are obviously only justifiable if complexes with metal centers of comparable electronic structures are involved. In our series, this would, for example, seem to be the case for systems with little or no preference for either TP or TAP structure (viz. d^0, d^1, (low-spin d^2), high-spin d^5, high-spin d^6, (d^9), and d^{10} on the basis of the ligand field model as outlined above) and the geometry is then the result of ligand dictation ($\phi \approx 28°$). For all other cases the electronic preferences cannot be neglected.[26]

Registry No. **1**, 96193-89-4; **2**, 96164-36-2; **3**, 96164-38-4; **4**, 96164-39-5; **5**, 96164-42-0; **6**, 96164-44-2; **7**, 96164-47-5; **8**, 88228-11-9; **9**, 96164-48-6; **10**, 96193-87-2; **11**, 72560-65-7; **12**, 96193-88-3; **13**, 96164-51-1; **14**, 88229-09-8; **15**, 96164-54-4; **16**, 92096-45-2; **17**, 96164-57-7; **18**, 96164-60-2; **19**, 96164-63-5.

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(21) (a) Avdeef, A.; Costamagna, J. A.; Fackler, J. P., Jr. *Inorg. Chem.* **1974**, *13*, 1854. (b) Avdeef, A.; Fackler, J. P., Jr. *Inorg. Chem.* **1975**, *14*, 2002.
(22) For additional definitions of shape parameters see also ref 14 and 23.
(23) Pignolet, L. H. *Top. Curr. Chem.* **1975**, *56*, 91.
(24) (a) Kepert, D. L. *Inorg. Chem.* **1972**, *11*, 1561. (b) Kepert, D. L. *Prog. Inorg. Chem.* **1977**, *23*, 1.
(25) Nikolov, G. St.; Trendafilova, N. S. *Inorg. Chim. Acta* **1983**, *68*, 29.
(26) $M(en)_3^{n+}$ complexes, for example, show the same general trends[6] although the range of the twist angles ϕ is much smaller (~49–54°).
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Articles

Contribution No. 858 from the Battelle-C. F. Kettering Research Laboratory,
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Synthetic Utility of Molybdenum–Diazene Adducts: Preparation, Reactions, and Spectral Properties of Oxo-Free and (^{18}O)Oxo Molybdenum Complexes

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Compounds of the type $Mo(LL)_2(DEAZ)_x$ (LL = S_2CNR_2, $S_2P(i\text{-}Pr)_2$, $S_2P(OEt)_2$; DEAZ = diethyl diazenedicarboxylate; x = 1, 2) are prepared from $Mo(CO)_2(LL)_2$. Their facile protonation by water and other reagents ($o\text{-}C_6H_4(XH)_2$: X_2 = S_2; O_2; S, O; S, NH; S, NMe) to release the hydrazine ($DEAZH_2$) has been used to prepare oxo-free and oxo-containing species. $o\text{-}C_6H_4(XH)_2$ and HOC_2H_4SH react with $Mo(S_2CNEt_2)_2(DEAZ)$ to produce $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4X_2)$ or $Mo(S_2CNEt_2)_2(OC_2H_4S)$. Some of these same compounds can be produced by oxo removal by these same reagents from $OMo(S_2CNEt_2)_2$. Some of these products can be oxidized to Mo(V) and Mo(VI) compounds by Cl_2 and O_2 to give $ClMo(S_2CNEt_2)_2(o\text{-}C_6H_4X_2)$ (X_2 = S_2; O, S; S, NMe) and $OMo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$, respectively. Hydrolysis of $Mo(S_2CNR_2)_2(DEAZ)_2$ produces $MoO_2(S_2CNR_2)_2$ and $DEAZH_2$. Hydrolysis of a reaction mixture containing $Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2$ and DEAZ gives a mixture of $MoO_2[S_2P(i\text{-}Pr)_2]_2$ and $Mo_2O_4[S_2P(i\text{-}Pr)_2]_2$, while $Mo(CO)_2(PPh_3)[S_2P(OEt)_2]_2$ and DEAZ, after hydrolysis, give some $Mo_2O_3[S_2P(OEt)_2]_4$. Complexes of stoichiometry $Mo^{18}O_2(LL)_2$, $Mo^{18}O(LL)_2$, $Mo_2{}^{18}O_3(LL)_4$, $Mo_2{}^{18}O_4(LL)_2$, and $Mo_2{}^{18}O_3S(LL)_2$ (LL = S_2CNR_2, $S_2P(OR)_2$, S_2PR_2; not all compounds were formed with each ligand) are produced by the reaction series (i) controlled hydrolysis with $H_2{}^{18}O$ of diazene adducts, $Mo(LL)_2(DEAZ)_2$, and (ii) reduction of $Mo^{18}O_2(LL)_2$ with tertiary phosphine. Reaction of $Mo_2O_4(LL)_2$ with H_2S gives $Mo_2O_3S(LL)_2$. By spectral comparisons with their ^{16}O analogues, definitive unambiguous assignments of both terminal and bridging molybdenum–oxygen stretching vibrations are made.

Introduction

There has been considerable recent interest in diazene complexes of transition metals,[1] particularly because of their potential involvement as intermediates in the catalyzed (both chemical and enzymic) reduction of dinitrogen to ammonia.[2-4] We have been particularly interested in molybdenum complexes of these moieties and have previously described the catalytic reduction of diazenes by the Mo(IV) species $OMo(S_2CNR_2)_2$, the crystal and molecular structure of $OMo(S_2CNMe_2)_2(C_6H_5CON_2COC_6H_5)$, and the possible relevance of the hydrolysis of the complexes $OMo(S_2CNR_2)_2$(diazene) to that displayed by molybdoenzymes (eq 1).[2,5,6] The preparation of[7,8] the compounds $Mo(S_2CNR_2)_2$-

$$OMo(S_2CNR_2)_2(RN_2R) + H_2O \rightarrow MoO_2(S_2CNR_2)_2 + RHN_2HR \quad (1)$$

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(1) See, for example: Ittel, S. D.; Ibers, J. A. *Inorg. Chem.* **1970**, *14*, 1183. Dickson, R. S.; Ibers, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2988. Nakamura, A.; Yoshida, T.; Cowie, M.; Otsuka, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2108. Bailey, N. A.; Frisch, P. D.; McCleverty, J. A.; Walker, N. W.; Williams, J. *J. Chem. Soc., Chem. Commun.* **1975**, 350. Carroll, J. A.; Sutton, D.; Cowie, M.; Gauthier, M. D. *J. Chem. Soc., Chem. Commun.* **1979**, 1058. Chatt, J.; Dilworth, J. R.; Dahlstrom, P. L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 786. Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 914. Butcher, A. V.; Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 921. Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 279. Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1979**, 1603.
(2) Newton, W. E.; Corbin, J. L.; McDonald, J. W. *Proc. Int. Symp. Nitrogen Fixation, 1st* **1976**, 53.
(3) Schrauzer, G. N.; Kiefer, G. W.; Tano, K.; Doemeny, P. A. *J. Am. Chem. Soc.* **1974**, *96*, 641.
(4) Enemark, J. H. In "Nitrogen Fixation"; Newton, W. E., Orme-Johnson, W. H., Eds.; University Park Press: Baltimore, MD, 1980; p 297.
(5) McDonald, J. W.; Corbin, J. L.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2056. Marabella, C. P.; Enemark, J. H.; Newton, W. E.; McDonald, J. W. *Inorg. Chem.* **1982**, *21*, 623.
(6) Schneider, P. W.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 8640.
(7) McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *J. Organomet. Chem.* **1975**, *92*, C25.

0020-1669/85/1324-2327$01.50/0

(DEAZ)$_x$ (x = 1, 2; DEAZ = diethyl diazenedicarboxylate) and the extremely facile protonation of the bound diazene with concomitant coordination of an oxo group from water has been utilized to synthesize a number of (^{18}O)oxo–molybdenum species in the IV, V, and VI oxidation states. These products have been subjected to infrared spectroscopy and the various molybdenum–oxygen vibrations assigned definitively to resolve the disagreements and misassignments in the literature. We also find that removal of these coordinated diazenes by protonation is a general reaction and have prepared a new series of Mo(IV) compounds via reaction of Mo(S$_2$CNEt$_2$)$_2$(DEAZ) with the acid forms of a variety of dinegative bidentate ligands, *o*-C$_6$H$_4$(XH)$_2$. Some of these same Mo(S$_2$CNEt$_2$)$_2$(*o*-C$_6$H$_4$X$_2$) compounds may also be prepared by direct reaction with OMo(S$_2$CNEt$_2$)$_2$. Herein, we also describe the synthesis, characterization, and reactivity of a number of compounds of the form Mo(S$_2$CNEt$_2$)$_2$L (L = C$_2$H$_4$OS, *o*-C$_6$H$_4$X$_2$; X = S$_2$; O$_2$; S, O; S, NH; S, NMe) and their oxidation to heptacoordinate Mo(V) monomers.

Experimental Section

Materials and Methods. All reactions were carried out under a dry inert atmosphere (argon or nitrogen) with use of standard techniques. All solvents were dried over molecular sieves and were degassed prior to use. The reagents HS$_2$P(*i*-Pr)$_2$, *o*-C$_6$H$_4$(SH)$_2$, *o*-C$_6$H$_4$(OH)(SH), and *o*-C$_6$H$_4$(NHMe)(SH) were synthesized by known[9-11] procedures, while *o*-C$_6$H$_4$(OH)$_2$, *o*-C$_6$H$_4$(NH$_2$)(SH), HOC$_2$H$_4$SH, and EtO$_2$CNNCO$_2$Et (DEAZ) were commercially available and used as received. H$_2$^{18}O (90–99% (^{18}O)oxygen) was purchased from Mound Laboratory, Miamisburg, OH.

Infrared spectra were recorded as KBr disks on a Beckman IR-20A spectrophotometer calibrated with polystyrene film, UV-visible spectra on a Cary 118C instrument, and NMR spectra on a Varian Associates A-60 spectrometer. EPR spectra were obtained on a Varian Associates 4502 spectrometer equipped with a Model V4560 modulation control unit, an X-band microwave bridge, and a Hewlett-Packard X 532 G frequency meter. Elemental analyses for C, H, and N were determined in this laboratory with a Perkin-Elmer 240 analyzer equipped with a Microjector from Control Equipment Corp. Chlorine analyses were determined by Galbraith Laboratories, Knoxville, TN.

Preparation of Mo(CO)$_2$(S$_2$CNEt$_2$)$_2$. Chlorine (~40 mL) was condensed onto solid Mo(CO)$_6$ (6.0 g) in a Schlenk tube immersed in a dry ice–acetone bath. The yellow slurry was stirred at −78 °C for 30 min and then removed from the bath and allowed to evaporate to dryness under a stream of argon. After pumping on the solid residue for 5 min to remove residual chlorine, ethanol (70 mL) was added, yielding a orange-red solution. *Caution! Vigorous gas evolution occurs on addition of ethanol, and the vessel must be vented during this step.* NaS$_2$CNEt$_2$ (9.4 g) in ethanol (75 mL) was added to the above solution, causing the immediate precipitation of an orange-red solid. After it was stirred at room temperature for 15 min, the reaction mixture was filtered and the solid washed with acetone (2 × 10 mL) and then extracted with dichloromethane until only sodium chloride remained on the frit. The extracts were evaporated to dryness under vacuum, and the residue was tirturated with diethyl ether, yielding the product, which was isolated by filtration, washed with ether, and dried in vacuo. The yield was 7.7 g (76%). Anal. Calcd for C$_{12}$H$_{20}$N$_2$MoO$_2$S$_4$: C, 32.1; H, 4.46; N, 6.25. Found: C, 32.3; H, 4.94; N, 6.41. The complex Mo(CO)$_2$[S$_2$CN(*n*-Pr)$_2$]$_2$ was similarly prepared. Anal. Calcd for C$_{16}$H$_{28}$N$_2$O$_2$S$_4$Mo: C, 38.1; H, 5.56; N, 5.56. Found: C, 37.3; H, 5.71; N, 5.44.

Preparation of Mo(CO)$_2$[S$_2$P(*i*-Pr)$_2$]$_2$. Chlorine (~30 mL) was condensed onto solid Mo(CO)$_6$ (4.0 g) and the reaction mixture treated in a fashion identical with that described above for Mo(CO)$_2$(S$_2$CNEt$_2$)$_2$. After evaporation of chlorine, the residue was dissolved in methanol (70 mL; *see above caution*) and HS$_2$P(*i*-Pr)$_2$ (6.0 mL) in methanol (70 mL) was added. The reaction mixture was evaporated under vacuum to ~30 mL, during which time the color changed from orange-red to green and a green solid crystallized. The product was isolated by filtration, washed with methanol, and dried in vacuo. The yield was 6.1 g, 78%. Anal. Calcd for C$_{14}$H$_{28}$O$_2$P$_2$S$_4$Mo: C, 32.7; H, 5.45. Found: C, 32.4; H, 5.78.

Preparation of Mo(CO)$_2$(S$_2$CNMe$_2$)$_2$. Because of its insolubility, extraction of this complex from coprecipitated sodium chloride (see above for the S$_2$SNEt$_2$ and S$_2$CN(*n*-Pr)$_2$ compounds) was not feasible and, therefore, the following substitution reaction on Mo(CO)$_2$[S$_2$P(*i*-Pr)$_2$]$_2$ was employed. Methanol (60 mL) was added to a mixture of Mo(CO)$_2$[S$_2$P(*i*-Pr)$_2$]$_2$ (0.75 g) NaS$_2$CNMe$_2$·2H$_2$O (0.58 g), causing the immediate formation of a red solid. After the mixture was stirred at room temperature for 30 min, the product was isolated by filtration, washed with methanol and ether, and dried in vacuo. The yield was 0.41 g, 72%. Anal. Calcd for C$_8$H$_{12}$N$_2$O$_2$S$_4$Mo: C, 24.5; H, 3.06; N, 7.14. Found: C, 24.8; H, 2.73; N, 7.01.

Preparation of Mo(S$_2$CNEt$_2$)$_2$(DEAZ). Diethyl diazenedicarboxylate (DEAZ; 0.42 g) was added to a solution of Mo(CO)$_2$(S$_2$CNEt$_2$)$_2$ (1.05 g) in benzene (50 mL). After it was stirred for 30 min at room temperature, the deep orange-brown reaction mixture was filtered, the filtrate evaporated to dryness under vacuum, and the residue triturated with hexane (75 mL). The resulting solid was isolated by filtration, washed with hexane, and dried in vacuo. The yield was 0.95 g, 71%. Anal. Calcd for C$_{16}$H$_{30}$N$_4$O$_4$S$_4$Mo: C, 33.9; H, 5.30; N, 9.89. Found: C, 33.9; H, 5.81; N, 9.93.

Preparation of Mo(S$_2$CNEt$_2$)$_2$(DEAZ)$_2$. DEAZ (0.50 g) was added to a solution of Mo(CO)$_2$(S$_2$CNEt$_2$)$_2$ (0.50 g) in dichloromethane (50 mL). After it was stirred for 2 h at room temperature, the reaction mixture was filtered, the filtrate evaporated to dryness, and the residue triturated with hexane (75 mL). The resulting solid was isolated by filtration, washed with hexane, and dried in vacuo. The yield was 0.50 g, 61%. Anal. Calcd for C$_{22}$H$_{40}$N$_6$O$_8$S$_4$Mo: C, 35.7; H, 5.41; N, 11.4. Found: C, 35.9; H, 5.57; N, 11.2.

Preparation of *cis*-Mo^{18}O$_2$(S$_2$CNEt$_2$)$_2$. DEAZ (0.452 g) was added to a benzene (50 mL) solution of Mo(CO)$_2$(S$_2$CNEt$_2$)$_2$ (0.50 g) and the mixture stirred at room temperature for 20 min. H$_2$^{18}O (0.60 mL) was then added and the solution heated under reflux for 50 min, during which time the color changed to yellow. After it was cooled, the reaction mixture was filtered and the filtrate evaporated to dryness under vacuum. Trituration of the residue with ether gave the yellow product (characterized by its IR spectrum), which was isolated by filtration, washed with ether, and dried in vacuo. The yield was 0.31 g, 66%. *cis*-Mo^{18}O$_2$(S$_2$CNR$_2$)$_2$ compounds (R = Me, *n*-Pr) were prepared similarly in ~60% yields.

Preparation of ^{18}OMo(S$_2$CNEt$_2$)$_2$. PPh$_2$Et (0.1 mL) was added to a 1,2-dichloroethane solution (25 mL) of Mo^{18}O$_2$(S$_2$CNEt$_2$)$_2$ (0.15 g) and the reaction mixture refluxed for 20 min. The resulting red solution was evaporated to dryness under vacuum and the residue triturated with ethanol (~25 mL), yielding the product, which was isolated by filtration, washed with ether, and dried in vacuo. The yield was 0.1 g (70%), and the product was identified by its IR spectrum. ^{18}OMo(S$_2$CNR$_2$)$_2$ compounds (R = Me, *n*-Pr) were prepared in ~60% yields by similar procedures.

Preparation of Mo$_2$^{18}O$_3$(S$_2$CNEt$_2$)$_4$. Dichloromethane (30 mL) was added to a mixture of ^{18}OMo(S$_2$CNEt$_2$)$_2$ (0.070 g) and Mo^{18}O$_2$(S$_2$CNEt$_2$)$_2$ (0.073 g) and the resulting solution stirred at room temperature for 45 min. The reaction mixture was evaporated to dryness under vacuum and the residue recrystallized from CH$_2$Cl$_2$/hexane, yielding the product, which was isolated by filtration, washed with hexane, and dried in vacuo. The yield was 0.08 g (56%), and the product was identified by its IR spectrum. Mo$_2$^{18}O$_3$(S$_2$CNR$_2$)$_4$ compounds (R = Me, *n*-Pr) were prepared similarly.

Preparation of Mo$_2$^{18}O$_4$[S$_2$P(*i*-Pr)$_2$]$_2$. DEAZ (0.68 g) was added to a solution of Mo(CO)$_2$[S$_2$P(*i*-Pr)$_2$]$_2$ (1.0 g) in 1,2-dichloroethane (75 mL). After 15 min, H$_2$^{12}O (0.060 mL) was added and the reaction mixture was stirred at room temperature for 1 h. The yellow precipitate was isolated by filtration, washed with ether, and dried in vacuo. The product (0.49 g, 80% yield) was identified as Mo$_2$O$_4$[S$_2$P(*i*-Pr)$_2$]$_2$ by its IR spectrum. Evaporation of the reaction mixture filtrate to dryness and trituration of the residue gave a solid identified (IR) as a mixture of Mo^{18}O$_2$[S$_2$P(*i*-Pr)$_2$]$_2$ and Mo$_2$^{18}O$_4$[S$_2$P(*i*-Pr)$_2$]$_2$.

Preparation of Mo$_2$^{18}O$_4$(S$_2$CNEt$_2$)$_2$. Dichloromethane (30 mL) and isopropyl alcohol (30 mL) were added to Mo$_2$^{18}O[S$_2$P(*i*-Pr)$_2$]$_2$ (0.13 g) and NaSCNEt$_2$ (0.086 g), and the reaction mixture was stirred at room temperature for 12 h. The product was isolated by filtration, recrystallized from CH$_2$Cl$_2$–petroleum ether, and identified by its IR spectrum.

Preparation of Mo$_2$^{18}O$_3$S[S$_2$P(*i*-Pr)$_2$]$_2$. Mo$_2$^{18}O$_4$[S$_2$P(*i*-Pr)$_2$]$_2$ (0.20 g) was dissolved in 1,2-dichloroethane (30 mL), and H$_2$S was bubbled into the reaction mixture under reflux. After 1 h, the solution was evaporated to dryness under vacuum and the residue triturated with ether to give the product, which was isolated by filtration, washed with ether, and dried in vacuo. A similar procedure gave Mo$_2$^{18}O$_3$S(S$_2$CNEt$_2$)$_2$ starting from Mo$_2$^{18}O$_4$(S$_2$CNEt$_2$)$_2$.

Preparation of Mo$_2$^{18}O$_3$[S$_2$P(OEt)$_2$]$_4$. DEAZ (0.40 g) was added to a solution of Mo(CO)$_2$(PPh$_3$)[S$_2$P(OEt)$_2$]$_2$ (0.50 g)[12] in 1,2-dichloro-

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(8) Newton, W. E.; McDonald, J. W. *Chem. Uses Molybdenum, Proc. Int. Conf., 2nd* **1976**, 25; *J. Less-Common Met.* **1977**, *54*, 51.

(9) Corbin, J. L.; Newton, W. E.; McDonald, J. W. *Org. Prep. Proced. Int.* **1975**, *7*, 309.

(10) Hunig, S.; Fleckenstein, E. *Justus Liebigs Ann. Chem.* **1970**, *738*, 192.

(11) Djerassi, C.; Gorman, M.; Markley, F. X.; Oldenburg, E. B. *J. Am. Chem. Soc.* **1955**, *77*, 568. Quast, H.; Schmitt, E. *Chem. Ber.* **1969**, *102*, 568.

Table I. Elemental Analytical Data for the Compounds $Mo(S_2CNEt_2)_2L^a$

L	% C	% H	% N
$C_6H_4S_2$	36.4 (36.1)	4.43 (4.51)	5.29 (5.26)
C_6H_4OS	37.0 (37.2)	4.61 (4.65)	5.45 (5.43)
C_6H_4NHS	36.8 (37.3)	4.85 (4.85)	8.07 (8.16)
C_6H_4NMeS	38.1 (38.5)	5.18 (5.10)	7.68 (7.94)
$C_6H_4O_2$	37.7 (38.4)	4.84 (4.80)	5.36 (5.60)
C_2H_4OS	30.3 (30.8)	4.93 (5.13)	5.93 (5.98)

[a] Found values with calculated values in parentheses.

ethane (50 mL). After 15 min, $H_2{}^{18}O$ (0.05 mL) was added and the solution was stirred for 3 h at room temperature. The reaction mixture was filtered and evaporated to dryness under vacuum, and the residue was triturated with methanol (50 mL), yielding the product (characterized by its IR spectrum), which was isolated by filtration, washed with methanol, and dried in vacuo. The yield was 0.02 g, 6%.

Preparation of $^{18}OMo[S_2P(OEt)_2]_2$. 1,2-Dichloroethane (25 mL) was added to $Mo_2{}^{18}O_3[S_2P(OEt)_2]_4$ (0.15 g) and PPh_3 (0.05 g) and the solution was stirred at room temperature for 2 h. The reaction mixture was evaporated to dryness under vacuum and the residue extracted with hexane (40 mL). Evaporation of the extract to dryness gave the product as a pink solid, which was shown by IR spectroscopy to contain some contaminating $OPPh_3$ and PPh_3.

Preparation of $Mo^{16}O_2(LL)_2$, $^{16}OMo(LL)_2$, $Mo_2{}^{16}O_3(LL)_4$, $Mo_2{}^{16}O_4(LL)_2$, and $Mo^{16}O_3S(LL)_2$. These compounds were all prepared by literature methods.[13-18]

Preparation of the Complexes $Mo(S_2CNEt_2)_2L$. (i) The synthetic procedure was basically the same for all complexes. DEAZ (0.207 g, 1.14 mmol) was added to $Mo(CO)_2(S_2CNEt_2)_2$ (0.50 g, 1.12 mmol) in benzene (40 mL). After 30 min at room temperature, the acid form of the ligand (H_2L, 1.2 mmol) was added and the reaction mixture was stirred for an additional 2 h. For H_2L = *o*-$C_6H_4(SH)_2$, *o*-$C_6H_4(NH_2)(SH)$, *o*-$C_6H_4(NMeH)(SH)$, the product precipitated, was isolated by filtration, was washed with diethyl ether, and was dried in vacuo. For H_2L = *o*-$C_6H_4(OH)_2$, *o*-$C_6H_4(OH)(SH)$, HSC_2H_4OH, no precipitate formed and so the reaction mixture was evaporated to dryness under vacuum and the residue triturated with ether. The resulting solid was filtered off, washed with ether, and dried in vacuo. The presence of the hydrazine, H_2DEAZ, in the reaction mixtures was confirmed by the IR spectra of the residue obtained by evaporating the ether washes to dryness. Elemental analytical data for the new complexes are found in Table I.

(ii) $OMo(S_2CNEt_2)_2$ (0.41 g, 1 mmol) was stirred in dichloromethane (30 mL) with *o*-benzenedithiol (0.154 g, 1.1 mmol) for 18 h. The dark brown precipitate of $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$ (0.4 g, 73%) was recrystallized from dichloromethane–ether. A similar procedure; but with *o*-$C_6H_4(SH)(XH)$ (4 mmol), gave dark brown $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4SX)$ (X = O, NH) in 78–80% yield. No reaction occurred with HSC_2H_4OH.

Reaction of $Mo(S_2CNEt_2)_2L$ with Pyridine *N*-Oxide. Dichloromethane (50 mL) was added to a mixture of $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$ (0.30 g, 0.563 mmol) and pyridine *N*-oxide (0.054 g, 0.568 mmol), and the solution was stirred at room temperature for 1 h. After filtration, the reaction mixture was evaporated to dryness under vacuum and the residue triturated with diethyl ether. The resulting dark brown solid was isolated by filtration, washed with diethyl ether, and dried in vacuo. The yield of $OMo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$ was 0.25 g, 18%. Anal. Calcd for $C_{16}H_{24}N_2MoOS_6$: C, 35.0; H, 4.38; N, 5.11. Found: C, 35.2; H, 4.44; N, 4.91.

Attempts to carry out similar oxidations of $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4OS)$ and $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4NMeS)$ resulted only in uncharacterized products.

Reaction of $Mo(S_2CNEt_2)_2L$ with Chlorine. $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$ (0.50 g, 0.940 mmol) was dissolved in dichloromethane (65 mL) and the reaction mixture placed under vacuum. Chlorine (11.8 mL, 0.470 mmol) was injected into the reaction vessel and the solution stirred for 30 min. After filtration and evaporation of the filtrate to dryness, the residue was triturated with diethyl ether (50 mL) and the resulting solid isolated by filtration, washed with diethyl ether, and dried in vacuo. The yield of $ClMo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$ was 0.50 g, 94%. Anal. Calcd for $C_{16}H_{24}N_2ClMoS_6$: C, 33.8; H, 4.22; N, 4.93; Cl, 6.26. Found: C, 33.7; H, 4.33; N, 4.94; Cl, 5.82.

The following compounds were similarly prepared: $ClMo(S_2CNEt_2)_2(o\text{-}C_6H_4OS)$ was obtained in 70% yield. Anal. Calcd for $C_{16}H_{24}N_2ClMoOS_5$: C. 34.8; H, 4.35; N, 5.07; Cl, 6.44. Found: C, 34.5; H, 4.46; N, 5.10; Cl, 5.67.

$ClMo(S_2CNEt_2)_2(o\text{-}C_6H_4NMeS)$ was obtained in 84% yield. Anal. Calcd for $C_{17}H_{27}N_3ClMoS_5$: C, 36.1; H, 4.78; N, 7.44; Cl, 6.29. Found: C, 35.2; H, 4.85; N, 7.20; Cl, 5.90.

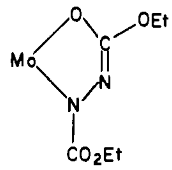
Results and Discussion

1. Synthesis of Diazene Adducts. As previously reported,[7] the Mo(II) complex $Mo(CO)_2(S_2CNEt_2)_2$ reacts with DEAZ to yield either $Mo(S_2CNEt_2)_2(DEAZ)$ (**1**) (eq 2) or $Mo(S_2CNEt_2)_2(DEAZ)_2$ (**2**) (eq 3) depending on the stoichiometry of the

$$Mo(CO)_2(S_2CNEt_2)_2 + DEAZ \rightarrow Mo(S_2CNEt_2)_2(DEAZ) + 2CO \quad (2)$$

$$Mo(CO)_2(S_2CNEt_2)_2 + 2DEAZ \rightarrow Mo(S_2CNEt_2)_2(DEAZ)_2 + 2CO \quad (3)$$

reactants. The nature of the diazene bonding in **1** and **2** is unknown but is likely to be unsymmetrical



because this mode of attachment is found in both $OMo(S_2CNMe_2)_2(C_6H_5CON_2COC_6H_5)$[5] and $Pt(PTol_3)_2(C_6H_5CON_2COC_6H_5)$.[19] The oxidation state of the metal in these complexes is also open to question, but **1** and **2** can be formally assigned as Mo(IV) and Mo(VI), respectively, if the diazene is assumed to add oxidatively to the Mo(II) species. The infrared spectra of the complexes contain strong bands in the 1700–1800-cm^{-1} region (1710 cm^{-1} for **1** and 1710 and 1765 cm^{-1} for **2**) assigned to ν(C═O) of the coordinated diazene along with the usual dithiocarbamate and DEAZ spectral patterns. The NMR spectra of the adducts are not particularly diagnostic, containing only a complex pattern of overlapping ethyl resonances arising from both the dithiocarbamate ligands and coordinated DEAZ.

Although both **1** and **2** have been isolated as solids with high degrees of purity, to facilitate synthetic experiments involving these complexes (see later), they are usually generated in situ by adding either 1 or 2 equiv. of DEAZ to solutions of $Mo(CO)_2(S_2CNEt_2)_2$. Similarly, no attempt was made to isolate the complexes analogous to **2** for L = S_2CNMe_2, $S_2CN(n\text{-}Pr)_2$, and $S_2P(i\text{-}Pr)_2$; instead, they were produced in solution by addition of 2 equiv of DEAZ to the corresponding dicarbonyl species.

2. Synthesis of (^{18}O)Oxo–Molybdenum Complexes. (a) *N*,*N*-Dialkyldithiocarbamates. As previously reported,[7] **1** and **2** react with H_2O in nonaqueous solvents to yield $OMo(S_2CNEt_2)_2$ and $MoO_2(S_2CNEt_2)_2$ respectively (see eq 4 and 5), with the diazene

$$MoL_2(DEAZ) + H_2O \rightarrow OMoL_2 + H_2DEAZ \quad (4)$$

$$MoL_2(DEAZ)_2 + H_2O \rightarrow MoO_2L_2 + 2H_2DEAZ \quad (5)$$

being liberated as the corresponding hydrazine in both hydrolysis reactions. Only stoichiometric amounts of H_2O are required for complete hydrolysis of the adducts, i.e., ~40 μL for 1 mmol of **2**. Thus, these reactions provide a unique and ideal method for preparing (^{18}O)oxo–molybdenum complexes by utilizing the

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(12) Chen, G. J.-J.; Yelton, R. G.; McDonald, J. W. *Inorg. Chim. Acta* **1977**, *22*, 249.

(13) Newton, W. E.; Bravard, D. C.; Corbin, J. L.; Searles, J. E.; McDonald, J. W. *Inorg. Chem.* **1974**, *13*, 1100.

(14) Barral, R.; Bocard, C.; Seree de Roche, I.; Sajus, L. *Kinet. Catal.* (*Engl. Transl.*) **1973**, *14*, 130. Matsuda, T.; Tanaka, K.; Tanaka, T. *Inorg. Chem.* **1979**, *18*, 454.

(15) Jowitt, R. N.; Mitchell, P. C. H. *J. Chem. Soc. A* **1969**, 2632; **1971**, 1702.

(16) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612.

(17) Chen. G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 697.

(18) Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5387.

(19) Ittel, S. D.; Ibers, J. A. *Inorg. Chem.* **1973**, *12*, 2290.

readily available, but expensive, $H_2{}^{18}O$ as the source of oxygen-18. $Mo^{18}O_2(S_2CNR_2)_2$ (R = Me, Et, *n*-Pr) is prepared by addition of $H_2{}^{18}O$ to a benzene solution of $Mo(S_2CNR_2)_2(DEAZ)_2$, which is generated in situ as described above. These *cis*-dioxo complexes are the precursors for the corresponding Mo(IV) compounds, ${}^{18}OMo(S_2CNR_2)_2$, which are synthesized with use of oxo abstraction[14] by PPh_2Et (eq 6). Combining equimolar amounts of

$$\mathrm{Mo^{18}O_2(S_2CNR_2)_2 + PPh_2Et \rightarrow {}^{18}OMo(S_2CNR_2)_2 + {}^{18}OPPh_2Et} \tag{6}$$

${}^{18}OMo(S_2CNR_2)_2$ and $Mo^{18}O_2(S_2CNR_2)_2$ produces the μ-oxo-bridged, dinuclear Mo(V) compounds $Mo_2{}^{18}O_3(S_2CNR_2)_4$, by the well-characterized[14-16] equilibrium shown in eq 7. As these

$$\mathrm{Mo^{18}O_2(S_2CNR_2)_2 + {}^{18}OMo(S_2CNR_2)_2 \rightleftharpoons Mo_2{}^{18}O_3(S_2CNR_2)_4} \tag{7}$$

dinuclear species are the least soluble,[16] concentration of the mixture results in their crystallization. The bis(μ-oxo)-bridged Mo(V) complexes $Mo_2{}^{18}O_4(S_2CNEt_2)_2$ are obtained by substitution of $Mo_2{}^{18}O_4[S_2P(i\text{-}Pr)_2]_2$ (see later) with NaS_2CNEt_2 in dichloromethane–isopropyl alcohol (eq 8). The less acidic isopropyl alcohol is used to circumvent oxygen exchange with the alcohol.

$$\mathrm{Mo_2{}^{18}O_4[S_2P(\mathit{i}\text{-}Pr)_2]_2 + 2NaS_2CNEt_2 \rightarrow Mo_2{}^{18}O_4(S_2CNEt_2)_2 + 2NaS_2P(\mathit{i}\text{-}Pr)_2} \tag{8}$$

Reaction with H_2S in boiling 1,2-dichloroethane gives $Mo_2{}^{18}O_3S(LL)_2$ (LL = S_2CNEt_2, $S_2P(i\text{-}Pr_2)$).

(b) Diisopropyldithiophosphinate. Addition of $H_2{}^{18}O$ to a 1,2-dichloroethane solution containing 1 equiv of $Mo(CO)_2[S_2P(i\text{-}Pr)_2]_2$ and 2 equiv of DEAZ results in the precipitation of a yellow solid. This product is the Mo(V) species $Mo_2{}^{18}O_4[S_2P(i\text{-}Pr)_2]_2$ and *not* $Mo^{18}O_2[S_2P(i\text{-}Pr)_2]_2$, which is expected by analogy (eq 5) with the dithiocarbamate systems. The formation of the Mo(V) complex apparently results from the initial generation of MoO_2L_2 (eq 9) followed by the relatively rapid internal

$$\mathrm{Mo[S_2P(\mathit{i}\text{-}Pr)_2]_2(DEAZ)_2 + 2H_2{}^{18}O \rightarrow Mo^{18}O_2[S_2P(\mathit{i}\text{-}Pr)_2]_2 + 2H_2DEAZ} \tag{9}$$

$$\mathrm{2Mo^{18}O_2[S_2P(\mathit{i}\text{-}Pr)_2]_2 \rightarrow Mo_2{}^{18}O_4[S_2P(\mathit{i}\text{-}Pr)_2]_2 + (\mathit{i}\text{-}Pr)_2P(S)S\text{-}S(S)P(\mathit{i}\text{-}Pr)_2} \tag{10}$$

reduction of this compound by ligand, yielding the disulfide (eq 10). Small amounts of $Mo^{18}O_2[S_2P(i\text{-}Pr)_2]_2$ contaminated with $Mo_2{}^{18}O_4[S_2P(i\text{-}Pr)_2]_2$ are detected by IR spectroscopy in the product from the filtrate, supporting the above mechanism. These phosphinate ligands are labile to substitution by dithiocarbamates, and this reactivity is utilized to prepare the complex $Mo_2{}^{18}O_4(S_2CNEt_2)_2$ (eq 8).

(c) Diethyl Dithiophosphate. Because the complex $MoO_2[S_2P(OEt)_2]_2$ has never been isolated, we concentrated on the preparation of the known[15,17] dinuclear Mo(V) species $Mo_2O_3[S_2P(OEt)_2]_4$. Addition of 2.5 equiv of DEAZ (1.5 equiv to attain the Mo(V) oxidation state and 1 equiv for reaction with PPh_3) to a 1,2-dichloroethane solution of $Mo(CO)_2(PPh_3)[S_2P(OEt)_2]_2$, followed by hydrolysis with $H_2{}^{18}O$, produces $Mo_2{}^{18}O_3[S_2P(OEt)_2]_4$. Reduction of this product with PPh_3 gives the Mo(IV) species ${}^{18}OMo[S_2P(OEt)_2]_2$. The yields in the preparation of both the Mo(V) and the Mo(IV) compounds are very poor, and this technique is certainly not recommended as a general synthetic procedure. The method did, however, yield sufficient amounts of products for the desired recording of their infrared spectra. The details of the spectral analysis are reported in part 4 (vide infra).

Table II. Visible Spectral Data

complex	visible spectrum[a,b]
$Mo(S_2CNEt_2)_2(C_6H_4S_2)$	431 (10700), 548 (1960)
$Mo(S_2CNEt_2)_2(C_6H_4OS)$	367 (5960), 480 (1460), 575 (1320)
$Mo(S_2CNEt_2)_2(C_6H_4NHS)$	430 (12300), 565 (1360)
$Mo(S_2CNEt_2)_2(C_6H_4NMeS)$	437 (9390), 570 (3460)[c]
$Mo(S_2CNEt_2)_2(C_6H_4O_2)$	395 (4550), 445 (4700), 520 (2780)
$Mo(S_2CNEt_2)_2(C_2H_4OS)$	350 sh (4870), 625 (550)
$OMo(S_2CNEt_2)_2(C_6H_4S_2)$	419 (6020), 549 (1460)
$ClMo(S_2CNEt_2)_2(C_6H_4S_2)$	437 (6070), 490 (4440)
$ClMo(S_2CNEt_2)_2(C_6H_4OS)$	365 sh (5500), 516 (4320)
$ClMo(S_2CNEt_2)_2(C_6H_4NMeS)$	417 (7300), 484 (5450), 605 (1540)

[a] Values in nm with molar absorptivities in parentheses. [b] 1,2-Dichloroethane solution. [c] Values are approximate due to decomposition of the complex under spectral conditions.

3. Synthesis and Reactivity of the Complexes $Mo(S_2CNEt_2)_2L$. The facile reactions of the Mo(II)–diazene adducts with water, plus the known[20] reactivity of DEAZ toward the oxidation of hydrazines, led us to utilize other protonic reagents for the removal of bound diazene. To that end, reactions of **1** (generated in situ as above) with a series of compounds of the form $o\text{-}C_6H_4(XH)_2$ (X = S_2; O_2; O, S; S, NH; S, NMe) and with $HSCH_2CH_2OH$ were attempted. In all cases, the reactions predictably yield new Mo(IV) complexes of the form $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4X_2)$ and $Mo(S_2CNEt_2)_2(SCH_2CH_2O)$ according to eq 11. Thus, as in

$$\mathrm{Mo(S_2CNEt)_2(DEAZ) + \mathit{o}\text{-}C_6H_4(XH)_2 \rightarrow Mo(S_2CNEt_2)_2(\mathit{o}\text{-}C_6H_4X_2) + H_2DEAZ} \tag{11}$$

the above hydrolysis reaction, diazene is removed as hydrazine and the doubly deprotonated form of the reactant is bound to the metal. It seems reasonable to postulate the complexes as six-coordinate Mo(IV) species containing two uninegative, bidentate dithiocarbamate ligands and one dinegative, bidentate moiety, but no structural evidence as to their exact nature now exists. These same compounds can also be prepared directly from $OMo(S_2CNEt_2)_2$ and $o\text{-}C_6H_4SH(XH)$ (X = S, O, NH) (eq 12).

$$\mathrm{OMo(S_2CNEt_2)_2 + \mathit{o}\text{-}C_6H_4SH(XH) \rightarrow Mo(S_2CNEt_2)_2(\mathit{o}\text{-}C_6H_4SX) + H_2O} \tag{12}$$

The spectral data for the new complexes are not particularly revealing. The IR spectra are consistent with their formulation as $Mo(S_2CNEt_2)_2L$, containing bands assignable to both S_2CNEt_2 and $o\text{-}C_6H_4X_2$ or SCH_2CH_2O and no Mo═O stretching frequencies in the 850–1000-cm^{-1} region. A well-defined N–H stretching frequency is observed at 3290 cm^{-1} in the spectrum of $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4NHS)$, but the other complexes contain no such spectrally diagnostic features. Visible spectral data for the highly colored new compounds are listed in Table II and are presented as an aid to future characterization with no attempt made to assign the various transitions.

Consistent with their formulation as Mo(IV) complexes, the species $Mo(S_2CNEt_2)_2L$ are EPR inactive. The complexes in dichloromethane solution at room temperature do, however, contain very weak EPR signals in the $g = 1.9\text{–}2.0$ region, which are indicative of the presence of monomeric Mo(V) compounds. The low intensity of the signals indicates that only insignificant amounts of these impurities are present. As evidenced by EPR spectral changes, $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4NHS)$ is unstable in dichloromethane solution and, with time, decomposes to a mixture of the known species $Mo(S_2CNEt_2)(o\text{-}C_6H_4NHS)_2$[21] and $[Mo(S_2CNEt_2)_4]^+$.[22]

Because of our general interest in the atom-transfer reactions of molybdenum complexes, we have carried out the reactions of the oxo-free Mo(IV) complexes $Mo(S_2CNEt_2)_2L$ (L = $o\text{-}C_6H_4S_2$, $o\text{-}C_6H_4OS$, $o\text{-}C_6H_4NMeS$) with both pyridine *N*-oxide (py-O) and chlorine since these reagents are known[23] to oxidize readily the oxomolybdenum(IV) species $OMo(S_2CNEt_2)_2$. $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$ readily abstracts an oxygen atom from pyridine *N*-oxide to yield the Mo(VI) complex OMo-

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[20] Bottaro, J. C. *J. Chem. Soc., Chem. Commun.* **1978**, 990.

[21] Pariyadath, N.; Newton, W. E.; Stiefel, E. I. *J. Am. Chem. Soc.* **1976**, *98*, 5388.

[22] Nieuwpoort, A. *Chem. Uses Molybdenum, Proc. Int. Conf., 1st* **1973**, 143.

[23] Newton, W. E.; Bravard, D. C.; McDonald, J. W. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 553. Mitchell, P. C. H.; Scarle, R. D. *J. Chem. Soc., Dalton Trans.* **1976**, 2552.

$(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$ (eq 13). In the absence of X-ray crystallographic data, the species is postulated to contain seven-coordinate molybdenum, a coordination number not uncommon for Mo(VI).[24] The product is characterized by a strong Mo=O stretching frequency at 885 cm^{-1} in the infrared. The abnormally low position of this band (e.g., the seven-coordinate $OMoCl_2(S_2CNEt_2)_2$ has ν(Mo=O) at 935 cm^{-1})[25] may reflect a decrease in the ability of the oxygen atom to back-donate to molybdenum because of the "soft" all-sulfur environment around the metal.

$$Mo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2) + py\text{-}O \rightarrow OMo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2) + py \quad (13)$$

In contrast to the clean oxygen atom abstraction that occurred with $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$, the complex $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4NMeS)$ reacted rapidly with pyridine *N*-oxide, but the infrared spectrum of the thus far uncharacterized product contains no ν(Mo=O). *No* reaction occurs between $Mo(S_2CNEt_2)_2(o\text{-}C_6H_4OS)$ and pyridine *N*-oxide in 1 h at room temperature. The ability of these oxo-free molybdenum(IV) complexes to undergo oxygen atom transfer is, thus, very sensitive to the ligating environment of the metal. This observation may highlight an important factor in such enzymes as xanthine oxidase and nitrate reductase, where we have suggested that the molybdenum-containing, substrate-binding prosthetic group may act as an oxygen atom transfer agent[13,26-28] rather than as a hydroxylase[28,29] as is generally accepted. Recent studies[30] on related oxomolybdenum complexes tend to reaffirm our suggestion.

The complexes $Mo(S_2CNEt_2)_2L$ ($L = o\text{-}C_6H_4S_2, o\text{-}C_6H_4OS, o\text{-}C_6H_4NMeS$) were all cleanly oxidized to $ClMo(S_2CNEt_2)_2L$ by exactly 0.5 mol of Cl_2 (eq 14). Consistent with their formulation as monomeric Mo(V) species, all three products exhibit strong EPR signals. The EPR spectrum of $ClMo(S_2CNEt_2)_2(o\text{-}C_6H_4S_2)$ contains a single signal at $g = 1.984$ with ^{95,97}Mo hyperfine of 37 G. The spectrum of $ClMo(S_2CNEt_2)_2(o\text{-}C_6H_4OS)$ contains one primary signal ($g = 1.969$ $A(^{95,97}Mo) = 40$ G) and a much weaker signal at $g = 1.978$. The EPR spectrum of $ClMo(S_2CNEt_2)_2(o\text{-}C_6H_4NMeS)$ also contains two signals ($g = 1.978$, $A(^{95,97}Mo) = 45$ G; $g = 1.965$ $A(^{95,97}Mo) = 39$ G), but in this case, the intensity ratio is ~1:2 as opposed to the ~1:20 ratio observed in the spectrum of $ClMo(S_2CNEt_2)_2(o\text{-}C_6H_4OS)$. The two EPR signals observed for $L = o\text{-}C_6H_4OS$ and $o\text{-}C_6H_4NMeS$ are likely to be due to two of the many possible isomers of $ClMo(S_2CNEt_2)_2L$.

$$Mo(S_2CNEt_2)_2L + {}^1/_2Cl_2 \rightarrow ClMo(S_2CNEt_2)_2L \quad (14)$$

Table III. Assignments of ν(Mo=O) in Oxygen-16 and Oxygen-18 Substituted *cis*-MoO_2^{2+} and MoO^{2+} Cores[a]

		ν(Mo=^{18}O)	
compd	ν(Mo=^{16}O)	found	calcd
$MoO_2[S_2CN(CH_3)_2]_2$	910 (vs), 874 (vs)	864 (vs), 835 (vs)	865, 831
$MoO_2[S_2CN(C_2H_5)_2]_2$	910 (vs), 877 (vs)	865 (vs), 836 (vs)	865, 834
$MoO_2[S_2CN(n\text{-}C_3H_7)_2]_2$[b]			
α	913 (vs), 878 (vs)	866 (vs), 839 (vs)	868, 837
β	911 (vs), 878 (vs)	864 (vs), 838 (vs)	866, 835
$MoO_2[S_2P(i\text{-}C_3H_7)_2]_2$	924 (vs), 890 (vs)	880 (vs), 851 (vs)	879, 846
$MoO[S_2CN(CH_3)_2]_2$	957 (vs)	910 (vs)	910
$MoO[S_2CN(C_2H_5)_2]_2$	962 (vs)	914 (vs)	915
$MoO[S_2CN(n\text{-}C_3H_7)_2]_2$	965 (vs)	917 (vs)	918
$MoO[S_2P(OCH_3)_2]_2$	967 (s)		
$MoO[S_2P(OC_2H_5)_2]_2$	972[c]	924 (s)	

[a] In cm^{-1}. [b] See text. [c] Obscured by ligand vibration and calculated from ^{18}O value.

4. Infrared Spectral Assignments of Oxomolybdenum Complexes.

The lack of consensus in the literature over the correct assignment of infrared absorption bands to various molybdenum-oxygen stretching vibrations, particularly those of the oxo-bridged dinuclear molybdenum(V) complexes,[13,15,31-36] arises mainly from the lack of dinuclear cores bound by simple ligands. The many absorption bands of ligands like the dithiocarbamates, when coordinated to molybdenum, make the resulting complex spectra difficult to analyze. Our synthesis of a series of oxygen-18 substituted compounds, using minimal amounts of $H_2{}^{12}O$, not only makes comparative studies of these products with their oxygen-16 counterparts possible but also allows definitive, unambiguous assignments of both terminal and bridging molybdenum-oxygen stretching frequencies to be made.

(a) Dioxomolybdenum(VI) and Oxomolybdenum(IV) Complexes. The structures of $MoO_2(LL)_2$ and $MoO(LL)_2$ ($LL = (n\text{-}C_3H_7)$)[37] substantiate earlier spectroscopically based suggestions that the former compounds contain the *cis*-MoO_2 grouping, while the latter approximate a square pyramid with an apical oxo ligand. Our infrared spectral assignments are listed in Table III and, except for $MoO[S_2P(OR)_2]_2$ ($R = C_2H_5$), are in good agreement with reported values. Two solid-state forms of $MoO_2[S_2CN(n\text{-}C_3H_7)_2]_2$, designated α and β in Table III, exist and are easily distinguishable by infrared spectroscopy[8] at ~600, 750, and 980 cm^{-1}. The α form has strong, unsplit bands at 610, 750, and 980 cm^{-1} while the β form is characterized by a 600-cm^{-1} band, plus two weaker split bands at 750 and 770 cm^{-1} and a weak doublet at 980 cm^{-1}. The difference at ~750 cm^{-1} becomes important in the consideration of assignments for $Mo_2O_3(LL)_4$. The "two-band" form of the ligand (at 750 and 770 cm^{-1}) is observed in $MoO[S_2CN(n\text{-}C_3H_7)_2]_2$. α is the form produced from acidified aqueous solutions of Na_2MoO_4 and $NaS_2CN(n\text{-}C_3H_7)_2$, while form β is the product of hydrolysis of $Mo(DEAZ)_2[S_2CN(n\text{-}C_3H_7)_2]_2$. β converts to α on recrystallization from diethyl ether, while α transforms into β on recrystallization from CH_2Cl_2 containing added $DEAZH_2$.

The previous erroneous assignment[15] of ν(Mo=O) in $Mo^{16}O[S_2P(OC_2H_5)_2]_2$ at 1000 cm^{-1} arises from the complicated vibrations of the P-O-C grouping of the ligand. This assignment always appeared unlikely because (i) all related $Mo^{16}O(S_2CNR_2)_2$ complexes have[6,15] ν(Mo=O) at ~960 cm^{-1} and (ii) $Mo^{16}O[S_2P(OCH_3)_2]_2$ has no ligand absorptions between 990 and 850 cm^{-1} but an intense band at 967 cm^{-1}, which is likely ν(Mo=O). After considerable effort, $Mo^{18}O[S_2P(OC_2H_5)_2]_2$ was synthesized and it exhibits a unique absorption at 924 cm^{-1} (ν(Mo=^{18}O)). Therefore, by calculation, ν(Mo=^{16}O) is expected at 972 cm^{-1} in $Mo^{16}O[S_2P(OC_2H_5)_2]_2$ but is hidden under a ligand vibration. Thus, the previous assignment[15] of ν(Mo=^{16}O) at 998 cm^{-1} in $Mo^{16}O[S_2P(OPh)_2]_2$ is also likely incorrect. All terminal Mo=O vibrations in these (^{16}O)oxo-molybdenum(IV) complexes lie at 965 ± 8 cm^{-1}.

(b) Bis(μ-oxo)bis[oxomolybdenum(V)] and (μ-Oxo)(μ-sulfido)bis[oxomolybdenum(V)] Complexes. Terminal molybdenum-oxygen stretching vibrations in $Mo_2{}^{16}O_4(LL)_2$ have been

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(24) Stiefel, E. I. *Prog. Inorg. Chem.* **1976**, *22*, 1.
(25) Dirand, J.; Ricard, L.; Weiss, R. *J. Chem. Soc., Dalton Trans.* **1976**, 278.
(26) Newton, W. E.; Watt, G. D.; McDonald, J. W. *Chem. Uses Molybdenum, Proc. Int. Conf., 3rd* **1979**, 259.
(27) Newton, W. E.; McDonald, J. W.; Yamanouchi, K.; Enemark, J. H. *Inorg. Chem.* **1979**, *18*, 1621.
(28) Stiefel, E. I.; Newton, W. E.; Watt, G. D.; Hadfield, K. L.; Bulen, W. A. *Adv. Chem. Ser.* **1977**, *No. 162*, 353.
(29) Bray, R. C. In "The Enzymes", 3rd ed.; Boyer, P. D., Ed.; Academic Press: New York, 1975; Vol. 12, p 299.
(30) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 3035.
(31) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 867.
(32) Selbin, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 712.
(33) Wing, R. M.; Callahan, K. P. *Inorg. Chem.* **1969**, *8*, 871.
(34) Newton, W. E.; Corbin, J. L.; McDonald, J. W. *J. Chem. Soc., Dalton Trans.* **1974**, 1044.
(35) Cotton, F. A.; Hunter, D. L.; Ricard, L.; Weiss, R. *J. Coord. Chem.* **1974**, *3*, 259.
(36) Miller, K. F.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 984; **1980**, *19*, 1818.
(37) Ricard, L.; Estienne, J.; Karagiannides, P.; Toledano, P.; Fischer, J.; Mitschler, A.; Weiss, R. *J. Coord. Chem.* **1974**, *3*, 277.

Table IV. Molybdenum–Oxygen Assignments for Species $Mo_2O_3(LL)_4$ and $Mo_2O_2X_2(LL)_2$[a,b]

compd	isotope	ν(Mo=O)	ν(MoOMo)	δ(MoOMo)	ν(MoSMo)
$Mo_2O_3[S_2CN(CH_3)_2]_4$	^{16}O	933 (vs)	753 (w)	437 (m)	
	^{18}O	886 (vs) [887]	715 (w) [716]	416 (m) [416]	
$Mo_2O_3[S_2CN(C_2H_5)_2]_4$	^{16}O	932 (vs)	743 (w)	437 (m)	
	^{18}O	885 (vs) [886]	706 (w) [707]	420 (m) [416]	
$Mo_2O_3[S_2CN(n\text{-}C_3H_7)_2]_4$	^{16}O	929 (vs)	*c* [747][d]	434 (m)	
	^{18}O	885 (vs) [883]	710 (w)	417 (m) [413]	
$Mo_2O_3[S_2P(OC_2H_5)_2]_4$	^{16}O	*c* [961][d]	764 (w)	427 (vw)	
	^{18}O	914 (s)	726 (w) [727]	409 (vw) [406]	
$Mo_2O_3[S_2P(OCH_3)_2]_4$	^{16}O	960 (s)	765 (m)	428 (vw)	
$Mo_2O_4[S_2P(i\text{-}C_3H_7)_2]_2$	^{16}O	980 (vs), 961 (m)	732 (s), 714 (w), 475 (m)		
	^{18}O	934 (vs), 913 (m) [932, 914]	701 (s), *c*, 457 (m) [696, 679, 452]		
$Mo_2O_4[S_2CN(C_2H_5)_2]$	^{16}O	973 (vs), 956 (m)	730 (s), 709 (w), 477 (m)		
	^{18}O	926 (vs), 910 (s) [925, 909]	696 (s), 672 (w), 455 (m) [694, 674, 454]		
$Mo_2O_3S[S_2P(i\text{-}C_3H_7)_2]$	^{16}O	977 (vs), 962 (s)	712 (s), 514 (w)		458 (m), 376 (w)
	^{18}O	930 (vs), 915 (s) [929, 915]	*c*, *c* [677, 489]		459 (m), 374 (w)
$Mo_2O_3S[S_2CN(C_2H_5)_2]_2$	^{16}O	969 (vs), 952 (s)	708 (m), 515 (m)		472 (m), 353 (m)
	^{18}O	922 (vs), 907 (s) [922, 905]	673 (m), 488 (m) [673, 490]		461 (m), 350 (m)

[a] All values in cm^{-1}. [b] Calculated values for ^{18}O vibration in brackets. [c] Obscured by ligand vibration. [d] Calculated from observed ^{18}O vibration.

assigned tentatively to one or more bands at ~950 cm^{-1} in complexes for LL = anions of amino acids and related compounds[38-42] and with LL = $\eta^5\text{-}C_5H_5$,[43] $R_2NCS_2^-$,[13] $ROCS_2^-$,[34] and OCS_2^{2-}.[34] Two bands should be observable in the infrared on the basis of the number, symmetry class, and activity of ν(Mo=O) vibrations, when these molecules, excluding the centrosymmetric[43,44] $(C_5H_5)_2Mo_2O_4$, are treated in the point group C_{2v}. Comparative studies of $Mo_2X_4(LL)_2$ (X = ^{16}O, ^{18}O; LL = $S_2CN(C_2H_5)_2$, $S_2P(i\text{-}C_3H_7)_2$), in which two absorptions centered at ~970 cm^{-1} shift to 920 cm^{-1} on substitution with oxygen-18, confirm this prediction (see Table IV). The related ν(Mo=O) bands in $(C_5H_5)_2Mo_2O_2X_2$ (X = O, S) occur at 925 and 920 cm^{-1}, respectively.[43] A similar treatment of the bridging vibrations indicates that, of the four bis(μ-oxo) bridge vibrational modes, three should be infrared active as suggested previously.[33] Previous attempts to assign the bis(μ-oxo) bridge vibrational modes have been limited to one band[39-43] at ~740 cm^{-1} or two bands[13,38] at ~740 and ~475 cm^{-1}. A comparison of the spectra of $Mo^{16}O_2(LL)_2$ and $Mo_2{}^{16}O_4(LL)_2$ (LL = $S_2CN(C_2H_5)_2$, $S_2P(i\text{-}C_3H_7)_2$) in the region 850–250 cm^{-1} indicates bands unique to the bis(μ-oxo) complexes at ~730 (s), ~710 (w), and ~475 (m) cm^{-1}. Confirmation of these assignments as the three infrared-active bridge modes comes from their shift to lower wavenumbers in the spectrum of $Mo_2{}^{18}O_4(LL)_2$ (Table IV). Our assignment of the third bis(μ-oxo) mode at ~475 cm^{-1} contrasts significantly with a previous[33] assignment at ~650 cm^{-1}. These data also allow differentiation among the six bands reported[43] as Mo–O–Mo related in $(C_5H_5)_2Mo_2O_4$. In C_{2h} symmetry, only two bridge bands should be infrared active and should correspond well with the assignments in $Mo_2O_4(LL)_2$. Those bands at 710 and 462 cm^{-1} satisfy these criteria.

The μ-oxo–μ-sulfido complexes $Mo_2O_3S(LL)_2$ (LL = $S_2CN(C_2H_5)_2$, $S_2P(i\text{-}C_3H_7)_2$) show a similar shift of the two terminal ν(Mo=O) modes on replacing ^{16}O with ^{18}O (see Table IV). Also, by comparison of the spectra of $Mo^{16}O_2(LL)_2$, $Mo_2{}^{16}O_4(LL)_2$, and $Mo_2{}^{16}O_3S(LL)_2$ (LL = $S_2P(i\text{-}C_3H_7)_2$, $S_2CN(C_2H_5)_2$), unique bands at ~710 (s), ~515 (w), ~460 (m), and ~365 (w) cm^{-1} are apparent in the last spectrum. The appearance of four infrared-active bridge modes is consistent with a lowering of the symmetry of the molecule to C_s. On substitution with oxygen-18, the two higher frequency absorptions shift to 673 and 488 cm^{-1}, but the absorptions at ~460 and ~365 cm^{-1} are hardly affected. The higher frequency pair is, therefore, primarily Mo–O–Mo in nature, while the lower frequency pair is Mo–S–Mo. These observations indicate that the coupling between the terminal and bridge modes is minimal as is that between the bent Mo–O–Mo and Mo–S–Mo bridges.

(c) Linear Monooxo-Bridged Molybdenum(V) Dimers. These $Mo_2O_3(LL)_4$ complexes have either a cis arrangement[37,45] of the $Mo_2O_3{}^{4+}$ core (overall C_2 symmetry) or a centrosymmetric trans structure.[46] $Mo_2O_3(S_2CNR_2)_4$ is an example of the former structure and $Mo_2O_3[S_2P(OR)_2]_4$ of the latter. The spectra of these complexes have presented the most problems in terms of the correct assignment of the various molybdenum–oxygen fundamental modes. Both structures should have a symmetric and an antisymmetric terminal molybdenum–oxygen stretching mode (ν(Mo=O)). However, as the Mo–O oscillators are somewhat insulated from one another by the oxo bridge, the coupling constant may be small but is probably observable by analogy with the bis(μ-oxo) systems. Similarly, two bridge vibrational modes are expected, with the antisymmetric (ν^a(MoOMo)) at higher frequency[35] than the symmetric (ν^s(MoOMo)). For the trans compounds, only the antisymmetric terminal and bridge vibrations should be infrared active.

(i) Bridge Modes. We sought to confirm our previous assignments[13,14] of the unique bands at ~745 cm^{-1} (ν(MoOMo)) and ~435 cm^{-1} in $Mo_2O_3(LL)_4$ (LL = S_2CNR_2, S_2COR) as bridge-related modes because ν^a(MoOMo) in $Mo_2O_3[S_2CN(n\text{-}C_3H_7)_2]_4$ has been suggested[35] to occur at 770 cm^{-1}, ~20 cm^{-1} higher than we would have predicted. This assignment[35] appears doubtful because of ligand bands at 770 cm^{-1} in both the oxomolybdenum(IV) complex and the β form of *cis*-$MoO_2[S_2CN(n\text{-}C_3H_7)_2]_2$. The assignment[15] in *trans*-$Mo_2O_3[S_2P(OR)_2]_4$ (R = C_2H_5, C_6H_5) for ν^a(MoOMo) at ~780 cm^{-1} also appears anomalously high because we find that the analogous $Mo_2O_3[S_2P(OCH_3)_2]_4$ complex has a unique band at 765 cm^{-1}. Oxygen-18 substitution in $Mo_2O_3[S_2P(OC_2H_5)_2]_4$ shows that a shoulder at 764 cm^{-1} on the 780-cm^{-1} band is ν^a(MoOMo), *not* the 780-cm^{-1} band itself, consistent with the absorption observed in $Mo_2O_3[S_2P(OCH_3)_2]_4$. The weak ~427-cm^{-1} band in $Mo_2O_3[S_2P(OR)_2]_4$ (R = CH_3, C_2H_5) could be a bridge deformation mode because it shifts to 409 cm^{-1} on ^{18}O substitution in the centrosymmetric R = C_2H_5 complex.

These results indicate that the assignment[15] of ν^a(MoOMo) at 785 cm^{-1} in $Mo_2{}^{16}O_3[S_2P(OC_6H_5)_2]_4$ is also likely in error and that the use of these data to make assignments[35] in $Mo_2O_3(S_2CNR_2)_4$ would be misleading. Our assignments of the two bridge-related modes in the dithiocarbamate complexes (R = CH_3, C_2H_5) were confirmed by ^{18}O substitution when the absorption bands at ~745 and ~435 cm^{-1} shifted to ~705 and ~420 cm^{-1} (Table IV). Also, as expected, the 770-cm^{-1} band did *not* shift

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(38) Melby, L. R. *Inorg. Chem.* **1969**, *8*, 349.
(39) Kay, A.; Mitchell, P. C. H. *J. Chem. Soc. A* **1970**, 2421.
(40) Spivack, B.; Dori, Z. *J. Chem. Soc. D* **1970**, 1716.
(41) Cotton, F. A.; Morehouse, S. M. *Inorg. Chem.* **1965**, *4*, 1377.
(42) Mitchell, P. C. H. *J. Chem. Soc. A* **1969**, 146.
(43) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1964**, 1567. Treichel, P. M.; Wilkes, G. R. *Inorg. Chem.* **1966**, *5*, 1182.
(44) Stevenson, D. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 3721.
(45) Blake, A. B.; Cotton, F. A.; Wood, J. S. *J. Am. Chem. Soc.* **1964**, *86*, 3024.
(46) Knox, J. R.; Prout, C. K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 2281.

on ^{18}O substitution of $\mathrm{Mo_2O_3[S_2CN(\textit{n}-C_3H_7)_2]_4}$, but a weak absorption at 710 cm^{-1} appears (ν^a(Mo^{18}OMo)), which places ν^a(Mo^{16}OMo) at 747 cm^{-1} by calculation, exactly in the range of its methyl and ethyl analogues. A band at 434 cm^{-1} also shifts concomitantly to 417 cm^{-1} and is assigned as δ(MoOMo) by analogy with the dithiophosphate complexes.

(ii) Terminal Modes. The terminal Mo–O stretching vibrations have been assigned,[13,15,34,35,47–49] to various infrared bands in the range 1005–910 cm^{-1}, with assignments[15,31,33] in the related xanthates going as high as 1047 cm^{-1}. For those complexes with *cis*-$\mathrm{Mo_2O_3}^{4+}$ cores, either one or two bands have been assigned by others to ν(Mo=O),[35,49] while we had assigned[13] single bands at ~935 cm^{-1} in the dithiocarbamate complexes. One aspect of this severe lack of agreement is exemplified by the proposed association[15] of ν(Mo=O) in $\mathrm{Mo_2O_3[S_2P(OR)_2]_4}$ with a ~975-cm^{-1} band. This assignment would indicate an ~40-cm^{-1} shift to higher wavenumbers compared to that band in $\mathrm{Mo_2O_3(S_2CNR_2)_4}$, a considerable increase over the usual ~10-cm^{-1} differences observed in comparing ν(Mo=O) in the OMo(LL)$_2$ complexes, for example (Table III). Further, ν(Mo=O) in $\mathrm{Mo_2O_3[S_2P(OCH_3)_2]_4}$ is clearly assignable at 960 cm^{-1}. As confirmed by the appearance of ν(Mo=^{18}O) at 914 cm^{-1}, ν(Mo=^{16}O) must be at 961 cm^{-1} in $\mathrm{Mo_2O_3[S_2P(OEt)_2]_4}$, which puts it directly under a ligand absorption. This erroneous ~975-cm^{-1} assignment has been used to support the assignment of cleanly separated symmetric and antisymmetric terminal modes in the $\mathrm{Mo_2O_3(S_2CNR_2)_4}$ spectra,[35] a second aspect of severe disagreement. With $\mathrm{Mo_2O_3(S_2CNR_2)_4}$ (R = $\mathrm{C_2H_5}$, *n*-$\mathrm{C_3H_7}$), we find no observable differences in the 1100–950-cm^{-1} region for the ^{16}O and ^{18}O complexes. Only the very strong band at ~930 cm^{-1} is affected by substitution with ^{18}O by shifting to 885 cm^{-1} (Table IV). These observations, coupled with our evidence indicating the erroneous assignment of ν(Mo=O) in $\mathrm{Mo_2O_3[S_2P(OR)_2]_4}$, show that there is *no* clearly observable second ν(Mo=O) for the *cis*-$\mathrm{Mo_2O_3}^{4+}$ core, certainly not in this region of the spectrum, although the C_2 symmetry of these complexes would appear to demand it. We suggest, therefore, that the single band at ~950 cm^{-1} encompasses both ν^s(Mo=O) and ν^a(MO=O). Thus, either the coupling between them is very small or the two Mo=O groups act as independent oscillators, insulated by the oxo bridge, requiring only one absorption band. This situation finds support in the very small shifts (±4 cm^{-1}) in frequency observed for ν(Mo=O) in the series $\mathrm{Mo_2O_2X_2}^{2+}$, where the bridging $\mathrm{X_2}$ varies from O, O through O, S to S, S.[50]

Thus, ν(Mo=O) has been definitively assigned for complexes of two ligand and structural types containing sulfur donor atoms as follows: (i) in MoO(LL)$_2$, ν(Mo=O) lies at 965 ± 8 cm^{-1}; (ii) for $\mathrm{Mo_2O_3(LL)_4}$, ν(Mo=O) is at 945 ± 16 cm^{-1}; (iii) in $\mathrm{Mo_2O_2X_2(LL)_2}$, ν(Mo=O) is at 975 ± 6 cm^{-1}; (iv) for $\mathrm{MoO_2(LL)_2}$, both ν(Mo=O) bands lie at 900 ± 24 cm^{-1}. These data show that ν(Mo=O) tends to increase inversely with oxidation state with the exception of $\mathrm{Mo_2O_2X_2(LL)_2}$, which has only one LL per Mo and a Mo–Mo bond. Previous assignments of ν(Mo=O) in $\mathrm{Mo_2O_3(LL)_4}$ at higher frequency than in MoO(LL)$_2$ and the arguments proposed[15] to explain this anomaly are erroneous. The hypothesis involving competition for the π-acceptor orbitals of molybdenum by the varying number and types of oxo ligands, therefore, appears adequate to explain the observed trend.[51] By similar methods, *all* expected vibrational modes for the μ-oxo, bis(μ-oxo), and μ-oxo–μ-sulfido bridges have been assigned for the first time. Unambiguous assignment of these various molybdenum–oxygen vibrational modes is of importance because they are useful monitors for oxidation state and/or stereochemical changes occurring during reaction. Further, easy spectroscopic identification of the various mononuclear and dinuclear molybdenum cores may find utility in probes of the molybdenum-containing centers in a wide variety of species of both biological and chemical origin.

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Registry No. **1**, 57088-09-2; **2**, 57034-65-8; $\mathrm{Mo(S_2CNEt_2)_2(C_6H_4S_2)}$, 96617-11-7; $\mathrm{Mo(S_2CNEt_2)_2(C_6H_4OS)}$, 96617-10-6; $\mathrm{Mo(S_2CNEt_2)_2(C_6H_4NHS)}$, 96617-16-2; $\mathrm{Mo(S_2CNEt_2)_2(C_6H_4NMeS)}$, 96617-17-3; $\mathrm{Mo(S_2CNEt_2)_2(C_6H_4O_2)}$, 96617-18-4; $\mathrm{Mo(S_2CNEt_2)_2(C_2H_4OS)}$, 96617-19-5; $\mathrm{OMo(S_2CNEt_2)_2}$, 96617-15-1; $\mathrm{ClMo(S_2CNEt_2)_2}$, 96617-14-0; $\mathrm{ClMo(S_2CNEt_2)_2}$, 96617-13-9; $\mathrm{ClMo(S_2CNEt_2)_2}$, 96617-12-8; $\mathrm{MoO_2[S_2CN(CH_3)_2]_2}$, 39248-36-7; $\mathrm{Mo^{18}O_2[S_2CN(CH_3)_2]_2}$, 63912-65-2; $\mathrm{MoO_2[S_2CN(C_2H_5)_2]_2}$, 18078-69-8; $\mathrm{Mo^{18}O_2[S_2CN(C_2H_5)_2]_2}$, 63912-66-3; $\mathrm{MoO_2[S_2CN(\textit{n}-C_3H_7)_2]_2}$, 18078-70-1; $\mathrm{Mo^{18}O_2[S_2CN(\textit{n}-C_3H_7)_2]_2}$, 63912-67-4; $\mathrm{MoO_2[S_2P(\textit{i}-C_3H_7)_2]_2}$, 63998-94-7; $\mathrm{MoO[S_2CN(CH_3)_2]_2}$, 63950-36-7; $\mathrm{Mo^{18}O[S_2CN(CH_3)_2]_2}$, 63912-68-5; $\mathrm{MoO[S_2CN(C_2H_5)_2]_2}$, 63950-40-3; $\mathrm{Mo^{18}O[S_2CN(C_2H_5)_2]_2}$, 63912-69-6; $\mathrm{MoO[S_2CN(\textit{n}-C_3H_7)_2]_2}$, 54515-55-8; $\mathrm{Mo^{18}O[S_2CN(\textit{n}-C_3H_7)_2]_2}$, 63912-54-9; $\mathrm{MoO[S_2P(OCH_3)_2]_2}$, 63950-38-9; $\mathrm{MoO[S_2P(OC_2H_5)_2]_2}$, 63950-39-0; $\mathrm{Mo^{18}O[S_2P(OC_2H_5)_2]_2}$, 63912-55-0; $\mathrm{Mo_2O_3[S_2CN(CH_3)_2]_4}$, 20023-85-2; $\mathrm{Mo_2{}^{18}O_3[S_2CN(CH_3)_2]_4}$, 63912-51-6; $\mathrm{Mo_2O_3[S_2CN(C_2H_5)_2]_4}$, 20023-86-3; $\mathrm{Mo_2{}^{18}O_3[S_2CN(C_2H_5)_2]_4}$, 63912-52-7; $\mathrm{Mo_2O_3[S_2CN(\textit{n}-C_3H_7)_2]_4}$, 53426-41-8; $\mathrm{Mo_2{}^{18}O_3[S_2CN(\textit{n}-C_3H_7)_2]_4}$, 63912-53-8; $\mathrm{Mo_2O_3[S_2P(OC_2H_5)_2]_4}$, 53494-96-5; $\mathrm{Mo_2{}^{18}O_3[S_2P(OC_2H_5)_2]_4}$, 96617-22-0; $\mathrm{Mo_2O_3[S_2P(OCH_3)_2]_4}$, 63950-37-8; $\mathrm{Mo_2O_4[S_2P(\textit{i}-C_3H_7)_2]_2}$, 63912-56-1; $\mathrm{Mo_2{}^{18}O_4[S_2P(\textit{i}-C_3H_7)_2]_2}$, 63943-20-4; $\mathrm{Mo_2O_4[S_2CN(C_2H_5)_2]_2}$; 55780-89-7; $\mathrm{Mo_2{}^{18}O_4[S_2CN(C_2H_5)_2]_2}$, 63943-19-1; $\mathrm{Mo_2O_3S[S_2P(\textit{i}-C_3H_7)_2]_2}$, 63912-57-2; $\mathrm{Mo_2{}^{18}O_3S[S_2P(\textit{i}-C_3H_7)_2]_2}$, 96617-21-9; $\mathrm{Mo_2O_3S[S_2CN(C_2H_5)_2]_2}$, 63912-48-1; $\mathrm{Mo_2{}^{18}O_3S[S_2CN(C_2H_5)_2]_2}$, 96633-11-3; $\mathrm{Mo(CO)_2(S_2CNEt_2)_2}$, 18947-43-8; $\mathrm{Mo(CO)_6}$, 13939-06-5; $\mathrm{Mo(CO)_2[S_2CN(\textit{n}-Pr)_2]_2}$, 96617-20-8; $\mathrm{Mo(CO)_2[S_2P(\textit{i}-Pr)_2]_2}$, 60965-90-4; $\mathrm{Mo(CO)_2(S_2CNMe_2)_2}$, 80664-77-3; $\mathrm{Mo(CO)_2(PPh_3)[S_2P(OEt)_2]_2}$, 63339-43-5; ^{18}O, 14797-71-8.

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(47) Colton, R.; Scollary, G. R. *Aust. J. Chem.* **1968**, *21*, 1427.
(48) Moore, F. W.; Larson, M. L. *Inorg. Chem.* **1967**, *6*, 998.
(49) Casey, A. T.; Mackey, D. J.; Martin, R. L.; White, A. H. *Aust. J. Chem.* **1972**, *25*, 477.
(50) Schultz, F. A.; Ott, V. R.; Rolinson, D. S.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1978**, *17*, 1758.
(51) Mitchell, P. C. H. *Q. Rev., Chem. Soc.* **1966**, *20*, 103.