CO)_2NO]PF_6$ all hydrogen atoms were localized in difference syntheses and isotropically included in the refinement. For the remaining compounds idealized positions of H atoms bound to carbon atoms were calculated (C–H = 0.96 Å, sp^3-hybridized atoms). CH_2 groups were refined as rigid moieties with fixed isotropic thermal parameters for the hydrogen atoms ($U_H = 1.2U_C$) and anisotropic thermal parameters for the carbon atoms.

During the refinement of the structure of $[L_2Mo_2O_4]ZnCl_4 \cdot H_2O$ the anisotropic thermal parameters and bond distances of the atoms N1, N4, S1, and S2 showed atypical values, indicating a restricted rotational disorder of L, which exchanged the donor positions N1 with S1 and N4 with S2, respectively. Subsequent refinement of the site occupation factors gave the following results: the site S1 is occupied by 0.791 (9)) S and 0.209 (9) N, the site S2 by 0.699 (10) S and 0.301 (10) N; the

Table II. Atom Positional Parameters (×10^4) for $[LMo(CO)_2NO]PF_6$ (Refined Hydrogen Atoms Omitted)

atom	x	y	z
Mo	−1112.8 (3)	−1165.5 (1)	1643.4 (3)
S	3541.4 (9)	467.1 (3)	8524.1 (8)
O1	1110 (3)	1299 (1)	1935 (2)
O2	8329 (3)	2147 (1)	7960 (3)
O3	8496 (3)	180 (1)	8234 (3)
N1	1612 (3)	1152 (1)	5836 (3)
N2	3180 (3)	1834 (1)	8294 (3)
N3	9510 (3)	557 (1)	8280 (3)
C1	2452 (4)	1733 (1)	5467 (4)
C2	3756 (4)	1903 (1)	6718 (3)
C3	4513 (4)	1666 (1)	9468 (4)
C4	5118 (4)	1015 (1)	9234 (4)
C5	3875 (4)	404 (1)	6447 (3)
C6	2401 (4)	570 (1)	5384 (3)
C7	1082 (3)	1240 (1)	601 (3)
C8	9361 (4)	1805 (1)	8073 (3)
P1	7159.5 (9)	1443.5 (3)	3696.5 (8)
F1	5483 (2)	1112 (1)	3180 (2)
F2	7114 (2)	1160 (1)	5401 (2)
F3	8820 (2)	1787 (1)	4222 (2)
F4	8124 (3)	855 (1)	3204 (3)
F5	6208 (2)	2037 (1)	4222 (3)
F6	7218 (3)	1732 (1)	2005 (2)

Table III. Atom Positional Parameters (×10^4) for $[LMo(NO)_2Cl]PF_6$

atom	x	y	z
Mo	3771.7 (8)	2852.2 (6)	5481.7 (4)
Cl	3334 (3)	4122 (2)	4224 (1)
S	3755 (3)	1876 (2)	6899 (1)
O1	3758 (9)	0616 (6)	4504 (4)
O2	7229 (7)	2881 (6)	5720 (4)
N1	1213 (8)	2881 (5)	5693 (4)
N2	3470 (8)	4420 (6)	6322 (4)
N3	5894 (9)	2893 (6)	5560 (4)
N4	3786 (8)	1498 (7)	4860 (4)
C1	661 (9)	3988 (7)	6090 (6)
C2	1927 (11)	4923 (8)	6078 (6)
C3	3605 (11)	4221 (7)	7292 (5)
C4	4424 (10)	3103 (8)	7423 (6)
C5	1670 (9)	1811 (7)	7083 (5)
C6	768 (9)	1854 (7)	6236 (5)
P	−1439 (2)	3390 (2)	8650 (1)
F1	−31 (6)	4186 (4)	8333 (3)
F2	−2832 (6)	2581 (4)	8942 (3)
F3	−207 (6)	2392 (4)	8917 (3)
F4	−2654 (6)	4366 (4)	8377 (3)
F5	−1585 (6)	2840 (4)	7695 (3)
F6	−1269 (6)	3924 (5)	9594 (3)

Table IV. Atom Positional Parameters ($\times 10^4$) for $[L_2Mo_2O_4]ZnCl_4 \cdot H_2O$

Mo1	x	y	z
Mo1	0102.6 (5)	7895.0 (3)	2854.2 (3)
Mo2	2049.6 (5)	7278.6 (3)	3806.5 (4)
S1[a]	−259 (2)	9222 (1)	4045 (1)
S2[a]	2324 (2)	6488 (2)	179 (1)
O1	443 (4)	7207 (3)	4010 (3)
O2	1714 (4)	8334 (3)	3025 (3)
O3	−181 (5)	7210 (3)	1923 (3)
O4	2295 (4)	6394 (3)	3151 (3)
N1[a]	−470 (4)	9105 (3)	1863 (4)
N2	−1843 (5)	7857 (4)	2837 (3)
N3	3972 (5)	7620 (4)	4127 (4)
N4[a]	2755 (4)	6308 (4)	5078 (3)
C1	1858 (6)	9154 (5)	1742 (5)
C2	2435 (6)	8274 (4)	1926 (4)
C3	2230 (6)	8173 (6)	3694 (5)
C4	−1814 (8)	9074 (6)	4005 (6)
C5	−218 (6)	172 (5)	3313 (4)
C6	67 (6)	9964 (5)	2371 (5)
C7	4702 (6)	6965 (5)	4806 (4)
C8	3989 (7)	6141 (5)	4942 (5)
C9	2881 (6)	8148 (5)	1074 (4)
C10	2186 (7)	7287 (5)	1059 (5)
C11	3797 (8)	8773 (5)	5299 (5)
C12	4240 (7)	8556 (5)	4420 (5)
Zn	3856.8 (7)	723.5 (5)	2442.5 (5)
Cl1	−4756 (1)	7098 (1)	2521 (1)
Cl2	−2938 (2)	5781 (1)	1335 (1)
Cl3	−5236 (2)	4662 (1)	2511 (1)
Cl4	−2506 (2)	5695 (2)	3944 (2)
Ow	−116 (7)	4100 (5)	4783 (5)

[a] These positions are partially occupied by nitrogen and sulfur (see Experimental Section).

Table V. Atom Positional Parameters ($\times 10^4$) for $LMoCl_3$

atom	x	y	z
Mo	9371.2 (2)	7500.0	665.6 (3)
Cl1	9629.5 (9)	9127.6 (9)	2626.6 (13)
Cl2	1191.7 (6)	7347.8 (11)	−214.7 (10)
Cl3	9552.7 (9)	5920.5 (9)	2718.8 (13)
S	7441.7 (6)	7658.4 (10)	1143.0 (9)
N1	8844 (1)	6209 (3)	−1213 (4)
N2	8978 (3)	8698 (4)	−1421 (5)
C1	8769 (3)	6722 (3)	−2896 (4)
C2	9283 (3)	8002 (4)	−2928 (4)
C3	7859 (3)	9147 (3)	−1545 (5)
C4	7282 (3)	9092 (4)	75 (5)
C5	6979 (3)	6520 (4)	−321 (5)
C6	7850 (3)	5615 (4)	−683 (4)

sites N1 and N4 are occupied by N and S in the reversed ratios. The *R* value improved significantly from 0.049 to 0.040.

Results and Discussion

Nitrosyl Complexes. $[LMo(CO)_2NO]PF_6$ was obtained by reaction of $LMo(CO)_3$ with $NaNO_2/HCl$ in water at room temperature. Prolonged reaction using $NaNO_2/HCl$ in excess gave the fully decarbonylated green dinitrosyl complex $[LMo(NO_2)Cl]PF_6$. During the reaction the yellow color of $[LMo(CO)_2NO]PF_6$ was observed. Starting from $LW(CO)_3$ the identical tungsten complexes could also be obtained. All compounds are stable to storage and may be exposed to air. The IR spectra of $[LMo(CO)_2NO]PF_6$ exhibited the CO stretching frequencies at 2010 and 1940 cm^{-1} and the NO stretching frequency at 1670 cm^{-1}. In $[LMo(NO)_2Cl]PF_6$ NO stretching frequencies were observed at 1790 and 1690 cm^{-1}, typical for dinitrosyl compounds with linear M–N–O groups. In the analogous 1,4,7-triazacyclononane complexes the respective vibrational frequencies are shifted to lower wave numbers by approximately 40 cm^{-1}.[9a]

Due to the asymmetrical donor set of the macrocyclic ligand substitution of one or three CO molecules by NO and Cl may produce isomeric compounds. According to the spectroscopic properties and the bond distances of $LMo(CO)_3$,[7a] the carbonyl group in trans position to the sulfur atom is less strongly bound than the carbonyl groups in the cis positions. One may expect therefore, that the former carbonyl ligand is replaced by NO at first. On the other side, the entering ligand NO is a better π-acceptor than CO. It may prefer, therefore, the positions trans to the N donor atoms, if the thioether group possesses some π-acidity. To distinguish between these two models, we elucidated the sterical arrangement of the ligands in $[LMo(CO)_2NO]PF_6$ and $[LMo(No)_2Cl]PF_6$ by structure determinations. Figure 1 shows ORTEP plots of the cations of both compounds, Tables II and III contain the final coordinates, and Tables VI and VII contain selected bonding parameters.

$LMo(CO)_2NO^+$ and $LMo(NO)_2Cl^+$ consist of octahedrally coordinated molybdenum atoms with facial coordination of the ligand L. In the former ion, the strong π-acid ligand NO is in trans position to an amino group, underlining the π-acceptor properties of the thioether group. In $LMo(NO)_2Cl^+$, the NO ligands occupy these positions for the same reason, leaving the position trans to the thioether group to the weakly π-accepting

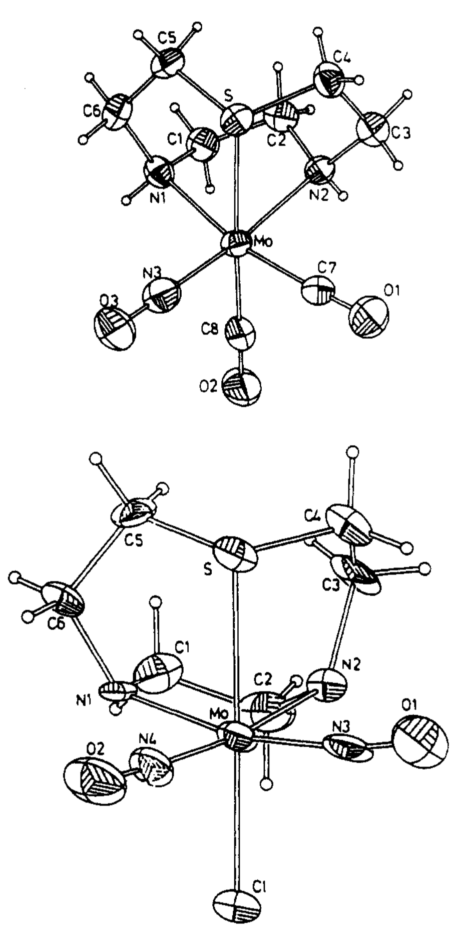

Figure 1. ORTEP diagrams of the $LMo(CO)_2NO^+$ (top) and $LMo(NO)_2Cl^+$ cations (bottom).

Table VI. Selected Bond Lengths (Å) and Angles (deg) for $[LMo(CO)_2NO]PF_6$

Mo–N1	2.244 (2)	Mo–C8	2.013 (3)
Mo–N2	2.256 (2)	N3–O3	1.175 (3)
Mo–N3	1.874 (3)	C7–O1	1.154 (3)
Mo–S	2.522 (1)	C8–O2	1.134 (4)
Mo–C7	1.942 (1)		
N1–Mo–S	80.43 (6)	N2–Mo–C8	95.8 (1)
N1–Mo–N2	77.31 (9)	S–Mo–C7	94.11 (8)
N2–Mo–S	77.10 (6)	S–Mo–N3	98.36 (8)
C7–Mo–N3	91.4 (1)	S–Mo–C8	172.17 (9)
C7–Mo–C8	89.6 (1)	N1–Mo–C7	169.4 (1)
C8–Mo–N3	88.5 (1)	N2–Mo–N3	174.2 (1)
N1–Mo–N3	98.5 (1)	Mo–N3–O3	179.4 (3)
N1–Mo–C8	94.8 (1)	Mo–C7–O1	177.5 (3)
N2–Mo–C7	92.6 (1)	Mo–C8–O2	176.5 (3)

Table VII. Selected Bond Lengths (Å) and Angles (deg) for $[LMo(NO)_2Cl]PF_6$

Mo–N1	2.222 (7)	Mo–N4	1.824 (7)
Mo–N2	2.234 (6)	Mo–Cl	2.440 (2)
Mo–S	2.447 (2)	N3–O1	1.164 (10)
Mo–N3	1.819 (7)	N4–O3	1.150 (10)
N1–Mo–S	81.4 (2)	N2–Mo–Cl	87.5 (2)
N1–Mo–N2	77.0 (2)	S–Mo–N3	88.9 (2)
N2–Mo–S	81.6 (2)	S–Mo–N4	94.3 (2)
N3–Mo–N4	92.2 (3)	S–Mo–Cl	166.5 (1)
N3–Mo–Cl	99.9 (2)	N1–Mo–N3	167.6 (3)
Cl–Mo–N4	95.7 (2)	N2–Mo–N4	172.5 (3)
N1–Mo–N4	96.2 (3)	Mo–N3–O1	171.4 (6)
N1–Mo–Cl	87.5 (2)	Mo–N4–O2	176.3 (7)
N2–Mo–N3	94.0 (3)		

or non-π-accepting chloro ligand. The Mo–NO bond distances, 1.874 (3) Å in $LMo(CO)_2NO^+$ and 1.819 (7) and 1.824 (7) Å in $LMo(NO)_2Cl^+$, differ considerably. The reason is probably the different number of strong π-acid ligands, which share the back-donation, although the positive charge at the central atom in $LMo(NO_2)Cl^+$ is higher. The Mo–N and Mo–S bond distances decrease with increasing positive charge at the coordination center in the order $LMo(CO)_3 > LMo(CO)_2NO^+ > LMo(NO)_2Cl^+$. The Mo–S distances vary from 2.526 (2) Å in $LMo(CO)_3$ to 2.447 (2) Å in $LMo(NO)_2Cl^+$. The remaining dimensions of $[LMo(CO)_2NO]PF_6$ and $[LMo(NO)_2Cl]PF_6$, are regular. The PF_6^- anions are involved in weak hydrogen bonds with the >NH groups of the macrocycle. The structures of the analogous 1,4,7-triazacyclononane complexes are unknown due to crystal disorder.[9a]

Oxidation Reactions. As observed for $L'Mo(CO)_3$ (L′ = 1,4,7-triazacyclononane) by Wieghardt and co-workers, [9]$LMo(CO)_3$ also easily undergoes oxidative-addition reactions with halogens (dissolved in trichloromethane) to divalent seven-coordinate complexes $LMo(CO)_3X_2$. By metathesis in ethanol, $LMo(CO)_3X^+$ ions (X = Cl, Br) can be obtained as air-stable PF_6^- salts. It is interesting that the thioether function of L is not attacked under these conditions. The IR spectra of the $LMo(CO)_3X^+$ salts contain three carbonyl stretching frequencies, whose wavenumbers differ only slightly from those for the analogous $L'Mo(CO)_3Br^+$, where the central atom is seven-coordinate as shown by a crystal structure determination.[9a] Prolonged reaction (~20 h) of $LMo(CO)_3$ with Br_2 in trichloromethane gave products whose IR spectra contain Mo=O stretching frequencies at 960 cm^{-1}. Probably ions of the formula $LMoOBr_2^+$ were formed. When the solvent was changed to acetonitrile, oxidation with Br_2 yielded within 0.5 h green solutions, from which dark green crystals precipitated. They gave similar IR spectra as mentioned above, and analyzed close to $[LMoOBr_2]Br$. Their hydrolysis in dilute HCl produced the dimeric $L_2Mo_2O_4^{2+}$ cation. It could be isolated as ClO_4^- and PF_6^- salts. A better preparative method to synthetize this dimer is the use of air to oxidize a solution of $LMo(CO)_3$ in 0.5 M $HClO_4$.

Salts containing the $L_2Mo_2O_4^{2+}$ unit show the typical absorptions in the IR and Raman spectra at 965, 940, 735, 715, 450, and 445 cm^{-1}, indicating a *syn*-Mo_2O_4 structure. The structure of $[L_2Mo_2O_4]ZnCl_4{\cdot}H_2O$ is discussed below. Orange solutions of $[L_2Mo_2O_4](ClO_4)_2$ are transformed upon acidification with concentrated HCl to dark green solutions; addition of sodium hydroxide changes the color back to orange. From the green solution, dark green, oddly shaped crystals of $[L_2Mo_2O_3Cl_2](ClO_4)_2$ could be precipitated by addition of solid $NaClO_4$. Absorption bands in the IR spectrum at 905 and 775 cm^{-1} can be assigned to $\nu_{Mo=O}$ and $\nu_{as(Mo-O-Mo)}$ of the Mo_2O_3 core.[10]

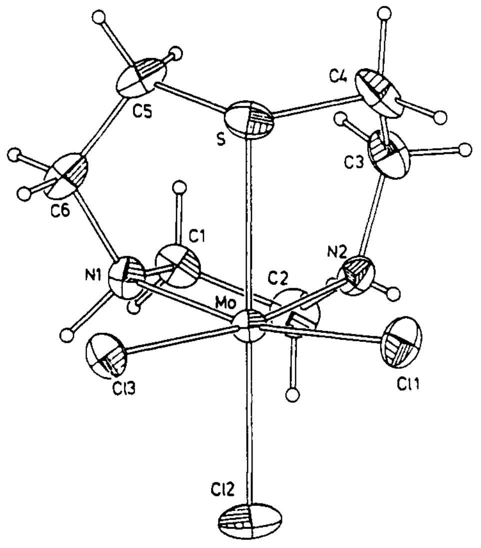

Figure 2. ORTEP diagram of $LMoCl_3$.

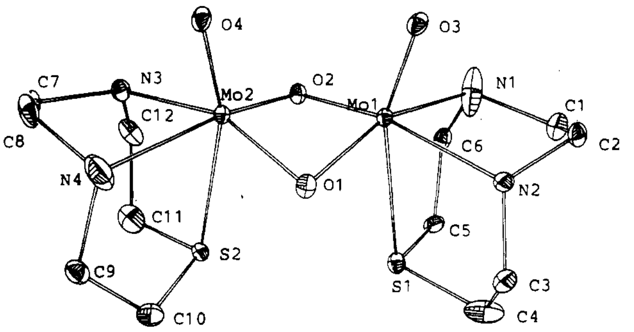

Figure 3. ORTEP diagram of the $L_2Mo_2O_4^{2+}$ cation.

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for $LMoCl_3$

Mo–N1	2.193 (3)	Mo–Cl1	2.425 (1)
Mo–N2	2.209 (4)	Mo–Cl2	2.408 (1)
Mo–S	2.467 (1)	Mo–Cl3	2.426 (1)
N1–Mo–S	81.8 (1)	N2–Mo–Cl1	95.3 (1)
N1–Mo–N2	77.6 (1)	N2–Mo–Cl2	91.5 (1)
N2–Mo–S	81.8 (1)	S–Mo–Cl1	88.6 (0)
Cl1–Mo–Cl3	93.8 (0)	S–Mo–Cl3	92.0 (0)
Cl1–Mo–Cl2	96.9 (0)	S–Mo–Cl2	171.8 (0)
Cl2–Mo–Cl3	93.7 (0)	N1–Mo–Cl1	168.8 (1)
N1–Mo–Cl3	92.4 (1)	N2–Mo–Cl3	168.8 (1)
N1–Mo–Cl2	92.0 (1)		

$LMoCl_3$ is easily prepared by action of air and HCl to $LMo(CO)_3$. It is stable in air for many weeks, but insoluble in most common organic solvents. The molecule is chiral. The five-membered chelate rings formed by L have λλλ or δδδ conformation (see Figure 2). It crystallizes in the acentric space group *Pn*2_1*a*, which contains both enantiomers. The Mo–N bond distances (see Table VIII) are rather short, reflecting the oxidation state of the central atom. Interestingly, the Mo–S bond is significantly longer than in $[LMo(NO)_2Cl]PF_6$ and the trans-positioned Mo–Cl bond is shorter than in the compound mentioned. This can be related to the π-acceptor properties of the thioether group. The Mo–N distances show generally a larger variation in complexes of the ligand L (from 2.193 (3) Å in $LMoCl_3$ to 2.317 (5) Å) in $LMo(CO)_3$) than in the analogous complexes of 1,4,7-triazacyclononane.[9b] Due to its high symmetry the latter ligand seems to be sterically more restricted.

Reaction of $LMoCl_3$ with HNO_3 leads to oxidation of the ligand L, even in dilute solutions. The IR spectra of colorless crystals, which were isolated after this treatment, contain a strong band at 1150 cm^{-1}, which has to be assigned to a S=O stretching frequency. Therefore, complexes containing the μ-oxo-bridged $Mo^{VI}_2O_5$ unit could not be prepared. Short reaction times give green solutions, which probably contain nitrosyl and dinitrosyl complexes.

Structure of $[L_2Mo_2O_4]ZnCl_4{\cdot}H_2O$. We applied successfully the recommendation of Cotton and co-workers[11] to use $ZnCl_4^{2-}$

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[10] (a) Chen, G. J. J.; McDonald, J. W.; Bravard, D. C.; Newton, W. E. *Inorg. Chem.* **1985**, *24*, 2327. (b) Mattes, R.; Scholand, H.; Mikloweit, U.; Schrenk, V. *Z. Naturforsch., B* **1987**, *42*, 599.

Table IX. Selected Bond Lengths (Å) and Angles (deg) for $[L_2Mo_2O_4]ZnCl_4 \cdot H_2O$

Mo1–O1	1.939 (5)	Mo2–O1	1.937 (5)
Mo1–O2	1.934 (5)	Mo2–O2	1.930 (4)
Mo1–O3	1.674 (5)	Mo2–O4	1.684 (5)
Mo1–N1	2.316 (5)[a]	Mo2–N3	2.226 (5)
Mo1–N2	2.237 (5)	Mo2–N4	2.355 (5)[a]
Mo1–S1	2.716 (2)[a]	Mo2–S2	2.682 (2)[a]
Mo1–Mo2	2.549 (1)		
O1–Mo1–O3	92.9 (2)	O1–Mo2–O4	82.5 (2)
O2–Mo1–O3	109.3 (2)	O2–Mo2–O4	109.8 (2)
O3–Mo1–S1	158.4 (2)	O4–Mo2–S2	161.7 (2)
S1–Mo1–N1	76.8 (2)	S2–Mo2–N3	74.4 (1)
S1–Mo1–N2	74.9 (1)	S2–Mo2–N4	82.3 (1)
N1–Mo1–N2	81.9 (2)	N3–Mo2–N4	79.0 (2)
Mo1–O1–Mo2	82.2 (2)	Mo1–O2–Mo2	85.5 (2)

[a] Bond Distances affected by rotational disorder of the ligand L (see text).

as a counterion to crystallize "difficult" cations. The orange compound contains the bis(μ-oxo)bis[oxo(1-thia-4,7-diazacyclononane)molybdenum(V)] cation with the Mo=O groups in the familiar syn position. In contrast to Wieghardt's results with the ligands 1,4,7-triazacyclononane[9] and 1,5,9-triazacyclododecane,[12] we did not observe the anti isomer, in which no sterical interactions are possible between the bulky macrocyclic ligands at the two molybdenum atoms. Figure 3 shows the cation, and Table IX contains selected bonding parameters. The overall dimensions in the $Mo_2O_4^{2+}$ core, with a Mo1–Mo2 distance of 2.549 (1) Å, are well in the range observed for similar compounds. The ligands L are rotationally disordered at Mo1 and Mo2. Each macrocycle is attached to the metal atom statistically in two different orientations, generated by a rotation about its pseudo-3-fold axis by 60°. Therefore, only one coordination site in the equatorial planes at the two molybdenum atoms is occupied exclusively by nitrogen; the other equatorial sites and the positions trans to the terminal oxo ligands, the axial sites, are occupied statistically by the sulfur and nitrogen donor atoms. The site occupation factors, varying at Mo1 and Mo2, could be determined quite precisely and are given in the Experimental Section. They show that the trans position is preferred by the thioether group with a probability of 70–80%. Two factors favor this configuration. (1) In an oxygen and nitrogen coordination sphere molybdenum (V) behaves as "hard acid". The sulfur donor is then forced to a "weak" coordination site, i.e., the position trans to the terminal oxo group. (2) Sulfur coordination in the site with the largest distance to the metal atom matches with the "asymmetric" nature of the macrocycle L (vide infra). The two (pure) Mo–N distances, Mo1–N2 and Mo2–N3 are 2.237 (5) and 2.226 (5) Å, respectively; they are in the same range as the literature data.[9,12] The other observed Mo–L distances are superimposed values of Mo–N and Mo–S bond lengths. From these data, the following approximate bond lengths (Å) can be extrapolated: Mo–S(equatorial), 2.50; Mo–S(axial), 2.75; Mo–N(axial), 2.40. As in $[L_2Cu](NO_3)_2$[5f] and $LCuBr_2$[5g] with strongly Jahn–Teller-distorted coordination polyhedra, the conformation of the five-membered chelate rings in $L_2Mo_2O_4^{2+}$ is not $\lambda\lambda\lambda$ or $\delta\delta\delta$ but rather $\delta\lambda\lambda$ (at Mo1) and $\lambda\delta\delta$ (at Mo2).

What causes the rotational disorder just discussed? If both trans positions (at Mo1 and Mo2) are occupied by sulfur, the interligand distance S1···S2 is approximately 3.26 Å. This is considerably smaller than the sum of the van der Waals radii of approximately 3.60 Å. If one ligand is rotated by 60°, S1 or S2 are replaced by nitrogen atoms and the repulsive nonbonding interaction is relaxed. It is not completely clear, why still approximately 50% of the $L_2Mo_2O_4^{2+}$ ions, as shown by the crystallographic results, retain the unfavorable configuration. In solution, equilibria probably exist between different configurations. Due to large lattice forces, more than one species is incorporated in to the crystals. These equilibria may cause the difficulties encountered by us to obtain crystals suitable for X-ray work and may also explain that some samples of $[L_2Mo_2O_4]X_2$ with X = ClO_4^-, PF_6^-, and $ZnCl_4^{2-}$ gave IR spectra that showed more than the expected number of bands in the $\nu_{Mo=O}$ region. Obviously the samples contained configurational isomers in different amounts.

Conclusions. This work shows that the ligating behavior of the N_2S ligand 1-thia-4,7-diazacyclononane toward molybdenum centers with varying coligands and oxidation states is very similar to the chemistry of 1,4,7-triazacyclononane, which has been explored by Wieghardt and co-workers. But it was impossible to oxidize molybdenum to the +VI oxidation state; under appropriate conditions the thioether group of L is oxidized to a sulfoxide group. In this respect it is interesting that 1-thia-4,7-diazacyclononane *S*-oxide[13] and 1,4,7-trithiacyclononane 1-oxide[2b] are still ligated in transition-metal complexes. A further difference from 1,4,7-triazacyclononane is the ability of 1-thia-4,7-diazacyclononane to act as a π-acceptor through the thioether group.

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Supplementary Material Available: Tables of thermal parameters for the non-hydrogen atoms, hydrogen atom parameters, bond distances and angles, and crystallographic data for $[LMo(CO)_2NO]PF_6$, $[LMo(NO)_2Cl]PF_6$, $LMoCl_3$, and $[L_2Mo_2O_4]ZnCl_4 \cdot H_2O$ (14 pages); tables of observed and calculated structure factors (54 pages). Ordering information is given on any current masthead page.

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