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Investigations of the Coordination Chemistry of Molybdenum with Facultative Tetradentate Ligands Possessing N_2S_2 Donor Sets. 4.[1,2] Crystal and Molecular Structures of $[Mo_2O_3(C_8H_{18}N_2S_2)_2]$ and $[Mo_2O_4(C_9H_{22}N_2S_2)_2]$

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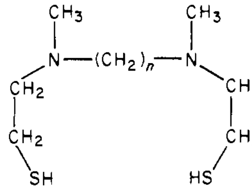
The reaction of $[MoO_2(acac)_2]$ with a twofold excess of *N,N'*-dimethyl-*N,N'*-bis(β-mercaptoethyl)ethylenediamine (LH_2) gives the deep purple compound $[Mo_2O_3(C_8H_{18}N_2S_2)]$, $[Mo_2O_3L_2]$, in low yield. X-ray crystallography shows that the molecule possesses a trans planar $[O{=}Mo{-}O{-}Mo{=}O]^{4+}$ core and that the ligand is present as a tetradentate, coordinating through sulfur and nitrogen donors. The complex crystallizes in space group *Pcab* with cell parameters a = 15.318 (3) Å, b = 17.957 (4) Å, and c = 18.298 (4) Å. The measured density of 1.70 g/cm^3 was in good agreement with the value of 1.72 g/cm^3 calculated on the basis of eight molecules in the unit cell. The structure has been refined to R_1 = 0.042 and R_2 = 0.048 on the basis of 2413 unique reflections with $F_o \geq 6\sigma(F_o)$. The analogous reaction of $[MoO_2(acac)_2]$ with the ligand *N,N'*-dimethyl-*N,N'*-bis(β-mercaptoethyl)propylenediamine ($L'H_2$) yields orange prisms of the compound $[Mo_2O_4(C_9H_{22}N_2S_2)_2]$, $[Mo_2O_4(L'H)_2]$. The complex crystallizes in the monoclinic space group $P2_1/a$ with unit cell dimensions a = 15.155 (5) Å, b = 12.446 (5) Å, and c = 16.195 (6) Å, and β = 101.99 (1)° with Z = 4 to give a calculated density of 1.55 g/cm^3 (observed density 1.54 g/cm^3). The structure was solved on the basis of 1907 unique reflections with $F_o \geq 6\sigma(F_o)$ and refined to final R values of 0.059 and 0.083. The complex possesses the $Mo_2O_4^{2+}$ core with molybdenum atoms coordinating to the thiolate sulfurs of the L' ligand. The unusual feature of the structure is that the two ligand amine nitrogens are not coordinated to the molybdenum, resulting in the 14-membered ring $(CH_2)_3N(CH_2)_2SMoOMo$-$S(CH_2)_2N$. One of the L'H nitrogens is protonated to produce a six-membered H-N-C-C-C-N ring with a chair conformation, and the ligand itself assumes an overall chair conformation.

Introduction

The chemistry of molybdenum is currently the subject of extensive research because of its recognized biochemical importance.[3,4] Research on the coordination chemistry of molybdenum–sulfur complexes[5,6] has been stimulated by recent electron paramagnetic resonance[7,8] and EXAFS[9-11] studies on molybdoenzymes other than nitrogenase that suggest thiolate sulfur as a donor to molybdenum. In addition, a basic group such as a nitrogen atom, or possible oxygen, is proposed to coordinate to molybdenum in xanthine oxidase. As part of our extensive investigations of the chemistry and structural systematics of molybdenum with sulfur-containing ligands,[6,12] we prepared oxo complexes of molybdenum with the facultative, potentially tetradentate N_2S_2 ligands L and L'. Although the Mo(VI) species $[MoO_2L]$ and $[MoO_2L']$[1] were readily synthesized, reduction of these species to Mo(V) dimers did not follow parallel paths. In the case of L, the μ-oxo dimer containing the $Mo_2O_3^{4+}$ core was produced by a variety of synthetic routes. On the other hand, with L' as ligand, reduction led preferentially to the formation of a species analyzing as $[Mo_2O_4(L'H)_2]$, whose infrared spectrum was consistent with the presence of the $Mo_2O_4^{2+}$ core (ν(Mo–O$_t$) 950 cm^{-1}; ν(Mo–O$_2$–Mo) 740 and 500 cm^{-1}) and hence suggested the protonation of L', which functioned as a bidentate ligand coordination exclusively through the thiolate sulfur donors. A preliminary report of the structure of $[Mo_2O_4(L'H)_2]$ has appeared.[2] This paper describes in detail the structures of the μ-oxo complex $[Mo_2O_3L_2]$ and of the μ-dioxo complex $[Mo_2O_4(L'H)_2]$ and compares these Mo(V) species to previously reported species possessing the $Mo_2O_3^{4+}$ and $Mo_2O_4^{2+}$ cores.



L, n = 2
L', n = 3

Experimental Procedures

The ligands LH_2 and $L'H_2$ were prepared as described previously.[13] The Mo(V) complexes $[Mo_2O_3L_2]$ and $[Mo_2O_4(L'H)_2]$ were prepared as described in part 2 of this series of papers.[14]

$[MoO_3L_3]$. Collection and Reduction of X-ray Data. The crystal used for the structure analysis was a purple needle with approximate dimensions 0.20 × 0.38 × 0.20 mm. A total of 25 reflections with 20° ≤ 2θ ≤ 40° were carefully aligned in the counter window of the Nicolet R3/m diffractometer. An autoindexing routine produced the unit cell dimensions recorded in Table I. Axial photographs and Delauney reduction of the unit cell dimensions revealed no hidden symmetry. The quality of the data crystal was checked by taking $\theta/2\theta$ scans of several strong low-angle reflections. The details of the data collection and reduction are given in Table I.

Structure Solution and Refinement. The structure of $[Mo_2O_3L_2]$ was solved by the conventional heavy-atom method. A Patterson map

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(1) For part 3 of this series see: Bruce, A.; Corbin, J. L.; Dahlstrom, P. L.; Hyde, J. R.; Minelli, M.; Spence, J.; Stiefel, E. I.; Zubieta, J. *Inorg. Chem.*, preceding paper in this issue.

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0020-1669/82/1321-0927$01.25/0

Table I. Crystal Data and Experimental Details of the X-ray Diffraction Study of $[Mo_2O_3L_2]$[a]

(A) Crystal Parameters at 21 °C[b]

a, Å	15.318 (3)	absences	$0kl$, $l = 2n + 1$; $k0l$, $k = 2n + 1$; $hk0$, $k = 2n + 1$
b, Å	17.957 (4)		
c, Å	18.298 (4)		
V, Å^3	5033.15	space group	*Pcab*[c]
mol wt	652	Z	8
cryst syst	orthorhombic	ρ(calcd), g/cm^3	1.72
$F(000)$	2656	ρ(obsd), g/cm^3	1.70[c]

(B) Measurement of Intensity Data

instrument	Nicolet R3/m diffractometer
radiation	Mo Kα ($\lambda\alpha_1$ 0.7093 Å), graphite monochromatized
scan technique	coupled θ(crystal)–2θ(counter)
scan range, deg	1.5
scan rate, deg/min	variable, 1–30 in 2θ
max 2θ, deg	45
bkgd measmts	stationary cryst, stationary counter; 20-s counts at each end of 2θ scan range
stds[e]	3 reflctns every 97 data reflctns
no. of reflctns collected	3844

(C) Treatment of Intensity Data

reductn to F_o^2 and $\sigma(F_o^2)$	corr for bkgd, attenuators, and Lorentz-polarization of monochromatized X radiation in the usual manner[f]
μ, cm^{-1}	13.20
obsd unique data, $F_o \geqslant 6\sigma(F_o)$	2413

[a] The computer programs used in this work are part of the integrated program package SHELXTL. [b] From a least-squares fit to the setting angles of 25 reflections. [c] A nonstandard setting of space group *Pbca* having the general equivalent positions (x, y, z), $(^1/_2 - x, {}^1/_2 + y, z)$, $(x, {}^1/_2 - y, {}^1/_2 + z)$, $(^1/_2 - x, -y, {}^1/_2 + z)$, and the centrosymmetrically related set. [d] Flotation. [e] Showed only random, statistical fluctuations. [f] Hyde, J.; Venkatasubramanian, K.; Zubieta, J. *Inorg. Chem.* 1978, *17*, 414.

was solved for the positions of the molybdenum atoms. Subsequent difference Fourier maps revealed the positions of all nonhydrogen atoms. No attempt was made to locate hydrogen atoms. All nonhydrogen atoms were refined anisotropically. Neutral-atom scattering factors and corrections for anomalous dispersion effects for the molybdenum and sulfur atoms were obtained from ref 15.

The final full-matrix least-squares refinements converged at $R_1 = 0.042$ and $R_2 = 0.049$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - F_c|)^2/\sum w|F_o|^2]^{1/2}$, with $w = 1/\sigma^2$. A final difference Fourier map showed no excursions of electron density greater than 0.8 e/Å^3; these peaks were found in reasonable positions for hydrogen atoms.

$[Mo_2O_4(L'H)_2]$. Collection and Reduction of X-ray Data. The crystal used for data collection was a parallelopiped with dimensions 0.30 × 0.25 × 0.35. Preliminary Weissenberg and precession photographs (Cu Kα, $\bar{\lambda}$ 1.5418 Å) show $2/m$ Laue symmetry with absences consistent with the space group $P2_1/a$. Final unit cell dimensions were produced by a least-squares fit to the setting angles of 25 reflections with $20° \geq 2\theta > 45°$. The details of the data collection and reduction are given in Table II.

Structure Solution and Refinement. The structure was solved as above with use of Patterson and Fourier methods. Refinement converged at $R_1 = 0.059$ and $R_2 = 0.083$, where R_1 and R_2 are defined as above. The final difference Fourier map showed excursions of electron density of 1.6 e/Å^3 in the vicinity of the molybdenum atoms. The resolution of the map was insufficient to allow location of hydrogen atoms.

Atomic positional and thermal parameters, topgether with standard deviations, are given in Tables III and IV for $[Mo_2O_3L_2]$ and $[Mo_2O_4(L'H)_2]$, respectively. Tables V and VI list selected interatomic bond lengths and angles for $[Mo_2O_3L_2]$ and $[Mo_2O_4(L'H_2)]$, respectively. Lists of observed and calculated structure factor amplitudes are provided as supplementary material. Perspective views of the geometries of $[Mo_2O_3L_2]$ and $[Mo_2O_4(L'H)_2]$, together with atom

Table II. Crystal Data and Experimental Details of the X-ray Diffraction Study of $[Mo_2O_4(L'H)_2]$[a]

(A) Crystal Parameters at 21 °C[b]

a, Å	15.155 (5)	absences	$0k0$, $k = 2n + 1$; $h0l$, $h = 2n + 1$
b, Å	12.446 (5)		
c, Å	16.195 (6)	space group	$P2_1/a$
β, deg	101.99 (1)	Z	4
V, Å^3	2988.1	ρ(calcd), g/cm^3	1.55
mol wt	698	ρ(obsd), g/cm^3	1.54 (2)[c]
$F(000)$	1360		
cryst syst	monoclinic		

(B) Measurement of Intensity Data

instrument	Picker FACS-I diffractometer
radiation	Mo Kα (λ 0.710 69 Å)
scan technique	coupled θ(cryst)–2θ(detector)
scan range, deg	1.5
scan rate, deg/min	1 in 2θ
max 2θ, deg	50
bkgd measmts	stationary cryst, stationary counter; 20-s counts at each end of 2θ scan range
stds[d]	3 reflctns every 97 data reflctns
no. of reflctns collected	2424

(C) Treatment of Intensity Data

reductn to F_o^2 and $\sigma(F_o^2)$	corr for bkgd, attenuators, and Lorenta-polarization in the usual manner
μ, cm^{-1}	11.13
obsd unique data, $F_o \geqslant 6\sigma(F_o)$	1907

[a] For a list of computer programs used in solution and refinement see: Stewart, J. M.; Kruger, G. J.; Ammon, H. L.; Dickinson, C.; Hall, S. R. Technical Report TR-192, University of Maryland, June 1972. [b] From a least-squares fitting of the setting angles of 12 reflections. [c] Flotation. [d] Showed only random, statistical fluctuations.

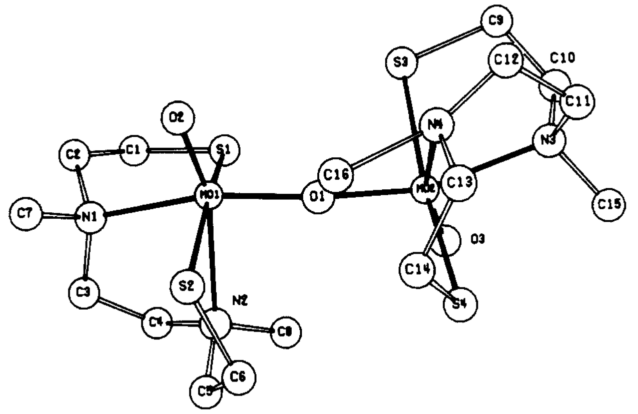

Figure 1. Structure of $[Mo_2O_3L_2]$ showing the atom labeling scheme and 50% probability thermal ellipsoids.

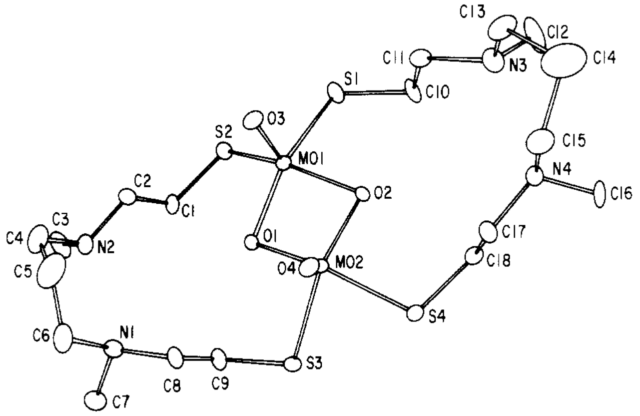

Figure 2. Structure of $[Mo_2O_4(L'H)_2]$ showing the atom labeling scheme and 50% probability thermal ellipsoids.

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(15) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72 ff.

Table III. Final Positional and Thermal Parameters for $[Mo_2O_3L_2]$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo1	0.368 06 (5)	0.151 14 (5)	0.454 75 (4)	2.11 (3)	2.22 (3)	2.00 (3)	−0.00 (4)	−0.01 (3)	0.06 (3)
Mo2	0.319 93 (5)	0.098 96 (5)	0.260 90 (4)	2.11 (3)	2.33 (3)	2.07 (4)	0.19 (4)	−0.18	0.05 (3)
S1	0.502 79 (16)	0.089 09 (15)	0.429 88 (14)	2.77 (12)	3.14 (13)	3.29 (13)	0.65 (11)	−0.07 (10)	−0.57 (11)
S2	0.502 77 (17)	0.248 49 (17)	0.471 61 (15)	3.24 (13)	4.13 (14)	3.39 (14)	1.33 (12)	0.29 (11)	−0.43 (13)
S3	0.368 35 (19)	−0.022 27 (15)	0.299 27 (15)	4.87 (14)	3.00 (13)	4.27 (14)	1.10 (12)	−1.76 (13)	−0.03 (11)
S4	0.226 35 (18)	0.206 35 (15)	0.228 13 (14)	4.37 (14)	3.22 (13)	2.96 (13)	1.05 (12)	−0.26 (12)	0.48 (11)
O1	0.337 15 (36)	0.130 44 (30)	0.357 45 (31)	2.08 (31)	2.19 (29)	2.64 (29)	0.58 (22)	−0.22 (23)	0.06 (23)
O2	0.310 37 (41)	0.093 83 (36)	0.508 05 (33)	3.50 (34)	3.83 (33)	2.83 (31)	0.00 (31)	−0.03 (27)	0.34 (29)
O3	0.399 72 (40)	0.134 34 (35)	0.210 57 (34)	3.15 (32)	3.84 (37)	3.08 (32)	0.38 (28)	0.41 (27)	−0.33 (28)
N1	0.448 28 (47)	0.193 48 (37)	0.552 43 (41)	3.34 (40)	1.99 (34)	2.75 (40)	−0.03 (31)	−0.26 (33)	0.06 (33)
N2	0.438 09 (48)	0.265 71 (40)	0.409 68 (40)	3.31 (40)	2.39 (39)	2.75 (40)	0.36 (33)	−0.17 (33)	0.30 (32)
N3	0.271 38 (55)	0.030 17 (42)	0.163 56 (41)	4.76 (49)	2.90 (42)	2.88 (42)	0.23 (37)	−0.77 (37)	−0.42 (34)
N4	0.172 85 (50)	0.059 19 (45)	0.298 15 (43)	2.94 (40)	4.33 (45)	3.66 (41)	−0.78 (37)	−0.29 (36)	0.03 (36)
C1	0.568 47 (59)	0.105 43 (55)	0.512 32 (51)	2.60 (44)	4.15 (54)	3.15 (48)	0.60 (45)	−1.32 (38)	−0.67 (45)
C2	0.510 34 (64)	0.131 33 (51)	0.575 84 (52)	3.61 (54)	3.04 (52)	3.37 (51)	1.21 (41)	−1.38 (43)	−0.08 (40)
C3	0.499 15 (65)	0.263 74 (54)	0.536 43 (56)	4.98 (55)	3.11 (53)	3.82 (55)	−1.80 (45)	−0.31 (48)	0.02 (46)
C4	0.520 91 (75)	0.275 09 (66)	0.455 33 (66)	5.99 (69)	6.84 (77)	5.62 (66)	−3.06 (59)	−1.29 (60)	1.30 (61)
C5	0.384 17 (84)	0.334 00 (62)	0.413 27 (80)	6.32 (86)	2.98 (60)	11.31 (104)	0.91 (58)	1.82 (76)	1.72 (66)
C6	0.287 59 (65)	0.316 23 (54)	0.401 90 (60)	3.75 (55)	2.89 (51)	5.59 (65)	−0.35 (43)	−1.70 (49)	1.73 (47)
C7	0.391 19 (67)	0.209 43 (57)	0.617 79 (50)	5.39 (66)	4.47 (57)	1.96 (46)	0.41 (50)	1.15 (44)	−0.50 (44)
C8	0.473 07 (83)	0.255 79 (66)	0.333 51 (61)	9.30 (86)	3.88 (61)	4.38 (67)	−0.36 (64)	4.01 (64)	0.18 (54)
C9	0.344 18 (77)	−0.082 84 (57)	0.220 05 (59)	7.79 (80)	3.30 (56)	4.62 (63)	1.78 (53)	−1.60 (56)	−1.66 (48)
C10	0.333 44 (70)	−0.034 59 (56)	0.151 57 (56)	5.27 (64)	3.50 (54)	4.25 (57)	1.54 (47)	−1.18 (50)	−1.27 (47)
C11	0.178 85 (74)	0.004 05 (62)	0.173 51 (59)	4.43 (61)	4.86 (62)	4.50 (60)	−1.95 (54)	−0.83 (52)	−0.78 (50)
C12	0.154 13 (66)	−0.011 54 (56)	0.253 24 (62)	5.10 (57)	5.19 (56)	4.58 (58)	−2.65 (46)	−0.74 (48)	−1.08 (52)
C13	0.102 36 (66)	0.114 35 (60)	0.285 44 (64)	3.04 (52)	5.06 (66)	6.21 (69)	1.52 (47)	0.45 (49)	0.82 (56)
C14	0.138 65 (69)	0.193 36 (61)	0.295 76 (57)	3.51 (54)	5.52 (64)	3.83 (55)	0.92 (51)	0.63 (48)	−0.91 (51)
C15	0.273 13 (79)	0.075 32 (58)	0.093 49 (51)	7.87 (78)	4.02 (62)	1.67 (47)	−0.15 (55)	−0.38 (50)	0.49 (43)
C16	0.172 21 (71)	0.036 40 (67)	0.377 82 (55)	4.46 (62)	7.85 (78)	2.66 (51)	−2.42 (58)	0.71 (48)	1.63 (54)

Table IV. Final Atomic Positional and Thermal Parameters for $[Mo_2O_4(L'H)_2]$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo1	0.22237 (7)	0.04155 (10)	0.32163 (5)	5.4 (1)	6.4 (2)	3.3 (1)	0.16 (7)	0.59 (5)	−0.51 (6)
Mo2	0.19946 (7)	−0.03563 (10)	0.16797 (5)	5.1 (1)	6.1 (2)	3.1 (1)	0.21 (7)	0.64 (6)	−0.18 (6)
S1	0.3354 (3)	0.0360 (4)	0.4368 (2)	7.9 (3)	8.3 (4)	5.8 (2)	1.0 (3)	−1.9 (2)	−1.3 (2)
S2	0.2415 (3)	0.2285 (4)	0.3660 (2)	8.1 (3)	6.6 (3)	5.4 (2)	0.8 (2)	0.2 (2)	−1.4 (2)
S3	0.1780 (2)	0.0588 (3)	0.0333 (1)	7.8 (3)	7.1 (3)	3.7 (2)	1.1 (2)	1.2 (2)	0.7 (2)
S4	0.3117 (3)	−0.1167 (4)	0.0996 (2)	6.9 (3)	8.1 (3)	4.2 (2)	1.2 (2)	1.5 (2)	0.0 (2)
O1	0.1740 (6)	0.1034 (7)	0.2106 (4)	6.5 (6)	4.0 (7)	3.7 (4)	1.4 (5)	0.7 (4)	0.1 (5)
O2	0.2879 (6)	−0.0662 (7)	0.2711 (4)	5.9 (6)	5.3 (6)	5.6 (4)	1.9 (5)	0.4 (4)	0.5 (5)
O3	0.1404 (6)	−0.0108 (9)	0.3645 (5)	6.8 (6)	8.3 (7)	5.0 (5)	−1.1 (6)	1.9 (5)	−0.9 (6)
O4	0.1116 (6)	−0.1195 (8)	0.1559 (5)	4.8 (6)	8.7 (8)	5.3 (5)	−1.4 (6)	1.0 (4)	−1.2 (6)
N1	−0.0308 (8)	0.2568 (11)	0.0613 (7)	6.7 (8)	8.0 (9)	6.3 (6)	−0.9 (8)	1.1 (6)	0.8 (8)
N2	0.0031 (8)	0.3437 (11)	0.2209 (7)	6.3 (8)	9.7 (1.0)	6.8 (7)	1.4 (8)	1.5 (6)	−1.3 (8)
N3	0.4021 (11)	−0.2942 (11)	0.4290 (7)	13.7 (12)	5.7 (9)	5.8 (7)	0.7 (9)	−0.1 (7)	−0.6 (7)
N4	0.3710 (8)	−0.3693 (10)	0.2666 (6)	8.6 (9)	6.3 (9)	5.7 (6)	1.5 (8)	1.5 (8)	0.3 (7)
C1	0.1651 (9)	0.3081 (12)	0.2875 (8)	5.9 (9)	5.2 (10)	7.1 (8)	1.4 (9)	2.1 (7)	0.5 (9)
C2	0.0658 (12)	0.2837 (15)	0.2882 (8)	8.5 (1.2)	12.0 (1.7)	6.2 (8)	2.9 (12)	2.1 (8)	1.9 (11)
C3	0.0148 (16)	0.4574 (17)	0.2300 (13)	4.0 (19)	9.2 (17)	10.8 (14)	5.8 (14)	3.2 (13)	−3.9 (13)
C4	−0.0908 (14)	0.3166 (23)	0.2196 (13)	7.6 (13)	15.0 (20)	11.2 (14)	−1.7 (15)	3.2 (11)	−5.1 (16)
C5	−0.1231 (17)	0.2308 (29)	0.1664 (21)	11.3 (20)	22.6 (34)	19.5 (27)	−8.6 (22)	9.8 (19)	−1.7 (29)
C6	−0.1288 (10)	0.2252 (18)	0.0753 (13)	4.6 (10)	12.9 (19)	12.4 (14)	−1.0 (11)	0.9 (9)	−5.3 (15)
C7	−0.0422 (15)	0.3349 (16)	−0.0111 (10)	13.0 (15)	8.0 (14)	7.4 (10)	1.8 (13)	1.5 (10)	1.9 (11)
C8	0.0189 (10)	0.1547 (12)	0.0459 (9)	7.8 (11)	2.8 (10)	6.7 (8)	1.8 (9)	0.4 (7)	0.7 (8)
C9	0.1176 (10)	0.1826 (13)	0.0435 (9)	6.3 (10)	5.3 (11)	7.9 (9)	0.5 (9)	1.8 (8)	2.1 (9)
C10	0.4152 (10)	−0.0918 (13)	0.4262 (9)	7.1 (10)	3.3 (11)	7.3 (9)	−0.2 (10)	−1.7 (8)	0.2 (9)
C11	0.3571 (15)	−0.1809 (16)	0.4457 (8)	17.6 (19)	6.2 (14)	4.6 (8)	1.3 (15)	3.1 (10)	−0.02 (87)
C12	0.4947 (17)	−0.3074 (17)	0.4738 (14)	16.7 (23)	8.8 (16)	12.7 (16)	4.6 (16)	−7.9 (15)	−1.4 (14)
C13	0.3368 (20)	−0.3807 (15)	0.4433 (13)	28.8 (33)	3.0 (13)	10.1 (14)	−1.8 (15)	10.3 (18)	−1.0 (12)
C14	0.3458 (27)	−0.4777 (30)	0.3879 (18)	25.7 (38)	20.8 (36)	12.9 (20)	−12.3 (31)	5.6 (23)	−1.4 (24)
C15	0.3051 (16)	0.4465 (18)	0.2928 (12)	15.6 (21)	11.0 (18)	8.2 (11)	3.1 (16)	3.0 (12)	1.5 (13)
C16	0.4473 (14)	−0.4245 (17)	0.2426 (13)	11.0 (15)	8.5 (14)	12.8 (15)	6.1 (13)	5.4 (13)	2.0 (13)
C17	0.3171 (11)	−0.3037 (15)	0.1965 (9)	8.0 (11)	7.7 (13)	6.1 (9)	1.5 (11)	−1.3 (8)	−1.2 (10)
C18	0.3778 (9)	−0.2073 (13)	0.1764 (8)	5.7 (9)	6.7 (12)	5.0 (7)	−1.6 (10)	1.3 (6)	−1.1 (8)

labeling schemes, are shown in Figures 1 and 2, respectively.

Results and Discussion

Structure of $[Mo_2O_3L_2]$. Each molybdenum atom of the discrete dimeric unit of $[Mo_2O_3L_2]$ is pseudooctahedrally coordinated to the mutually cis oxo groups and the thiolato sulfur and amine nitrogen atoms. The thiolato sulfur donors assume the preferred mutually trans configuration and are found cis to the oxo groups. The amine nitrogen donors are thus mutually cis and trans to the oxo groups. The two octahedral units about the molybdenum atoms share one vertex at the bridging oxo group, O1. The central unit O═Mo—O—Mo═O is planar, consistent with the diamagnetism of the complex and general bonding considerations.

Although a number of complexes possessing the $Mo_2O_3^{4+}$ core of the types $[Mo_2O_3(AB)_4]^{16-22}$ and $[Mo_2O_3(ABC)_2]^{23-25}$

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Table V. Selected Bond Lengths (Å) and Angles (Deg) for $[Mo_2O_3L_2]$

Mo1-S1	2.390 (3)	C3-C4	1.53 (2)
Mo1-S2	2.483 (3)	C4-N2	1.54 (2)
Mo1-O1	1.880 (6)	N2-C5	1.48 (2)
Mo1-O2	1.672 (7)	N2-C8	1.50 (1)
Mo1-N1	2.298 (8)	C5-C6	1.53 (2)
Mo1-N2	2.461 (8)	S2-C6	1.84 (1)
Mo2-S3	2.405 (4)	S3-C9	1.85 (1)
Mo2-S4	2.476 (3)	C9-C10	1.53 (2)
Mo2-O1	1.874 (6)	C10-N3	1.52 (1)
Mo2-O3	1.657 (7)	N3-C11	1.51 (2)
Mo2-N3	2.286 (9)	N3-C15	1.52 (1)
Mo2-N4	2.462 (9)	C11-C12	1.53 (2)
S1-C1	1.84 (1)	C12-N4	1.55 (2)
C1-C2	1.54 (2)	N4-C13	1.48 (1)
C2-N1	1.52 (1)	N4-C16	1.51 (1)
N1-C3	1.52 (1)	C13-C14	1.54 (2)
N1-C7	1.51 (1)	S2-C14	1.84 (1)
S1-Mo1-S2	162.9 (1)	S3-Mo2-S4	162.6 (1)
S1-Mo1-O1	86.9 (2)	S3-Mo2-O1	87.4 (2)
S1-Mo1-O2	106.2 (3)	S3-Mo2-O3	106.3 (3)
S1-Mo1-N1	80.8 (2)	S3-Mo2-N3	80.8 (2)
S1-Mo1-N2	87.2 (2)	S3-Mo2-N4	86.6 (2)
S2-Mo1-O1	94.6 (2)	S4-Mo2-O1	94.3 (2)
S2-Mo1-O2	89.6 (3)	S4-Mo2-O3	89.7 (3)
S2-Mo1-N1	92.5 (2)	S4-Mo2-N3	92.5 (2)
S2-Mo1-N2	75.9 (2)	S4-Mo2-N4	76.2 (2)
O1-Mo1-O2	107.3 (3)	O1-Mo2-O3	107.9 (3)
O1-Mo1-N1	159.6 (3)	O1-Mo2-N3	160.3 (3)
O1-Mo1-N2	87.5 (3)	O1-Mo2-N4	87.3 (3)
O2-Mo1-N1	91.8 (3)	O3-Mo2-N3	90.7 (3)
O2-Mo1-N2	160.3 (3)	O3-Mo2-N4	160.2 (3)
N1-Mo1-N2	75.8 (3)	N3-Mo2-N4	76.3 (3)
Mo1-S1-C1	104.1 (4)	Mo2-S3-C9	103.9 (4)
S1-C1-C2	110.5 (7)	S3-C9-C10	109.0 (8)
C1-C2-N1	112.0 (8)	C9-C10-N3	112.4 (9)
C2-N1-C3	109.7 (8)	C10-N3-C11	111.1 (8)
C2-N1-C7	106.2 (7)	C10-N3-C15	105.9 (8)
C3-N1-C7	107.0 (8)	C11-N3-C15	106.7 (8)
Mo1-N1-C2	108.2 (6)	Mo2-N3-C10	108.8 (6)
Mo1-N1-C3	113.7 (6)	Mo2-N3-C11	112.6 (6)
Mo1-N1-C7	111.7 (6)	Mo2-N3-C15	111.4 (6)
N1-C3-C4	113.9 (9)	N3-C11-C12	113.8 (9)
C3-C4-N2	109.8 (10)	C11-C12-N4	108.2 (9)
C4-N2-C5	111.1 (8)	C12-N4-C13	109.2 (8)
C4-N2-C8	105.9 (8)	C12-N4-C16	106.4 (8)
C5-N2-C8	106.7 (8)	C12-N4-C16	109.5 (8)
Mo1-N2-C4	108.8 (6)	Mo2-N4-C12	105.1 (6)
Mo1-N2-C5	112.6 (6)	Mo2-N4-C13	115.7 (6)
Mo1-N2-C8	11.4 (6)	Mo2-N4-C16	110.5 (6)
N2-C5-C6	110.7 (10)	N4-C13-C14	109.2 (9)
C5-C6-S2	108.0 (8)	Mo2-S4-C14	99.3 (4)
Mo1-O1-Mo2	171.2 (4)		

Table VI. Selected Bond Lengths (Å) and Angles (Deg) for $[Mo_2O_4(L'H)_2]$

Mo1-Mo2	2.623 (1)		
Mo1-S1	2.447 (4)	Mo2-S3	2.440 (3)
Mo1-S2	2.434 (4)	Mo2-S4	2.434 (4)
Mo1-O1	1.954 (7)	Mo2-O1	1.933 (9)
Mo1-O2	1.946 (9)	Mo2-O2	1.950 (7)
Mo1-O3	1.68 (1)	Mo2-O4	1.671 (9)
S2-C1	1.83 (1)	S1-C10	1.86 (2)
C1-C2	1.54 (2)	C10-C11	1.49 (2)
C2-N2	1.49 (2)	C11-N3	1.59 (3)
N2-C3	1.43 (3)	N3-C12	1.45 (3)
N2-C4	1.46 (2)	N3-C13	1.51 (3)
C4-C5	1.40 (4)	C13-C14	1.53 (2)
C5-C6	1.46 (4)	C14-C15	1.58 (3)
C6-N1	1.60 (2)	C15-N4	1.51 (3)
N1-C7	1.50 (2)	N4-C16	1.46 (3)
N1-C8	1.52 (2)	N4-C17	1.50 (3)
C8-C9	1.55 (2)	C17-C18	1.59 (2)
C9-S3	1.82 (2)	C18-S4	1.82 (1)
S1-Mo1-S2	76.9 (1)	S3-Mo2-S4	76.7 (1)
S1-Mo1-O1	143.6 (3)	S3-Mo2-O1	83.6 (2)
S1-Mo1-O2	83.7 (3)	S3-Mo2-O2	143.2 (3)
S1-Mo1-O3	108.8 (2)	S3-Mo2-O4	103.9 (2)
S2-Mo1-O1	83.9 (3)	S4-Mo2-O1	138.1 (3)
S2-Mo1-O2	137.9 (3)	S4-Mo2-O2	83.6 (3)
S2-Mo1-O3	107.6 (3)	S4-Mo2-O4	107.7 (3)
O1-Mo1-O2	90.7 (4)	O1-Mo2-O2	91.2 (3)
O1-Mo1-O3	111.4 (4)	O1-Mo2-O4	112.8 (4)
O2-Mo1-O3	113.2 (5)	O2-Mo2-O4	111.6 (4)
Mo2-Mo1-O3	106.9 (2)	Mo1-Mo2-O4	106.6 (2)
Mo1-S2-C1	107.1 (5)	Mo2-S4-C18	106.5 (5)
S2-C1-C2	111.6 (10)	S4-C18-C17	110.4 (9)
C1-C2-N2	111.9 (13)	C17-N4-C16	113.0 (13)
C2-N2-C3	112.1 (13)	C17-N4-C15	105.8 (13)
C2-N2-C4	111.6 (14)	C15-N4-C16	112.5 (14)
N2-C4-C5	108.4 (13)	N4-C15-C14	106.6 (19)
C4-C5-C6	116.8 (29)	C15-C14-C13	108.2 (24)
C4-C6-N1	105.6 (15)	C14-C13-N3	109.3 (23)
C6-N1-C7	129.9 (13)	C13-N3-C11	106.4 (15)
C6-N1-C8	112.1 (12)	C13-N3-C12	116.1 (15)
C7-N1-C8	113.0 (12)	C11-N3-C12	114.5 (13)
N1-C8-C9	109.3 (12)	N3-C11-C10	109.1 (16)
C8-C9-S3	108.8 (10)	C11-C10-S1	107.4 (12)
C9-S3-Mo2	107.6 (5)	C10-S1-Mo1	107.0 (5)

have been structurally characterized, where AB is a bidentate lignd and ABC is a tridentate group, $[Mo_2O_3L_2]$ provides the first example of a complex of this general class with a tetradentate ligand. The complexes of the type $[Mo_2O_3(AB)_4]$ are of two symmetry types: $[Mo_2O_3(S_2CNEt)_4]$,[16] $[Mo_2O_3(S_2CSC_3H_7)_4]$[19], and $[Mo_2O_3(S_2CNPr_2)_4]$[18] have a cis configuration of the terminal oxo groups of the Mo_2O_3 unit while $[Mo_2O_3[S_2P(OEt)_2]_4]$[17] and $[Mo_2O_3(C_5H_4NS)_4]$[22] possess a trans Mo_2O_3 chain with rigorous inversion symmetry. The five-coordinate structures $[Mo_2O_3(ABC)_2]$, where ABC is $CH_3N(C_2H_4S)_2$[23] $S(C_2H_4S)_2$,[24] or $O(C_2H_4S)_2$,[25] display only the trans chain configuration. The present compound $[Mo_2O_3L_2]$ possesses the trans arrangement of the O═Mo—O—Mo═O unit.

The bond lengths and angles in the $Mo_2O_3^{4+}$ unit are similar to those reported for other μ-oxo dimers of this type, as illustrated in Table V. The $Mo_2O_3^{4+}$ unit is essentially invariant to changes in coordination numbers or to changes in ligand type.

The Mo–N amine distances are nonequivalent, reflecting the relative trans influences of the bridging and terminal oxo group and the inherent strain of the ligand. Thus, the average Mo–N distance for the amine group trans to the bridging oxygen is 2.292 (9) Å while the average Mo–N distance for the trans terminal oxo amine nitrogen is lenghtened to 2.462 (8) Å. Molybdenum–amine nitrogen distances in oxo–molybdenum(V) dimers fall in the range 2.205 (6)–2.448 (8) Å, depending on the nature of the trans donor as illustrated in Table VII.

An unusual feature of the structure is the nonequivalence of the Mo–S bond lengths, which fall into two groups: the Mo–S distances for the thiolate donors in the five-membered chelate ring containing the amine nitrogen trans to the bridging oxo group at 2.398 (3) Å and the Mo–S bond lengths for those in the five-membered rings with the amine nitrogens trans to the terminal oxo group at 2.480 (3) Å. This effect is not observed in other examples of Mo(V) complexes with thiolate

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Table VII. Comparison of Relevant Structural Parameters for Dimeric Mo(V) Containing the $Mo_2O_3^{4+}$ Core

complex	Mo–O_t[a]	Mo–O_b	O_t–Mo–O_b	Mo–L_{tt}[b]	Mo–L_{tb}	Mo–L_c	ref
$[Mo_2O_3L_2]$	1.672 (7) 1.657 (7)	1.880 (6) 1.874 (6)	107.3 (3) 107.9 (3)	2.461 (8), N 2.462 (9), N	2.298 (8), N 2.286 (9), N	2.390 (3), S 2.483 (3), S 2.405 (4), S 2.476 (3), S	this work
$[Mo_2O_3(S(C_2H_4S)_2)_2]$	1.642 (16)	1.873 (2)	108.1 (7)		2.482 (6), S	2.360 (7), S 2.346 (8), S	24
$[Mo_2O_3(O(C_2H_4S)_2)_2]$	1.659 (7)	1.849 (6)			2.160 (8)0	2.342 (4), S 2.365 (4), S	25
$[Mo_2O_3(MeN(C_2H_4S)_2)_2]$	1.671 (8)	1.860 (1)	105.5 (3)		2.236 (10), N	2.347 (3), S 2.365 (4), S	23
$[Mo_2O_3(S_2COEt)_4]$	1.65 (2)	1.86 (2)	104 (1)	2.70 (2)	2.54 (1)	2.49 (1)	16
$[Mo_2O_3(S_2P(OEt)_2)_4]$	1.65 (1)	1.86 (2)	103 (1)	2.801 (5)	2.547 (5)	2.47 (1)	17
$[Mo_2O_3(S_2CSPr_2)_4]$	1.67 (1)	1.87 (1)	103 (1)	2.68 (1)	2.53 (1)	2.48 (4)	18
$[Mo_2O_3(S_2CNPr)_4]$	1.69 (1)	1.84 (1)	104.4 (7)	2.694 (6)	2.565 (6)	2.489 (6)	19
$[Mo_2O_3(C_6H_4NS)_4]$	1.673 (4)	1.853 (1)	105.9 (2)	2.305 (5), N	2.185 (5), N	2.463 (2)	22

[a] Abbreviations: O_t, terminal oxo group; O_b, bridging oxo group; L_c, ligand cis to O_t and O_b; L_{tt}, ligand trans to O_t; L_{tb}, ligand trans to O_b. [b] All Mo–L distances are metal–sulfur distances unless otherwise identified.

Table VIII. Selected Structural Parameters[a] for Oxomolybdenum(V) Dimers Having Ligands with Thiolate and Amine Donors, or Both

complex	geometry	Mo–Mo	Mo–Mo–O_t	Mo–S	Mo–N	ref
$[Na_2Mo_2O_4(cys)_2]$[b]	octahedral	2.569 (2)	99.5 (6)	2.490 (6)	2.23 (2)	32
$Mo_2O_4(his)_2 \cdot 3H_2O$[c]	octahedral	2.552			2.23	33
$[Mo_2O_4(Et\text{-}cys)_2]$	trigonal bipyramidal	2.562 (3)	102.5 (6)	2.380 (8)	2.219 (3)	34
$[Mo_2O_2S_2(Me\text{-}cys)_2]$	trigonal bipyramidal	2.804 (4)	101.8 (5)	2.380 (1)	2.24 (3)	35
$[Mo_2O_2S_2(his)_2] \cdot 1.5H_2O$[c]	octahedral	2.848 (4)	103.0 (1)		2.254 (9)	36
$Cs_2[Mo_2O_2S_2EDTA] \cdot 2H_2O$[d]	octahedral	2.799 (1)	100.5		2.448 (8)	37
$[Mo_2O_2S_2(his)_2] \cdot 1.5H_2O$[b]	octahedral	2.82 (1)	103 (1)	2.50 (1)	2.27 (3)	38
$[Mo_2O_3(SC_2H_4O)(oxine)_2]$[e]	octahedral	2.628 (1)		2.484 (2)		39
$(R_4N)_2[Mo_2O_4(SPh)_4]$	square pyrimidal	2.677 (2)		2.451 (4)		30
$(C_5H_{10}NH_2)_2[Mo_2O_3(SCH_2CH_2O)_3]$	octahedral	2.676 (1)		2.412 (3) 2.507 (2)[f]		40
$[Mo_2O_4(L'H)_2]$	square pyramidal	2.623 (1)	106.7 (2)	2.439 (3)		this work
$[Mo_2O_3(S(C_2H_4S)_2)_2]$	trigonal bipyramidal	*h*		2.353 (8) 2.482 (6)[g]		24
$[Mo_2O_3(O(C_2H_4S)_2)]_2$	trigonal bipyramidal	*h*		2.354 (4)		25
$[Mo_2O_3(MeN(C_2H_4S)_2)]$	trigonal bipyramidal	*h*		2.345 (4)	2.236 (10)	23
$[Mo_2O_3L_2]$	octahedral	*h*		2.398 (3)[i] 2.480 (3)[j]	2.292 (9)[k] 2.462 (9)[l]	this work

[a] Bond lengths in angstroms, angles in degrees. [b] Cysteine O trans to O_t. [c] Histidine O trans to O_t. [d] EDTA nitrogen trans to O_t. [e] The molybdenum atoms are bridged by an oxo group and by the thiolate sulfur and oxygen atoms of the 2-mercaptoethanol. [f] Nonequivalent Mo–S distances. [g] Thioether sulfur trans to the bridging oxo group. [h] Mo–O–Mo linkage rather than short Mo–Mo distance. [i] Sulfur donor in chelate ring with amine nitrogen trans to the bridging oxo group. [j] Sulfur donor in chelate ring with amine nitrogen trans to the terminal oxo group. [k] Nitrogen trans to the bridging oxo group. [l] Nitrogen trans to the terminal oxo group.

sulfur ligands or with dithioacid donors (Tables VII and VIII) and presumably reflects the steric constraints imposed by the "toC–N–Mo–N–C five-membered ring. This effect has been discussed for the dimeric iron species Fe_2L_2[26] and the monomeric molybdenum(VI) complexes [MoO_2L], [MoO(N_2R_2)L],[27] and [Mo(N_2R)$_2$L].[27]

The requirement of forming three five-membered chelate rings with the metal results in a tightly wrapped ligand chain and appears to produce pronounced differences in the bond lengths and significant deviations of the Mo–valence angles from those anticipated for regular octahedral geometry. The internal chelate ring angles are thus 80.8, 87.2, and 75.9° for S1–Mo–N1, S2–Mo–N2, and N1–Mo–N2, respectively. This severe accumulation of strain causes the $\overline{\mathrm{C{-}N{-}Mo{-}S{-}C}}$ rings to fold back toward the metal–diamine plane, as previously noted.[26]

The ligand geometry of [$Mo_2O_3L_2$] is similar to that observed for other complexes of L.[26] The methylene carbon atoms are on opposite sides of the S–Mo–N planes, thus producing $\overline{\mathrm{C{-}N{-}Mo{-}S{-}C}}$ rings with asymmetric skew conformations.[28] The methyl groups are on opposite sides of the N–Mo–N planes as in [Zn_2Cl_2L]$_2$·$2H_2O$.[29]

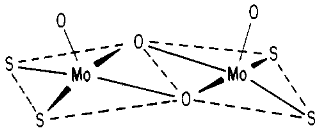

Figure 3. Schematic view of the edge-sharing, square-pyramidal molybdenum coordination geometry in [$Mo_2O_4(L'H)_2$], illustrating the cis-bent arrangement of the tetragonal planes.

Structure of [$Mo_2O_4(L'H)_2$]. Under similar reaction conditions to those employed to synthesize [$Mo_2O_3L_2$], we found that the analogous μ-oxo dimer of L′ could not be isolated but that the μ-dioxo species [$Mo_2O_4(L'H)_2$] formed preferentially. As illustrated in Figure 2, the complex forms discrete dimeric units with each molybdenum enjoying pseudo-square-pyramidal geometry, provided by the bridging oxo groups, and apical terminal oxo ligand, and the sulfur donors of L′. The two square-pyramidal units share an edge through the bridging oxygen ligands to produce the common cis-bent configuration

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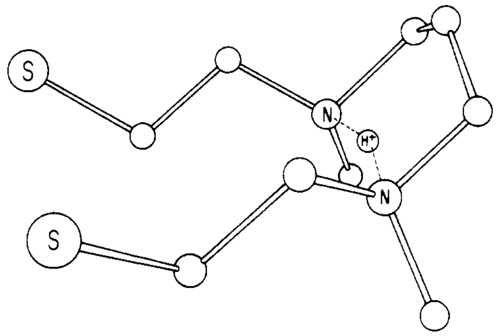

Figure 4. Schematic view of the ligand folding in $[Mo_2O_4(L'H)_2]$, illustrating the six-membered H–N–C–C–C–N ring and the chair conformation of the bridging bidentate ligand.

with a dihedral angle of 149.9° between the S1S2O1O2 and the S3S4O1O2 planes (Figure 3). The molybdenum atoms are displaced an average of 0.71 Å from the S_2O_2 basal planes in the direction of the terminal oxo group that defines the apex.

The structural parameters within the $Mo_2O_4^{2+}$ core are unexceptional and similar to those observed for $[Mo_2O_4(SPh)_4]^{2-}$,[30] $Mo_2O_4(S_2CN(C_2H_5)_2)_2$,[31] and other Mo(V) dimers with the $Mo_2O_4^{2+}$ core listed in Table VIII.

The average Mo–S distance of 2.439 (4) Å is similar to Mo–S bond lengths of 2.451 (4) and 2.406 (3) Å observed for $(R_4N)_2[Mo_2O_4(SPh)_4]$[30] and $(Et_4N)_2[Mo_2S_4(SCH_2CH_2S)_2]$,[41] respectively. These Mo–thiolate sulfur distances are significantly longer than those observed for complexes possessing the $Mo_2O_3^{2+}$ core, where a range of 2.340–2.350 Å has been observed for complexes of the $[Mo_2O_3(ABC)_2]$ class. Although somewhat similar Mo–S distances occur for $[Mo_2O_3L_2]$ and $[Mo_2O_3(C_6H_4NS)_4]$,[22] the inherent strain of the chelate rings is most likely responsible for lengthening of the bond distances to the 2.390–2.490-Å range in these cases. In the case of the complexes with the $Mo_2O_4^{2+}$ core, the Mo–S bond distances may reflect in part the trans influence of the multiply bonded bridging oxo groups.

The most unusual geometric feature of $[Mo_2O_4(L'H)_2]$ is the 14-membered chelate ring formed by the coordination of only the 2 thiolate atoms of the potentially tetradentate N_2S_2 ligand. The nitrogen atoms participate in the hydrogen-bonded six-membered ring H–N–C–C–C–N, similar to that observed for $[Fe(L'H)(NO)_2]$.[42] Figure 4 shows that the amine nitrogens are oriented in such a way so as to direct their lone-pair orbitals toward a common point, producing a chair conformation of the protonated diamine portion of the ligand. The intraligand N–N distance of 2.74 (1) Å, compared to 3.22 (1) Å in $(FeL')_2$ where L′ functions as a tetradentate ligand and to a van der Waals diameter of approximately 3.0 Å for nitrogen,[43] lends support for the amine nitrogens as the site for protonation. Other examples of large chelate rings containing potentially coordinating nitrogen atoms include $[Fe(L'H)(NO)_2]$[42] and $[Ph_2NCH_2N(Me)CH_2CH_2N(Me)CH_2PPh_2][Mo(CO)_4]$.[44]

Conclusion. Reduction of Mo(VI) starting materials of the type $[MoO_2(N_2S_2)]$ under the usual reaction conditions leads to the isolation of different Mo(V) dimeric species for L and L′. While $[MoO_2L]$ reacts smoothly to yield $[Mo_2O_3L_2]$, the usual product of these reactions, the reduction of $[MoO_2L']$ passes through an intermediate purple stage to produce $[Mo_2O_4(L'H)_2]$, a species possessing a 14-membered ring. The stability of the large ring in $[Mo_2O_4(L'H)_2]$ may be due in part to the stability of the H–N–C–C–C–N ring, which adopts the low-energy chair conformation.[42] That L does not form an analogous complex, $[Mo_2O_4L_2]^{2-}$, and does not form complexes possessing the $Mo_2O_2S_2^{2+}$ or $Mo_2S_4^{2+}$ cores reflects the steric constraints imposed by the dimethylene bridge between the amine nitrogens, effectively preventing the ligand from achieving the conformation required to bring the amine nitrogens into a suitable orientation for protonation while simultaneously providing an intraligand S–S distance of 6.5 Å, necessary to achieve bridging bidentate character.

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Registry No. $Mo_2O_3L_2$, 80287-00-9; $Mo_2O_4(L'H)_2$, 69593-51-7.

Supplementary Material Available: Listings of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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