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Preparation and Characterization of Binuclear Complexes of Molybdenum(III) and Molybdenum(V) via Oxidative Decarbonylation. Reactions of $LMo(CO)_3$ (L = 1,5,9-Triazacyclododecane) and Crystal Structure of *anti*-$[L_2Mo_2O_4](ClO_4)_2{\cdot}2H_2O$

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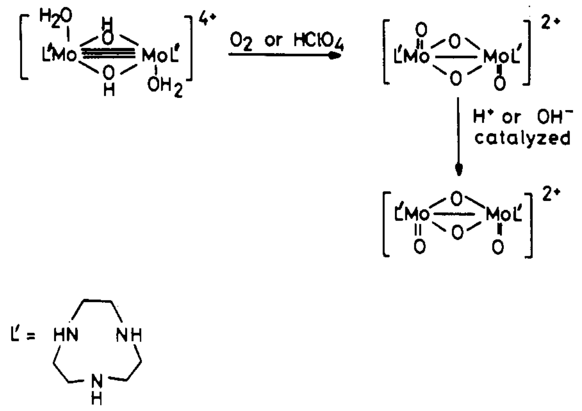
The cyclic triamine 1,5,9-triazacyclododecane (L), $C_9H_{21}N_3$, reacts with $Mo(CO)_6$ in Decalin at 150 °C to yield yellow, air-stable $LMo(CO)_3$ (**1**). Oxidation of **1** with bromine, nitrous acid (or $NOBF_4$), or hydrochloric acid in the presence of O_2 affords the monomeric complexes $[LMo(CO)_3Br](Br_3)$, $[LMo(CO)_2NO]BF_4$, and $LMoCl_3$, respectively. Oxidative decarbonylation of **1** in $HClO_4$ with O_2 gives the two isomers purple *anti*-$[L_2Mo_2O_4](ClO_4)_2{\cdot}2H_2O$ and yellow *syn*-$[L_2Mo_2O_4](ClO_4)_2{\cdot}H_2O$. Reduction of the former with zinc amalgam in aqueous solution in the presence and absence of coordinating acids (HBF_4, formic acid, acetic acid, hydrochloric acid) affords diamagnetic, green, dimeric bis(μ-hydroxo)-bridged species of molybdenum(III): $[L_2Mo_2(\mu\text{-}OH)_2(OH)_2]I_2{\cdot}2H_2O$, $[L_2Mo_2(\mu\text{-}OH)_2(\mu\text{-}HCOO)]I_3{\cdot}2H_2O$, $[L_2Mo_2(\mu\text{-}OH)_2(\mu\text{-}CH_3CO_2)]I_3$, and $[L_2Mo_2(\mu\text{-}OH)_2Cl_2](ClO_4)_2$. Purple *anti*-$[L_2Mo_2O_4](ClO_4)_2{\cdot}2H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.515$ (8) Å, $b = 11.11$ (2) Å, $c = 16.56$ (3) Å, $\beta = 92.3$ (1)°, $V = 1565$ (1) Å^3, and $d_{calcd} = 1.77$ g/cm^3 for $Z = 2$ and $M_r = 833.4$. Least-squares refinement of the structure based on 3216 observations led to final discrepancy indices of $R = 0.039$ and $R_w = 0.045$. The structure consists of dimeric cations with an *anti*-dioxobis(μ-oxo)dimolybdenum(V) core (edge-sharing octahedra); the short Mo–Mo distance of 2.586 (1) Å and the diamagnetism of the compound indicate a Mo–Mo single bond. The four-membered Mo_2O_2 ring is planar. In alkaline aqueous solutions the purple *anti*-$[L_2Mo_2O_4]^{2+}$ complex isomerizes irreversibly to the yellow syn isomer. The kinetics of this reaction have been measured, and a possible mechanism is discussed. This isomerization has also been demonstrated by using ^{95}Mo NMR spectroscopy.

Introduction

In a series of papers[2-4] we have recently reported the preparation of binuclear complexes of molybdenum in high oxidation states (V and VI) via oxidative decarbonylation of the mononuclear complex $L'Mo(CO)_3$ with nitric acid in aqueous solution[3] (L′ is the small macrocyclic triamine, 1,4,7-triazacyclononane). An alternative route to these products used $L'MoCl_3$ as starting material for the syntheses of binuclear (μ-hydroxo)-bridged, diamagnetic Mo(III) complexes that were readily oxidized to Mo(V) dimers by oxygen or perchlorate.[2,4] An interesting observation is the oxidation of $[L'_2Mo_2(\mu\text{-}OH)_2(H_2O)_2]^{4+}$ (Scheme I), which yielded the first example for a binuclear complex with an *anti*-$[Mo_2O_4]^{2+}$ core.[2a]

Scheme I



This complex was subsequently shown to be irreversibly isomerized to the thermodynamically more stable *syn*-$[L'_2Mo_2O_4]^{2+}$ species[4] by H$^+$ or OH$^-$.

We have now extended these studies by using the larger macrocycle 1,5,9-triazacyclododecane (L). We report the syntheses and structural characterization of mononuclear and binuclear complexes of molybdenum containing this ligand, which we summarized in Scheme II.

Experimental Section

The ligand, 1,5,9-triazacyclododecane (L = [12]aneN_3), was prepared according to a literature procedure.[5]

$LMo(CO)_3$ (1). A suspension of $Mo(CO)_6$ (2 g, 7.6 mmol) and [12]aneN_3 (1.2 g, 7.0 mmol) in 100 mL of Decalin was carefully heated to 150 °C for 15 min (*Caution*! CO effervescence!) under an argon atmosphere. After the solution was allowed to cool to room temperature, yellow microcrystals were filtered off, washed with benzene and ether, and air-dried (yield 2.1 g, 85%).

$[LMo(CO)_3Br](Br_3)$ (2). A suspension of **1** (0.2 g, 0.57 mmol) in $CHCl_3$ (20 mL) was combined with a solution of bromine (1 mL) in $CHCl_3$ (10 mL) under argon. This solution was refluxed for 5 min, then the yellow-brown precipitate was filtered off, washed with $CHCl_3$ and ether, and air-dried (yield 0.25 g, 65%).

$[LMoCl_3]{\cdot}H_2O$ (3). A mixture of **1** (1.5 g, 4.3 mmol) in 1.2 M hydrochloric acid (10 mL) was allowed to stand at room temperature in the presence of air for 2 days, after which time a yellow-brown precipitate was filtered off, washed with ethanol and ether, and air-dried (yield 0.1 g, 5%).

***anti*-$[L_2Mo_2O_4](ClO_4)_2{\cdot}2H_2O$ (4).** A suspension of **1** (1 g, 2.8 mmol) in 0.5 M $HClO_4$ (25 mL) was stirred in the presence of air for 4 h. Purple crystals slowly precipitated from the deep-red solution; these were recrystallized twice from hot ethanol (yield 0.4 g, 34%).

The purple iodide salt was obtained from an aqueous solution of the perchlorate salt after addition of solid NaI.

***syn*-$[L_2Mo_2O_4](ClO_4)_2{\cdot}H_2O$ (5).** The volume of the red mother liquor containing **4** was reduced to 15 mL under reduced pressure at 50 °C. After the mixture was allowed to stand for 12 h in the refrigerator yellow crystals precipitated; these were filtered off, washed with ethanol and ether, and air-dried (yield 0.3 g, 25%).

$[L_2Mo_2(\mu\text{-}OH)_2(OH)_2]I_2{\cdot}2H_2O$ (6). A deoxygenated solution of **4** (0.6 g, 0.72 mmol) in water (50 mL) under an argon atmosphere was treated with zinc amalgam at room temperature for 12 h. This solution was then added to a saturated, oxygen-free solution (5 mL) of NaI (10 g). The green crystals precipitated after 8 h were filtered off and dried under argon (yield 0.2 g, 62%).

$[L_2Mo_2(\mu\text{-}OH)_2Cl_2](ClO_4)_2$ (7). The reduction of **4** (0.6 g, 0.72 mmol) in 0.3 M HCl (50 mL) under an argon atmosphere with zinc amalgam affords a deep green solution. Addition of $NaClO_4$ (1 g) and cooling to 2 °C produced green crystals (yield 0.3 g, 54%).

$[L_2Mo_2(\mu\text{-}OH)_2(\mu\text{-}CH_3CO_2)]I_3$ (8). The reduction of **4** (0.6 g, 0.72 mmol) in 1 M acetic acid (50 mL) with zinc amalgam under an argon

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(1) (a) Ruhr-Universität. (b) University of Arizona.

(2) (a) Wieghardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Angew. Chem.* **1983**, *95*, 499; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 491. (b) Wieghardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Inorg. Chem.* **1984**, *23*, 94.

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Scheme II

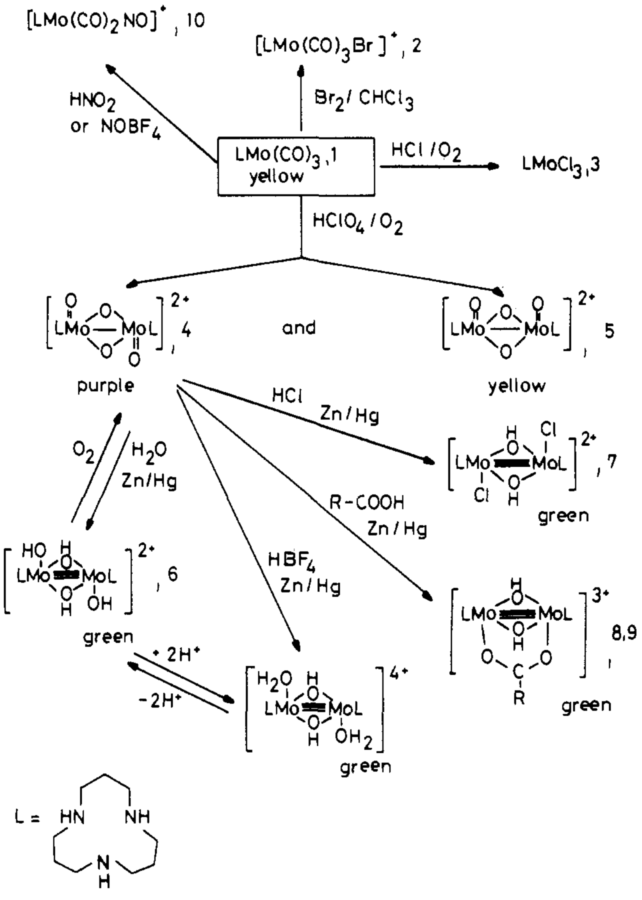

Table I. Crystallographic Data and Data Collection Parameters at 22 °C

formula	$C_{18}H_{46}N_6O_{14}Cl_2Mo_2$
fw	833.4
space group	$P2_1/c$
a, Å	8.515 (8)
b, Å	11.11 (2)
c, Å	16.56 (3)
β, deg	92.3 (1)
V, Å^3	1565 (1)
Z	2
d_{calcd}, g/cm^3	1.77
cryst size, mm	0.35 × 0.3 × 0.42
μ(Mo Kα), cm^{-1}	28.3
diffractometer	Syntex R3
radiation	Mo Kα (λ = 0.71069 Å)
monochromator	graphite
scan method	ω-scan; 2θ: 2–60°
no. of unique data ($I > 3\sigma(I)$)	3216
no. of variables refined	231
std reflcns	2 every 150 reflcns, no decay obsd
largest shift/esd, final cycle	0.08
octants	$\pm h,+k,+l$
R factor	0.039
R_w factor	0.045

atmosphere affords a green solution, which yielded green crystals upon addition of NaI (3 g) (yield 0.2 g, 28%).

$[L_2Mo_2(\mu\text{-}OH)_2(\mu\text{-}HCO_2)]I_3\cdot 2H_2O$ (9). The μ-formato complex was prepared by the preceding method using 1 M formic acid (yield 0.4 g, 54%).

$[LMo(CO)_2NO]BF_4$ (10). Solid $NOBF_4$ (1.5 g, 12.8 mmol) was added to a stirred suspension of 1 (0.7 g, 2.0 mmol) in water (20 mL). Within 3 h a clear, orange solution was obtained. When $NaBF_4$ was added (1 g) and the mixture cooled to 2 °C overnight, orange crystals precipitated, which were filtered off, washed with ether, and air-dried. (Yield 0.2 g, 23%).

The same product was obtained by using 0.4 M nitric acid (20 mL), although in smaller yields.

Table II. Atom Coordinates (×10^4)

atom	x	y	z
Mo	4702.4 (4)	3.2 (3)	5709.8 (2)
O1	3388 (3)	454 (3)	4907 (2)
O2	5006 (8)	702 (5)	6414 (3)
N1	5968 (5)	−1755 (3)	6540 (2)
N2	−2412 (4)	763 (4)	3684 (2)
N3	3892 (5)	−2294 (3)	5220 (3)
C1	1004 (6)	−918 (5)	5734 (4)
C2	5185 (7)	−3008 (4)	4887 (3)
C3	7070 (6)	−2585 (4)	6122 (4)
C4	3867 (7)	−1628 (5)	7548 (3)
C5	5126 (7)	−2372 (5)	7187 (3)
C6	1046 (7)	−2093 (6)	5238 (4)
C7	6240 (7)	−3550 (4)	5582 (4)
C8	2303 (7)	−1589 (5)	7020 (3)
C9	2406 (7)	−2271 (6)	4727 (4)
Cl	8529 (2)	−300 (1)	8417 (1)
O3	7364 (10)	282 (7)	8765 (7)
O4	−1299 (20)	−1424 (8)	8699 (10)
O5	−91 (11)	281 (10)	8576 (7)
O6	−1626 (9)	−432 (11)	7617 (4)
O_w	900 (12)	1340 (6)	6905 (5)

Table III. Selected Bond Distances (Å) and Angles (deg)

Mo–O1	1.946 (3)	Mo–N2	2.265 (4)
Mo–O1′	1.956 (3)	Mo–N3	2.346 (4)
Mo–O2	1.706 (6)	Mo–Mo	2.586 (1)
Mo–N1	2.277 (4)		
O1–Mo–O1′	97.0 (1)	N2–Mo–O1′	84.7 (1)
O1–Mo–N1	85.2 (1)	Mo–O1–Mo′	83.0 (1)
O1–Mo–N3	92.6 (1)	O2–Mo–N1	90.4 (2)
O1–Mo–O2	100.7 (2)	O2–Mo–N2	86.2 (2)
N1–Mo–N2	90.6 (1)	O2–Mo–O1′	105.6 (2)
N1–Mo–N3	75.1 (1)	O2–Mo–Mo′	110.0 (2)
N2–Mo–N3	75.5 (1)	N3–Mo–Mo′	93.5 (1)

A table of elemental analyses of all new complexes is available as supplementary material.

X-ray Structural Determination of *anti*-$[L_2Mo_2O_4](ClO_4)_2\cdot 2H_2O$ (4). A purple crystal of 4 was attached to a glass fiber and mounted on a Syntex R3 four-circle diffractometer. Preliminary examinations showed that the crystal belonged to the monoclinic system, space group $P2_1/c$. The unit cell dimensions were obtained by a least-squares fit of 25 strong reflections. The data are summarized in Table I. Intensity data were measured by θ–2θ scans at 22 °C and were corrected for Lorentz and polarization effects. An empirical absorption correction was carried out.[6] The function minimized during least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ with final convergence to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.039$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.045$, where $w = 1/\sigma^2(F)$. The structure was solved via Patterson and Fourier syntheses. The positions of hydrogen atoms were not located and were not calculated. All non-hydrogen atoms were refined with use of anisotropic thermal parameters (supplementary material). During all calculations the analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $i(\Delta f'')$ terms.[7] The final atomic parameters are given in Table II, and bond distances and angles are given in Table III. A list of observed and calculated structure factors and a list of anisotropic thermal parameters are available as supplementary material.

Instrumentation. The ^{95}Mo NMR data were obtained on a Bruker WM 250 NMR spectrometer equipped with a 10-mm molybdenum probe (16.3 MHz). Preacquisition delays of 100–200 μs were used to reduce the effect of probe ringing.[8,9] Spectra were recorded at ambient temperature (22 °C) unless specified, and 2 M $Na_2[MoO_4]$ in D_2O (effective pH = 11) was used as external standard.

Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer.

The magnetic susceptibilities of powdered samples were measured by using the Faraday method between 98 and 293 K (Sartorius microba-

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[6] Computations were carried out by using the SHELXTL system (Revision 3.0, July 1981) by G. M. Sheldrick, University of Göttingen.

[7] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

[8] Minelli, M.; Young, C. G.; Enemark, J. H. *Inorg. Chem.* **1985**, *24*, 1111.

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Table IV. Selected Spectroscopic Data (IR, UV-Visible) of Complexes (L = 1,5,9-Triazacyclododecane)

complex	IR, cm^{-1}	electronic spectra λ, nm (ε, L mol^{-1} cm^{-1})
$LMo(CO)_3$	ν(CO): 1875 (vs), 1740 (vs), 1710 (sh)	
$[LMo(CO)_3Br](Br_3)$	ν(CO): 1995 (m), 1940 (vs), 1905 (s)	
$[LMo(CO)_2NO](BF_4)$	ν(CO): 2000 (s), 1900 (vs) ν(NO): 1650 (vs)	
trans-$[L_2Mo_2O_4]I_2 \cdot 2H_2O$	ν(Mo═O): 930 (s) ν_{as}(Mo—O): 750 (m)	269 (8.6×10^3), 337 (2.4×10^3), 547 (510)
cis-$[L_2Mo_2O_4](ClO_4)_2 \cdot H_2O$	ν(Mo═O): 950 (vs) ν(Mo—O): 750 (m)	251 (8.9×10^3), 299 (4.8×10^3), 388 (sh, 360)
$[L_2Mo_2(\mu\text{-}OH)_2(OH)_2]^{2+}$		391 (1.2×10^3), 600 (220), 640 (190)[a] 411 (640), 434 (sh), 598 (72), 660 (60)[b]
$[L_2Mo_2(\mu\text{-}OH)_2(\mu\text{-}CH_3CO_2)]^{3+}$	ν_{as}(CO): 1520 (m) ν_s(CO): 1450 (s)	288 (830), 405 (750), 690 (68), 730 (sh)[a]
$[L_2Mo_2(\mu\text{-}OH)(\mu\text{-}HCO_2)_2]^{3+}$	ν_{as}(CO): 1540 (m) ν_s(CO): 1350 (s)	414 (814), 711 (108)[a]

[a] Measured in H_2O. [b] Measured in 0.1 M CH_3SO_3H.

lance, Bruker B-E 10 C 8 research magnet, and Bruker B-VT 1000 automatic temperature control). Diamagnetic corrections were applied with use of published tables.[10]

IR spectra were recorded on a Beckmann Acculab 10 instrument (KBr disks).

Kinetic measurements were made on a UNICAM SP 1700 spectrophotometer interfaced to a Commodore PET 4001 computer for data acquisition and analysis.

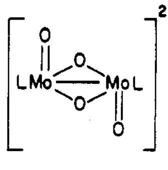
Kinetic Measurements. The OH^--catalyzed isomerization reactions 4 → 5 were run in alkaline aqueous solutions (LiOH) under pseudo-first-order conditions (excess $[OH^-]$) under an argon atmosphere. The ionic strength was adjusted to 0.25 M with $LiClO_4$. Pseudo-first-order rate constants were calculated by using a least-squares program[11] where the absorptions at the beginning of the reaction ($t = 0$) and after the completed reaction ($t = \infty$) were treated as variables. The observed and calculated values differed only within the uncertainty of the last digit of the readings of the instrument.

Results and Discussion

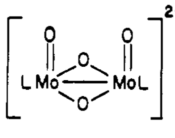
Syntheses of Complexes. The synthetic routes to mononuclear and binuclear complexes of molybdenum containing the facially coordinated tridentate ligand 1,5,9-triazacyclododecane are summarized in Scheme II. This ligand reacts with $Mo(CO)_6$ in Decalin at 150 °C to give yellow, diamagnetic **1** in excellent yields. Complex **1** is air stable in both the solid state and in solution. **1** is soluble in dimethylformamide, acetonitrile, or dimethyl sulfoxide but is insoluble in H_2O. The ν(C═O) stretching frequencies observed in the infrared spectrum are consistent with the C_{3v} local symmetry of *fac*-$LM(CO)_3$ (Table IV).

Oxidation of complex **1** with bromine in chloroform yields the diamagnetic, yellow, seven-coordinate, cationic species $[LMo(CO)_3Br]^+$. The ν(CO) stretching frequencies increased due to the increased oxidation number of the molybdenum center ($Mo^0 \rightarrow Mo^{II}$). The oxidation of **1** with nitrous acid or $NOBF_4$ in aqueous solution affords air-stable $[LMo(CO)_2NO]BF_4$. Slow air oxidation of **1** in 1.2 M hydrochloric acid at room temperature gives $LMoCl_3 \cdot H_2O$ (**3**) as a yellow-brown precipitate in low yield (6%). The effective magnetic moment of **3** at 293 K of 3.6 μ_B is consistent with a monomeric six-coordinate complex of molybdenum(III).

When **1** is reacted with 0.5 M perchloric acid in the presence of air at room temperature, a clear deep red solution is obtained from which purple crystals of **4** precipitated. The isomeric yellow **5** is precipitated from a reduced volume of the above mother liquor.



4, *anti*-dioxo, purple



5, *syn*-dioxo, yellow

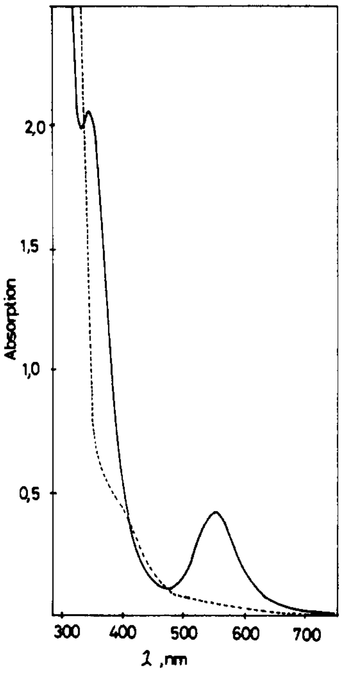


Figure 1. Electronic spectra of **4** ((—), 10^{-3} M, 1-cm cell) and **5** ((···), 1.5×10^{-3} M, 1-cm cell).

Thus both isomers are generated via oxidative decarbonylation of **1**.

Both perchlorate salts are diamagnetic due to a Mo–Mo single bond (see below). The electronic spectra of the two isomers are quite different (Figure 1); the purple anti isomer exhibits an intense band at 547 nm, which is not observed for the syn isomer. The nature of this transition is unclear. In the infrared spectrum one ν(Mo═O) and one ν(Mo—O—Mo) frequency is observed for both isomers (Table IV), although for the syn isomer *two* ν(Mo═O) and ν(Mo—O—Mo) bands, respectively, are allowed.

The anti isomer is stable in aqueous solutions at room temperature for at least 2 days in the absence of oxygen. In alkaline solutions a rapid hydroxide-catalyzed anti → syn isomerization is observed (see below). Both isomers are very slowly oxidized by oxygen in solution with decomposition. Reduction of *anti*-**4** in aqueous solution with zinc amalgam in the presence and absence of coordinating acids such as hydrochloric acid, formic acid, acetic acid, or HBF_4 leads to dimeric, green, bis(μ-hydroxo)-bridged complexes of molybdenum(III) (Scheme II). All these complexes are diamagnetic, and together with their characteristic electronic spectra, strong Mo–Mo bonds are proposed—most probably of bond order 3.[2] Both **6** and the respective diaqua species are very reactive toward oxidation by O_2 in solution and in the solid state; purple **4** is the sole product in both cases.

Crystal Structure. Crystals of purple **4** consist of discrete, well-separated $[L_2Mo_2O_4]^{2+}$ cations, ClO_4^- anions, and molecules

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(10) Figgis, B. N.; Lewis, J. In "Techniques of Inorganic Chemistry"; Jonassen, H. B., Weissberger, A., Eds.; Wiley-Interscience: New York, 1965; Vol. 4, p 137.

(11) DeTar, D. F. *Comput. Chem.* **1978**, *2*, 99.

Table V. ^{95}Mo NMR Data[a]

complex	solvent	chem shift,[d] ppm	line width, Hz	ref
$[(C_5H_5)Mo(CO)_3]^-$	CH_2Cl_2	−2120	20	20
$([9]aneS_3)Mo(CO)_3$	$MeNO_2$	−1350	30	21
$[(HB(3,5\text{-}Me_2pz)_3)Mo(CO)_3]^-$	DMF	−1149	80	*e*
$L''Mo(CO)_3$	Me_2SO	−1092	169	*e*
$LMo(CO)_3$	CH_2Cl_2	−1001	10	*e*
$L'Mo(CO)_3$	CH_2Cl_2	−866	20	*e*
$(C_5H_5)Mo(CO)_2(NO)$[b]	MeCN	−1584	<40	19
$(HB(3,5\text{-}Me_2pz)_3)Mo(CO)_2(NO)$	CH_2Cl_2	−746	60	19
$[L'Mo(CO)_2(NO)]BF_4$[c]	H_2O	−616	110	*e*
$[LMo(CO)_2(NO)]ClO_4$	H_2O	−580	90	*e*
$[L''Mo(CO)_2(NO)]PF_6$	MeCN	−437	80	*e*
anti-$[L_2Mo_2O_4](PF_6)_2$	MeCN	320	680	*e*
anti-$[L'_2Mo_2O_4]I_2$	H_2O	342	250	*e*
syn-$[L_2Mo_2O_4](ClO_4)_2$	H_2O	548	700	*e*
		527		
	MeCN	547	700	
		521		
	MeCN (80 °C)	575	650	
syn-$[L_2'Mo_2O_4]I_2$	H_2O	586	250	*e*

[a] L″ = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane; $HB(3,5\text{-}Me_2pz)_3^-$ = hydridotris(3,5-dimethylpyrazolyl)borate; DMF = *N,N*-dimethylformamide. [b] $J_{^{95}Mo-^{14}N}$ = 46 Hz at 343 K. [c] $J_{^{95}Mo-^{14}N}$ = 39 Hz at 373 K, partly resolved triplet. [d] Chemical shifts relative to 2 M Na_2MoO_4 in D_2O at pH 11. [e] This work.

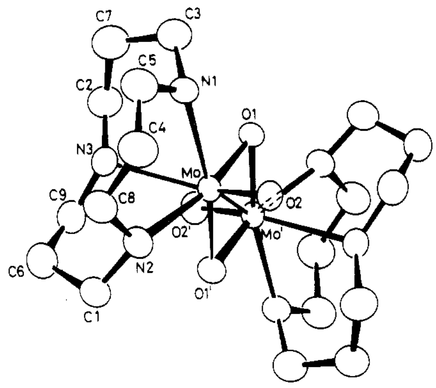

Figure 2. View of the cation *trans*-$[L_2Mo_2O_4]^{2+}$.

of water of crystallization. Figure 2 shows the molecular geometry and the atomic labeling scheme for the $[L_2Mo_2O_4]^{2+}$ core. Bond distances and angles are summarized in Table III.

The structure of the $[Mo_2O_4]^{2+}$ core is within experimental error identical with that of purple *anti*-$[L'_2Mo_2O_4]^{2+}$ reported previously.[1] The four-membered Mo_2O_2 ring is planar, in contrast to the well-known puckered ring of yellow *syn*-$[Mo_2O_4]^{2+}$ cores. The bond distances of terminal and bridging oxo groups to molybdenum agree well with other structures of this type. The short Mo–Mo distance of 2.586 (1) Å is in the range 2.55–2.60 Å observed for oxo-bridged Mo(V) dimers,[2a] which together with the diamagnetism of $[L_2Mo_2O_4]^{2+}$ is indicative of a Mo–Mo bond order of 1. The terminal oxo groups exert a strong trans influence on the Mo–N bond lengths (2.346 vs. 2.277 Å for nitrogens trans to oxo bridges). The O_t–Mo–Mo′ and N3–Mo–Mo′ bond angles are markedly greater than 90°, in agreement with a significant displacement of the molybdenum atoms from the idealized center of the N_3O_3 donor sets due to metal–metal bonding.

From comparisons of the crystal structures of *anti*- and *syn*-$[L'_2Mo_2O_4]^{2+}$,[1,4] we have recently proposed that the thermodynamic stability of the syn isomer containing puckered Mo_2O_2 rings may be due to a small but significant increased overall nonbonding distance of terminal and bridging oxygens as compared to that of its anti analogue[4] with planar Mo_2O_2 rings. This effect was most clearly shown by comparing the sum of the three O–Mo–O bond angles in the syn and anti isomers.[4]

Theoretical calculations on the *syn*- and *anti*-$[Mo_2S_4(S_2C_2H_4)_2]^{2-}$ ions have shown that direct Mo–Mo bonding interaction is more stable in the syn isomer.[12] Recent theoretical studies[13] on *syn*-$[Mo_2O_2S_2(S_2)_2]^{2-}$ show that the syn isomer is also stabilized by a direct π-bonding interaction between the two Mo=O units. Such a stabilizing π interaction is precluded by the geometry of the anti isomer.

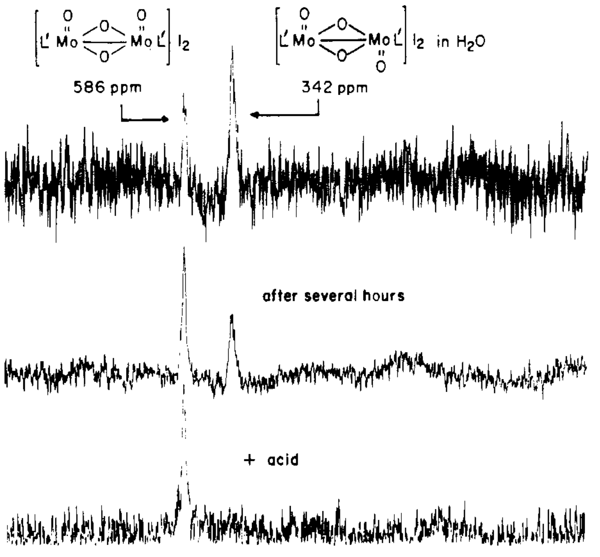

Figure 3. ^{95}Mo NMR spectra of *anti*- and *syn*-$[L'_2Mo_2O_4]^{2+}$ isomers (L′ = 1,4,7-triazacyclononane).

Other factors in addition to $O_t\cdots O_b$ repulsions and Mo–Mo bonding may be important in determining the most stable structure of $[L_2Mo_2O_4]^{2+}$ and $[L'Mo_2O_4]^{2+}$ complexes. Such factors include steric interactions among the coordinated ligands[14,15] and inter- and intramolecular hydrogen bonding involving the terminal oxo groups and the N–H groups of the ligand.[16]

^{95}Mo NMR Data. The yellow *syn*-$[L'_2Mo_2O_4]^{2+}$ and the purple *anti*-$[L'_2Mo_2O_4]^{2+}$ complexes are readily distinguished by ^{95}Mo NMR spectroscopy (Table V, Figure 3). Moreover, the interconversion of the anti isomer into the more stable syn isomer may be followed by ^{95}Mo NMR; Figure 3 shows the spectra of a sample containing both anti and syn isomers of $[L'_2Mo_2O_4]^{2+}$ at the beginning of an experiment, after several hours, and, finally, after the addition of several drops of $HClO_4$ (which rapidly catalyzes the isomerization). This is a further demonstration of the utility

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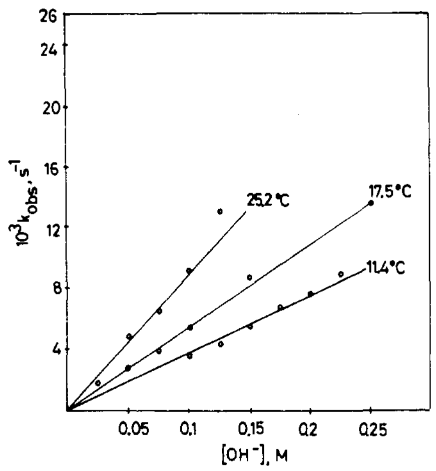

Figure 4. Plot of k_{obsd} (s^{-1}) vs. [OH^-] (M) for the anti → syn isomerization reaction of **4** (I = 0.25 M ($LiClO_4$)).

of ^{95}Mo NMR in monitoring the course of solution processes.[17] The two isomers of $[L_2Mo_2O_4]^{2+}$ display similar characteristic chemical shifts, that of the syn isomer, **5**, (average 535 ppm) being significantly more deshielded than that of the anti isomer, **4**, (320 ppm). Interestingly, two overlapping resonances are observed for the syn isomer (ca. 550 and 520 ppm) at room temperature. However, at 80 °C in MeCN a broad single resonance is observed; the presence of two conformers at room temperature is implied. Also, in contrast to the L′ system, but in keeping with other spectroscopic data, the anti to syn conversion in acidic solution is not observed by ^{95}Mo NMR in the case of **4**.

The tricarbonyl-molybdenum(0) complexes exhibit resonances that range from −2120 to 866 ppm (Table V). The variation of chemical shift with N-donor ligand follows the order L′ < L < L″ < $HB(3,5\text{-}Me_2pz)_3^-$. The $HB(3,5\text{-}Me_2pz)_3^-$ ligand also forms the most shielded N_3 ligand complex in the dicarbonyl nitrosyl series described below. The $([9]aneS_3)Mo(CO)_3$ complex is more shielded than the triaza complexes above; an analogous shielding trend has been observed for thioether and secondary amine complexes containing the MoO_2^{2+} moiety.[18] The $[(C_5H_5)Mo(CO)_3]^-$ complex exhibits the most shielded resonance of this series.

The dicarbonylnitrosylmolybdenum(0) complexes are deshielded by several hundred ppm compared to their tricarbonyl analogues. The shielding order observed in the triaza complexes of the dicarbonylnitrosyl series is the opposite of that found in the tricarbonyl series above. The ^{95}Mo–^{14}N spin–spin coupling (39 Hz) observed for the $[L'Mo(CO)_2(NO)]^+$ complex at 373 K is comparable to that found in similar complexes.[19] No ^{95}Mo–^{14}N coupling was observed for the other triaza complexes. Again the cyclopentadienyl complex exhibits the most shielded resonance of the series.

Kinetics and Mechanism of the Anti → Syn Isomerization. Aqueous solutions of purple **4** are stable at 25 °C for at least 2 days. Even in 1 M $HClO_4$ at 25 °C no change of the electronic spectrum was observed after 2 days, in contrast to its triazacyclononane analogue, which isomerizes under these conditions to the yellow cis isomer.[1] However, in alkaline solutions **4** rapidly changes color from purple to yellow. The final spectrum is identical with that of a genuine solution of **5**. The kinetics of this isomerization reaction were followed at 547 nm, the absorption maximum of purple **4**, with [OH^-] in large excess (pseudo-first-order conditions). Plots of absorbance changes, log ($A_t - A_\infty$), against time, t, were linear to at least 5 half-lives of the reaction. Observed first-order rate constants are listed in Table VI. The dependence of the rate constants, k_{obsd}, on [OH^-] is linear, eq 1 (Figure 4). The rate law derived for this base-

Table VI. Kinetic Data for the Anti → Syn, OH^--Catalyzed Isomerization Reaction of **4**

T, °C	[OH^-],[a] M	10^3k_{obsd}, s^{-1}	k, M^{-1} s^{-1}
11.4	0.10	3.7	0.040
	0.125	4.2	
	0.15	5.5	
	0.175	6.7	
	0.20	7.5	
	0.225	8.4	
17.5	0.05	2.6	0.056
	0.075	3.7	
	0.10	5.6	
	0.15	8.7	
	0.25	13.6	
25.2	0.025	1.68	0.104
	0.05	4.85	
	0.075	6.40	
	0.10	9.1	
	0.125	12.6	

$\Delta H^* = 11.3 \pm 1.3$ kcal mol^{-1} $\Delta S^* = -25 \pm 4$ cal mol^{-1} K^{-1}

[a] [Complex] = 5×10^{-4} M, I = 0.25 M ($LiClO_4$).

$$k_{obsd} = k[OH^-] \tag{1}$$

catalyzed reaction may be expressed as in eq 2–4. Equation 4

$$anti\text{-}[L_2Mo_2O_4]^{2+} + OH^- \overset{K_1}{\rightleftharpoons} \{[L_2Mo_2O_4(OH)]^+\} \tag{2}$$

$$\{[L_2Mo_2O_4(OH)]^+\} \xrightarrow{k_b} syn\text{-}[L_2Mo_2O_4]^{2+} + OH^- \tag{3}$$

$$\text{rate} = \frac{k_bK_1[OH^-]}{1 + K_1[OH^-]}[\text{complex}] \tag{4}$$

simplifies to the observed second-order rate law, eq 1, if $K_1[OH^-] < 1$; and the observed second-order rate constant k is a composite of k_bK_1.

These observed second-order rate constants at 25 °C are quite similar for the isomerization reaction of $[L'_2Mo_2O_4]^{2+}$ [1] (0.13 M^{-1} s^{-1}) and **4** (0.10 M^{-1} s^{-1}), but for the reaction of $[L'_2Mo_2O_4]^{2+}$ with OH^- the experimental rate law is of the form shown in eq 4 with $K_1 = 9$ M^{-1} and $k_b = 0.015$ s^{-1}.[1]

The reactive intermediate $\{[L_2Mo_2O_4(OH)]^+\}$, which is thought to be generated by nucleophilic attack of OH^- at a Mo(V) center trans to a terminal oxogroup (I_a mechanism), is converted in the rate-determining step to the syn isomer.[2b] It seems plausible that this interconversion is not significantly affected by the differing steric demands of L′ and L—once the intermediate is formed. Thus, k_b may be similar for both reactions. On the other hand, the preequilibrium, eq 2, may well be shifted to the left-hand side due to the increased bulkiness of L, and K_1 may be rather small.

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Registry No. **1**, 97703-29-2; **2**, 97703-31-6; **3**, 97689-66-2; **4**, 97747-92-7; **5**, 97689-68-4; **6**, 97689-69-5; **7**, 97689-71-9; **8**, 97689-72-0; **9**, 97689-73-1; **10**, 97689-75-3; *trans*-$[L_2Mo_2O_4]I_2$, 97805-11-3; $[(HB(3,5\text{-}Me_2pz)_3)Mo(CO)_3]^-$, 47637-78-5; $L''Mo(CO)_3$, 93646-59-4; $L'Mo(CO)_3$, 88253-24-1; $[L'Mo(CO)_2(NO)]BF_4$, 97689-77-5; $[L''Mo(CO)_2(NO)]PF_6$, 97689-79-7; $[LMo(CO)_2(NO)](BF_4)_2$, 97689-76-4; *anti*-$[L_2Mo_2O_4](PF_6)_2$, 97805-12-4; *anti*-$[L'_2Mo_2O_4]I_2$, 85923-30-4; $Mo(CO)_6$, 13939-06-5; Mo, 7439-98-7.

Supplementary Material Available: Tables of thermal parameters of non-hydrogen atoms, observed and calculated structure factor amplitudes, and elemental analyses of complexes (21 pages). Ordering information is given on any current masthead page.

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