Reaction of $ReOCl_3(PPh_3)_2$ with $NaEt_2NCS_2 \cdot 3H_2O$ in acetone solution[45,46] forms the well-characterized $Re_2O_3(Et_2NCS_2)_4$[46,47] which contains a linear O=Re—O—Re=O backbone. When the reaction is run in methanol, rather than acetone, the product isolated is *t*-$ReO(OMe)(dtc)_2$.[46] This material is easily converted to $Re_2O_3(dtc)_4$ in methylene chloride. The reaction of $ReOCl_3(PPh_3)_2$ pyridine in wet benzene leads to isolation of $Re_2O_3(py)_4Cl_4$,[48] another linear backbone, whereas reaction in ethanol[37] leads to the formation of $ReO_2(py)_4^+$. Addition of ethanol to $Re_2O_3(py)_4Cl_4$ results in formation of *t*-$ReO(OEt)py)_2Cl_2$ which is further converted to $ReO_2(py)_4^+$ upon addition of wet pyridine.[48]

The formation of the $M_2O_3^{4+}$ unit in $Re_2O_3(dtc)_4$,[45] $Re_2O_3(py)_4Cl_4$,[47] and $K_4Re_2O_3(CN)_8$[13] has been postulated to involve an intermediate *t*-$MO(OH)L_4$ species, which dimerizes and dehydrates to form the *t*-$M_2O_3^{4+}$ core.

Of special interest is the observation that the alkoxide species $ReO(OMe)(dtc)_2$ and $ReO(OEt)(Py)_2Cl_2$ are easily converted to $Re_2O_3(dtc)_4$ and *t*-$ReO_2(py)_4^+$, respectively.[46,48] In the case of $TcO(OMe)(CN)_4^{2-}$, there is no evidence for such a transformation under the mild conditions utilized in the rhenium complexes. Whether this behavior is due to the presence of cyanide ion or represents a fundamental difference between technetium and rhenium cannot be clearly ascertained at this time.

The isolation of $K_4Tc(CN)_7 \cdot 2H_2O$, $K_2TcO(CN)_5 \cdot 4H_2O$, $K_3TcO_2(CN)_4$, and $(n\text{-}Bu_4N)_2TcO(OMe)(CN)_4$ clearly demonstrates that technetium does indeed form a wide variety of cyanide complexes which parallel the known chemistry of its third-row congener, rhenium.

Acknowledgment. This work was performed under USPHS Grant 1 R01GM23270 and Department of Energy Contract E(11-1)4115. We wish to thank Dr. W. Natter and the M.I.T. Spectroscopy Laboratory for their help in obtaining Raman spectra on the complexes.

Registry No. **3**, 73466-61-2; **4**, 73396-83-5; $K_4Tc(CN)_7$, 73396-81-3; $K_2TcO(CN)_5$, 73396-80-2; $(NH_4)_2TcI_6$, 40694-78-8; $(NH_4)_2TcBr_6$, 29462-54-2; $TcO_2(py)_4ClO_4$, 73396-79-9; $n\text{-}Bu_4NTcOCl_4$, 71341-65-6.

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Binding and Activation of Enzymic Substrates by Metal Complexes. 5.[1] Synthesis, Structure, and Properties of Some Acetylenic Complexes of Oxomolybdenum(IV) Dithiocarbamates

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Received July 11, 1979

Reaction of $OMo(S_2CNR_2)_2$ (R = Me, Et) with various acetylenes ($C_2R^1R^2$: $R^1 = R^2 = H$; $R^1 = R^2 = Ph$; $R^1 = H$, $R^2 = Ph$; $R^1 = R^2 = CO_2Me$; $R^1 = R^2 = CF_3$; $R^1 = R^2 = COC_6H_5Me$; $R^1 = H$, $R^2 = CO_2Me$) produces the 1:1 complexes $OMo(S_2CNR_2)_2(C_2R^1R^2)$. These reactions have equilibrium constants in the range $\sim 20\,000\ M^{-1}$ (for $R^1 = R^2 = CO_2Me$) to $\sim 20\ M^{-1}$ (for $R^1 = R^2 = H$). Infrared spectroscopy indicates that these products are better described as complexes of Mo(VI) formed by oxidative addition of the acetylenic bond to Mo(IV). The structure of $OMo(S_2CNMe_2)_2(C_2R_2)$ ($R = COC_6H_5Me$) also conforms to this description. The acetylenic C–C bond is 1.267 Å and is perpendicular to the metal–oxygen bond (1.686 Å). The molybdenum–acetylenic carbon bonds are rather short (2.12 Å). NMR spectrometry indicates significant acetylene-to-metal π-electron donation from the position of the deshielded resonance of the bound acetylene in line with the shorter M–C bond. Variable-temperature NMR spectra show all these complexes to have similar structures in solution, which are fluxional, and that the stereochemistry determined in the solid state is conserved in solution. The reaction of $OMo(S_2CNR_2)_2(C_2R^1R^2)$ with water in air gives $Mo_2O_4(S_2CNR_2)_2$ for $R^1 = R^2 = CO_2Me$, for $R^1 = R^2 = CF_3$, and for $R^1 = H$, and $R^2 = CO_2Me$, but with $R^1 = R^2 = COC_6H_5Me$, the complex is stable toward hydrolysis. Under argon, one or the other or both of $OMo(S_2CNR_2)_2$ and $Mo_2O_4(S_2CNR_2)_2$ are formed depending on the conditions. The fate of the acetylenic moiety varies. With alcohols, a thiourethane is formed for $R^1 = R^2 = CO_2Me$ or CF_3 and for $R^1 = H$ and $R^2 = CO_2Me$. The latter also produces dimethyl (*N,N*-dimethyldithiocarbamato)fumarate. No reaction occurs with $R^1 = R^2 = COC_6H_5Me$. With R_2NH, except for $R^1 = R^2 = CF_3$ where no reaction occurs, all complexes give $OMo(S_2CNR_2)$ and dimethyl 2-(dialkylamino)maleate.

There are only few well-defined molybdenum(IV) complexes but the chemistry they undergo may well be very important in elucidating the role of molybdenum in enzymes. Molybdenum(IV) has been implicated in the redox cycle of a variety of molybdoenzymes,[3–5] e.g., xanthine oxidase and sulfite oxidase, and certain of its complexes have been used in model studies of these enzymes[6–10] and nitrogenase.[6,10–14] We have

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0020-1669/80/1319-1997$01.00/0

sought to extend our previous studies[6,10,13,15] of the reactions of oxobis(*N,N*-dialkyldithiocarbamato)molybdenum(IV), $[OMo(S_2CNR_2)_2]$, and herein we report the synthesis of a series of complexes of acetylenes with these coordinatively unsaturated species. Some of the properties and reactions of these complexes are described together with the structure of $OMo(S_2CNMe_2)_2(MeC_6H_4C(O)C_2C(O)C_6H_4Me)$ as determined by X-ray methods.

Experimental Section

Materials and Methods. All reactions were carried out under an argon atmosphere by using standard techniques. All solvents were dried over molecular sieves and degassed prior to use. The compounds $OMo(S_2CNR_2)_2$ (R = Me, Et), $MeC_6H_4C(O)C{\equiv}CC(O)C_6H_4Me$ (ditoluoylacetylene, DTA) and $HC{\equiv}CCO_2Me$ (methyl propiolate, MP) were prepared by literature[8,16-18] methods. Dimethyl acetylenedicarboxylate (DMAC), phenylacetylene, and diphenylacetylene were purchased from Aldrich Chemical Co., and hexafluoro-2-butyne (HFB) was purchased from the Hynes Chemical Co. All were used without further purification.

Infrared spectra were recorded on a Beckman IR-20A spectrophotometer, ^1H NMR spectra on a Varian A-60 instrument (results reported as ppm from Me_4Si) and ^{19}F NMR spectra on a Varian A56-60 instrument. Elemental analyses for CHN were determined in this laboratory by using a Hewlett-Packard 185 analyzer. Gas chromatography (GLPC) was performed with a Hewlett-Packard 5750 dual-flame instrument using 10% UCW-982 on Chromosorb W.

Synthesis of Adducts. $OMo(S_2CNMe_2)_2$(DTA). A slurry of $OMo(S_2CNMe_2)_2$ (0.75 g) in CH_2Cl_2 (40 mL) was treated with a solution of DTA (0.62 g) in CH_2Cl_2 (20 mL). After being stirred at room temperature for 1 h, the yellow-brown solution was filtered to remove a small amount of insoluble material and the filtrate evaporated to dryness under vacuum. Trituration of the residue with diethyl ether gave a yellow solid (1.19 g, 91% yield), which was isolated by filtration, washed with diethyl ether, and dried in vacuo. Anal. Calcd for $C_{24}H_{26}N_2MoO_3S_4$: C, 46.9; H, 4.23; N, 4.56. Found: C, 47.1; H, 4.21; N, 4.37.

The following compounds of the general form $OMo(S_2CNR_2)_2$(Ac) were prepared similarly.

$OMo(S_2CNEt_2)_2$(DTA)·0.25CH_2Cl_2: yield 94%. Anal. Calcd for $C_{28.25}H_{34.5}N_2Cl_{0.5}MoO_3S_4$: C, 49.0; H, 4.99; N, 4.05. Found: C, 48.8; H, 5.10; N, 3.99.

$OMo(S_2CNMe_2)_2$(DMAC): yield 89%. Anal. Calcd for $C_{12}H_{18}N_2MoO_5S_4$: C, 29.2; H, 3.65; N, 5.68. Found: C, 29.4; H, 3.90; N, 5.32.

$OMo(S_2CNEt_2)_2$(DMAC): yield 50%. Anal. Calcd for $C_{16}H_{26}N_2MoO_5S_4$: C, 34.9; H, 4.76; N, 5.09. Found: C, 35.3; H, 5.06; N, 4.84.

$OMo(S_2CNMe_2)_2$(MP): yield 80%. Anal. Calcd for $C_{10}H_{16}N_2MoO_3S_4$: C, 27.5; H, 3.70; N, 6.42. Found: C, 27.2; H, 3.66; N, 6.10.

$OMo(S_2CNEt_2)_2$(MP): yield 70%. Anal. Calcd for $C_{14}H_{24}N_2MoO_3S_4$: C, 34.1; H, 4.88; N, 5.69. Found: C, 33.6; H, 4.81; N, 5.26.

$OMo(S_2CNMe_2)_2$(HFB). HFB was bubbled for 10 min into a slurry of $OMo(S_2CNMe_2)_2$ (0.5 g) in CH_2Cl_2 (60 mL). After being stirred at room temperature for 30 min, the reaction mixture was filtered and the filtrate evaporated to dryness under vacuum. Trituration of the residue with hexane gave a yellow-brown solid (0.58 g, 79% yield), which was isolated by filtration, washed with hexane, and dried in vacuo. Anal. Calcd for $C_{10}H_{12}N_2F_6MoOS_4$: C, 23.4; H, 2.34; N, 5.45. Found: C, 23.0; H, 2.35; N, 5.24.

The following compound was prepared similarly.

$OMo(S_2CNEt_2)_2$(HFB): yield 75%. Anal. Calcd for $C_{14}H_{20}N_2F_6MoOS_4$: C, 29.5; H, 3.53; N, 4.91. Found: C, 28.3; H, 3.64; N, 4.58.

Hydrolysis of $OMo(S_2CNMe_2)_2$(Ac) in Air. The adduct with Ac = MP (0.25 g) was dissolved in ethanol-free $CHCl_3$ (40 mL) in air and 1 mL of H_2O was added. The solution initially went purple and then lightened, and after it was stirred for 16 h, the greenish precipitate was filtered off, washed with CCl_4, ethanol, and diethyl ether, and dried in vacuo. The yield of $Mo_2O_4(S_2CNMe_2)_2$ was 0.12 g, 84%. Anal. Calcd for $C_6H_{12}N_2Mo_2O_4S_4$: C, 14.5; H, 2.44; N, 5.64. Found: C, 14.3; H, 2.44; N, 5.19 (confirmed by IR spectrum). The filtrate and CCl_4 washes were evaporated to dryness, redissolved in CCl_4, filtered, and then dissolved in $CDCl_3$, and a known quantity of CH_3CN was added as an internal standard. Integration of the NMR spectrum showed *trans*-$(Me_2NCS_2)CH{=}CH(CO_2Me)$ to be present in 84.5% yield based on initial MP content. The preparation and properties of the olefin are given below.

A similar experiment with Ac = DMAC (0.25 g) gave $Mo_2O_4(S_2CNMe_2)_2$ (0.1 g, 80% yield. Anal. Calcd for $C_6H_{12}N_2Mo_2O_4S_4$: C, 14.5; H, 2.44; N, 5.64. Found: C, 14.9; H, 2.42; N, 5.10 (confirmed by IR spectrum). Examination of the filtrate and CCl_4 washings by NMR (as above) showed the absence of both *cis*- and *trans*-$(MeO_2C)(H)C{=}C(S_2CNMe_2)(CO_2Me)$.

A saturated solution of $OMo(S_2CNMe_2)_2$(DTA) in $CDCl_3$ was monitored by NMR spectrometry after the addition of an excess of water. No spectral changes were observed over a 20-h period. A similar experiment with $OMo(S_2CNMe_2)_2$(HFB) resulted in the precipitation of $Mo_2O_4(S_2CNMe_2)_2$, which was removed when the remaining solution showed no resonances attributable to $OMo(S_2CNMe_2)_2$(HFB).

Hydrolysis of $OMo(S_2CNR_2)_2$(Ac) under Argon. $OMo(S_2CNMe_2)_2$(MP) (0.5 g) was stirred for 18 h in acetone–water (10:1, 55 mL) under argon. The solvent was then removed in vacuo and the dark residue extracted with benzene–hexane (1:1, 2 × 25 mL). The tan-pink residue of $OMo(S_2CNMe_2)_2$ (0.3 g, 75%) was found (IR) to be contaminated with minor amounts of $MoO_2(S_2CNMe_2)_2$ and $Mo_2O_4(S_2CNMe_2)_2$.[10] The benzene–hexane extracts were treated as above, and NMR integration indicated *trans*-$(Me_2NCS_2)HC{=}CH(CO_2Me)$ (52% yield, based on initial MP content). A similar anaerobic experiment run in ethanol-free $CHCl_3$ and with CCl_4 (2 × 25 mL) extraction gave a tan residue (0.2 g) containing mainly $Mo_2O_4(S_2CNMe_2)_2$ (by IR). The CCl_4 extracts, after treatment and spectral study (see above), showed *trans*-$(Me_2NCS_2)HC{=}CH(CO_2Me)$ (68%).

When $OMo(S_2CNEt_2)_2$(MP) was stirred in acetone–water (10:1) solution under argon, slightly impure tan-pink $OMo(S_2CNEt_2)_2$ (0.2 g, 48%) and *trans*-$(Et_2NCS_2)HC{=}CH(CO_2Me)$ (52%) were produced. The identical experiment in ethanol-free $CHCl_3$ gave a 57% yield of the organic product, while the major metal-containing product was impure (by IR[10]) $Mo_2O_4(S_2CNEt_2)_2$ (0.12 g).

When $OMo(S_2CNMe_2)_2$(DMAC) (0.5 g) was used in either of these solvent systems, no $(MeO_2C)CH{=}C(S_2CNMe_2)(CO_2Me)$ was observed. The tan-to-yellow residues (0.4 g) contained not only some $Mo_2O_4(S_2CNMe_2)_2$ but also other product(s) exhibiting ν(C=O) at ~1750 cm^{-1} but no ν(C=C) between 1800 and 2000 cm^{-1} in their IR spectra.

Preparation of Methyl *cis*-3-(*N,N*-Dimethyldithiocarbamato)-acrylate, *cis*-(Me_2NCS_2) (H)C=C(H)(CO_2Me). The cis ester has been only sketchily described in the literature.[19] It was prepared by the dropwise addition of Me_2NCS_2Na and acetic acid (4 mmol each) in MeOH (8 mL) to methyl propiolate[4] (4 mmol) in MeOH (8 mL) at 0 °C. After the solution was stirred for 30 min, H_2O (8 mL) was added and the product filtered (69% yield, mp 108–109 °C). Recrystallization from MeOH–H_2O gave the pure cis ester, mp 110–111 °C. Anal. Calcd for $C_7H_{11}NO_2S_2$: C, 40.95; H, 5.40; N, 6.82. Found: C, 41.19; H, 5.46; N, 6.94. NMR ($CDCl_3$): 3.52,

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3.67 (br, 6 H, $(CH_3)_2N$–), 3.87 (s, 3 H, CH_3O–), 6.23 (d, J = 10.2 Hz, α-H), 8.68 (d, J = 10.2 Hz, β-H).

Preparation of Methyl *trans*-3-(*N*,*N*-Dimethyldithiocarbamato)-acrylate, *trans*-$(Me_2NCS_2)(H)C{=}C(H)(CO_2Me)$. The unreported trans methyl ester was most expeditiously prepared by a simultaneous isomerization–esterification. The cis acid[20] (500 mg) was refluxed 10 h with concentrated HBr (0.2 mL) and MeOH (50 mL), and the solvent was removed. Ether (50 mL) was added, and the solution was washed (H_2O, 5% $NaHCO_3$), dried (Na_2SO_4), and evaporated to give 422 mg of a 3:1 trans–cis mixture (NMR). Purification could be accomplished by repeated recrystallization from 3:1 hexane–benzene, or better by chromatography on silica gel (benzene as solvent) to give broad needles, mp 103.5–104.5 °C. Anal. Calcd for $C_7H_{11}NO_2S_2$: C, 40.95; H, 5.40; N, 6.82. Found: C, 40.72; H, 5.52; N, 6.83. NMR ($CDCl_3$): 6.27 (d, J = 15.9 Hz, α-H), 8.78 (d, J = 15.9 Hz, β-H); other peaks same as cis ester.

Preparation of Dimethyl (*N*,*N*-Dimethyldithiocarbamato)fumarate, $(Me_2NCS_2)(CO_2Me)C{=}C(H)(CO_2Me)$. A solution of Me_2NCS_2Na and acetic acid (10 mmol each) in MeOH (10 mL) was added dropwise at 0 °C to a solution of DMAC (10 mmol) in MeOH (10 mL). Water (20 mL) was added and the yellow product (41.3%) filtered after 30 min. Recrystallization was accomplished by dissolving in ether (25 mL), filtering to remove any diadduct,[21] and adding hot hexane. Chilling gave yellow prisms (mp 88–9.5 °C) after several recrystallizations. Anal. Calcd for $C_9H_{13}NO_4S_2$: C, 41.05; H, 4.97; N, 5.32. Found: C, 40.91; H, 4.95; N, 5.33. NMR ($CDCl_3$): 3.58 (s, 6 H, $(CH_3)_2N$–), 3.89, 3.92 (s, 3 H each, CH_3O–), 7.18 (s, 1 H, =CH). The fumarate stereochemistry is assumed by analogy to the known trans addition of dithiocarbamate to propiolate (above) as well as the general rule of trans addition of nucleophilic sulfur to triple bonds.[22] No evidence for a second isomer was seen (NMR) in the crude reaction mixture.

Reaction of $OMo(S_2CNMe_2)_2(Ac)$ with Secondary Amines. A slurry of the adduct (1.0 g, Ac = DMAC) in CH_2Cl_2 (50 mL) was treated with gaseous Me_2NH (150 mL). After being stirred at room temperature for 16 h, the reaction mixture was evaporated to dryness under vacuum and the residue triturated with methanol. The resulting pink solid was isolated by filtration, washed with methanol, and dried in vacuo. The compound (0.63 g, 90% yield) was identified as $OMo(S_2CNMe_2)_2$ by its infrared spectrum.

The methanolic filtrate was evaporated and the gummy residue recrystallized successively from hexane–CH_2Cl_2 and MeOH–H_2O to yield colorless prisms, mp 80–2 °C, shown to be dimethyl 2-dimethylaminomaleate $(MeO_2C)(Me_2N)C{=}C(H)(CO_2Me)$ by comparison with a synthetic sample[23] (NMR, GLPC, and mixture melting point behavior). For quantitation, the reaction was repeated and followed by GLPC (160 °C). The maleate was formed in a yield of 0.91 mol/mol of Mo.

The reactions of $OMo(S_2CNMe_2)_2(Ac)$ (Ac = MP, DTA, HFB) with Et_2NH were monitored by following changes in the NMR spectra of reaction mixtures. For Ac = MP and DTA, the products were shown to be $OMo(S_2CNMe_2)_2$ and $R(Et_2N)C{=}C(H)R'$, with authentic samples of the latter compounds prepared in situ by addition of $NHEt_2$ to $RC{\equiv}CR'$. *No* reaction occurred between $HNEt_2$ and $OMo(S_2CNMe_2)_2(HFB)$.

Reactions of the Adducts with Methanol. $OMo(S_2CNMe_2)_2$-(DMAC). Methanol (0.05 mL) was added to a solution of the adduct (0.0306 g, 0.062 mmol) in CH_2Cl_2 (1.0 mL). After 2 h, GLPC analysis (135 °C) of the reaction mixture showed the apparent presence of $MeOC(S)NMe_2$ (0.055 mmol). A larger scale reaction provided sufficient product for separation by preparative GLPC and identification (NMR) by comparison with an authentic sample (65% yield) prepared by the method used by Harris[24,25] for the analogous ethyl compound. The product distilled at 54 °C (4 mm) (lit. bp 68 °C (10 mm). Attempts to identify the molybdenum- and acetylene-containing products of the reaction were unsucessful, yielding only ill-defined and apparently impure solids.

$OMo(S_2CNMe_2)_2(HFB)$. Similarly, the reaction of the adduct (0.264 g, 0.153 mmol) with methanol (1.0 mL) in 1,2-dichloroethane (4.0 mL) gave $MeOC(S)NMe_2$ (0.431 mmol) as determined by GLPC. Attempts to characterize the other reaction products were again unsuccessful.

$OMo(S_2CNMe_2)_2(MP)$. A large excess of methanol was added to a saturated solution of the adduct with Ac = MP in $CDCl_3$ and the changes in the NMR spectrum of the reaction mixture were monitored. After 2 h, the spectrum showed the presence of $MeOC(S)NMe_2$ and *trans*-$(MeCO_2)(H)C{=}C(H)(S_2CNMe_2)$ (see above) in a ~3:2 ratio. A similar experiment with Ac = DTA showed no spectral changes after 18 h at room temperature.

Determination of Equilibrium Constants. For $HC{\equiv}CPh$, 4 mL of a 10^{-3} M solution of $OMo(S_2CNR_2)_2$ (R = Me, Et) in dichloromethane was placed in a spectrophotometric cell under Ar and the initial visible spectrum recorded. The solution was then thermostated at 20 °C, 10-μL aliquots of $HC{\equiv}CPh$ were successively added, and the spectrum was recorded following each addition. The absorbance of the reaction mixture at 490 nm was measured for each [$HC{\equiv}CPh$] and the equilibrium constant (K_{eq}) was determined from the relationship previously used[15] for calculating K_{eq} for the binding of C_2H_2 (eq 1), where ϵ_{App} is the apparent molar absorptivity at 490 nm and

$$\epsilon_{App} = (\epsilon_1 - \epsilon_{App}/K_{eq}[HC{\equiv}CPh]) + \epsilon_2 \quad (1)$$

ϵ_1 and ϵ_2 are the molar absorptivities of $OMo(S_2CNR_2)_2$ and $OMo(S_2CNR_2)_2(HC{\equiv}CPh)$, respectively. The same method was used for $PhC{\equiv}CPh$, except that separate solutions of $OMo(S_2CNR_2)_2$ containing varying amounts of the acetylene were placed in the spectrophotometric cell. For determination of K_{eq} for the binding of DMAC to $OMo(S_2CNEt_2)_2$, a somewhat different procedure was employed. In this case, K_{eq} was so large that at [DMAC] = 5×10^{-2} M, *only* $OMo(S_2CNEt_2)_2$(DMAC) was present in solution, and its molar absorptivity at 490 mm (effectively zero) could be determined directly. The spectrum of a reaction mixture containing 2.52×10^{-4} M $OMo(S_2CNEt_2)_2$ and 3.96×10^{-4} M DMAC was then recorded, and, from the known molar absorptivity of $OMo(S_2CNEt_2)_2$, the equilibrium concentrations of the reactants and products (and thus K_{eq}) could easily be calculated. K_{eq} was found to be 22 000 ± 1000 M^{-1} for Ac = DMAC, 14 ± 1 M^{-1} for $PhC{\equiv}CPh$, 25 ± 1 M^{-1} for $PhC{\equiv}CH$, and 16 ± 1 M^{-1} for C_2H_2.

The equilibrium constant for the C_2H_2 adduct[15] was confirmed from a NMR study. $OMo(S_2CNEt_2)_2$ (0.248 g, 0.608 mmol) was dissolved in C_2H_2-saturated 1,2-dichloroethane (3 mL) and equilibrated at 35 °C, and the NMR spectrum was recorded. 1,2-Dichloroethane served the purpose of separating the methyl triplet signal of the ethyl groups of uncomplexed $OMo(S_2CNEt_2)_2$ from the same resonance of the 1:1 adduct, $OMo(S_2CNEt_2)_2(C_2H_2)$. Integration of these signals and the two singlets due to free and complexed C_2H_2 allowed the concentrations of free C_2H_2, free $OMo(S_2CNEt_2)_2$, and $OMo(S_2CNEt_2)_2(C_2H_2)$ to be calculated. Under these conditions, 44.2% of $OMo(S_2CNEt_2)_2$ was bound as the 1:1 adduct and K_{eq} was found to be 18 M^{-1}.

The equilibrium constants for the C_2R_2 complexes (with $R_2 = Ph_2$; H_2; Ph, H) determined herein agree very closely with those reported recently.[12]

Crystal Data. Suitable crystals of $OMo(S_2CNMe_2)_2DTA{\cdot}C_6H_6$ were obtained from benzene–ether solutions. They are monoclinic with a = 15.110(3) Å, b = 20.061 (5) Å, c = 11.518 (2) Å, β = 109.09 (2)°, V = 3297.2 Å, mol wt 692, d_{obsd} = 1.40 g/cm^3 for Z = 4, d_{calcd} = 1.394 g/cm^3, and $\mu \mp$ 6.67 cm^{-1}. Systematic absences for $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, indicate that the correct space group is $P2_1/c$.

The unit cell dimensions and their estimated standard deviations were obtained at room temperature (20 ± 2 °C) with Mo Kα radiation (λ = 0.709 26 Å) by using the method outlined by Busing for four-circle diffractometers.[26] The experimental density was measured in cyclohexane–bromoform mixtures.

Data Collection. A crystal was shaped to a rough cube of approximately 150 μm edge and sealed in a Lindemann glass capillary. All quantitative data were obtained from a Picker four-circle dif-

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(21) A diadduct was characterized also ($C_{12}H_{20}N_2O_4S_4$). The crude product was consistent with the presence of the two possible diastereoisomeric succinates. The dominant one (mp 134.5–135 °C dec) could be separated by crystallization from $CHCl_3$–EtOH.
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Table I. Fractional Coordinates and Anisotropic Temperature Factors for $OMo(S_2CNMe_2)_2DTA$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.16282 (2)	0.59279 (1)	0.73237 (3)	0.0287 (2)	0.0445 (2)	0.0408 (1)	0.0013 (1)	0.0119 (1)	−0.0032 (2)
O	0.1032 (2)	0.5715 (1)	0.5859 (2)	0.042 (1)	0.060 (2)	0.040 (1)	0.009 (1)	0.007 (1)	−0.006 (1)
S_1	0.22408 (8)	0.69860 (7)	0.6696 (1)	0.0530 (8)	0.0576 (8)	0.0719 (9)	−0.0023 (5)	0.0330 (7)	0.0058 (6)
S_2	0.08517 (8)	0.68726 (5)	0.7894 (1)	0.0471 (7)	0.0435 (6)	0.0631 (8)	0.0020 (5)	0.0273 (6)	−0.0015 (5)
S_3	0.30437 (7)	0.61680 (7)	0.9423 (1)	0.0349 (6)	0.0727 (8)	0.0510 (7)	−0.0017 (5)	0.0123 (5)	−0.0168 (6)
S_4	0.31767 (7)	0.54707 (7)	0.7286 (1)	0.0357 (6)	0.075 (1)	0.0491 (7)	0.0062 (5)	0.0169 (5)	−0.0102 (6)
O_2	0.2639 (2)	0.4325 (1)	0.9542 (2)	0.045 (1)	0.073 (2)	0.047 (2)	0.016 (1)	0.002 (1)	−0.005 (1)
O_3	0.0235 (2)	0.5764 (1)	0.9773 (2)	0.039 (1)	0.062 (2)	0.048 (2)	−0.002 (1)	0.012 (1)	−0.012 (1)
N_1	0.4668 (2)	0.5807 (2)	0.9177 (3)	0.031 (2)	0.094 (3)	0.061 (2)	0.003 (2)	0.009 (2)	−0.006 (2)
N_2	0.1434 (2)	0.8054 (2)	0.7316 (3)	0.055 (2)	0.043 (2)	0.064 (2)	−0.001 (2)	0.013 (2)	0.006 (2)
C_1	0.0862 (2)	0.5407 (2)	0.8288 (3)	0.027 (2)	0.044 (2)	0.041 (2)	−0.004 (2)	0.008 (1)	−0.003 (1)
C_2	0.1521 (2)	0.5029 (2)	0.8235 (4)	0.031 (2)	0.042 (2)	0.044 (2)	−0.002 (2)	0.007 (1)	−0.002 (2)
C_3	0.2035 (2)	0.4395 (2)	0.8550 (4)	0.029 (2)	0.054 (2)	0.040 (2)	0.004 (2)	0.011 (2)	0.001 (2)
C_4	0.1794 (2)	0.3858 (2)	0.7616 (3)	0.030 (2)	0.044 (2)	0.043 (2)	0.001 (1)	0.010 (1)	0.006 (1)
C_5	0.2189 (3)	0.3232 (2)	0.7923 (5)	0.055 (3)	0.059 (3)	0.056 (3)	0.017 (2)	0.002 (2)	0.005 (2)
C_6	0.1935 (4)	0.2714 (2)	0.7101 (5)	0.077 (4)	0.048 (3)	0.073 (4)	0.018 (3)	0.015 (3)	0.001 (3)
C_7	0.1296 (3)	0.2797 (2)	0.5955 (5)	0.058 (3)	0.051 (3)	0.061 (3)	−0.004 (2)	0.020 (2)	−0.007 (2)
C_8	0.0920 (3)	0.3427 (2)	0.5634 (4)	0.065 (3)	0.055 (3)	0.050 (3)	0.002 (2)	0.012 (2)	−0.002 (2)
C_9	0.1150 (3)	0.3945 (2)	0.6450 (4)	0.051 (2)	0.041 (3)	0.049 (2)	0.005 (2)	0.007 (2)	0.004 (2)
C_{10}	0.0983 (6)	0.2219 (4)	0.5083 (8)	0.116 (7)	0.067 (4)	0.086 (5)	0.001 (4)	0.022 (5)	−0.025 (4)
C_{11}	0.0073 (2)	0.5535 (2)	0.8745 (4)	0.037 (2)	0.036 (2)	0.042 (2)	0.002 (2)	0.014 (2)	0.003 (2)
C_{12}	−0.0891 (2)	0.5397 (2)	0.7925 (3)	0.030 (2)	0.037 (2)	0.043 (2)	0.007 (1)	0.014 (1)	−0.001 (1)
C_{13}	−0.1088 (3)	0.5236 (2)	0.6702 (4)	0.034 (2)	0.069 (3)	0.045 (2)	0.003 (2)	0.015 (2)	−0.006 (2)
C_{14}	−0.2003 (3)	0.5101 (2)	0.5985 (4)	0.047 (2)	0.088 (4)	0.045 (2)	−0.001 (2)	0.011 (2)	−0.019 (2)
C_{15}	−0.2729 (3)	0.5113 (2)	0.6470 (4)	0.029 (2)	0.077 (3)	0.060 (3)	0.002 (2)	0.007 (2)	−0.015 (2)
C_{16}	−0.2518 (3)	0.5269 (2)	0.7702 (5)	0.037 (2)	0.073 (3)	0.066 (3)	0.007 (2)	0.026 (2)	−0.009 (2)
C_{17}	−0.1614 (3)	0.5414 (2)	0.8417 (4)	0.041 (2)	0.068 (3)	0.043 (2)	0.004 (2)	0.016 (2)	−0.008 (2)
C_{18}	−0.3719 (4)	0.4945 (5)	0.5687 (7)	0.034 (3)	0.149 (7)	0.096 (5)	−0.013 (4)	0.013 (3)	−0.049 (5)
C_{19}	0.3740 (2)	0.5814 (2)	0.8703 (4)	0.035 (2)	0.059 (3)	0.052 (2)	0.001 (2)	0.013 (2)	0.000 (2)
C_{20}	0.5158 (4)	0.6125 (4)	0.0357 (7)	0.037 (3)	0.126 (6)	0.083 (5)	−0.003 (3)	0.000 (3)	−0.011 (4)
C_{21}	0.5252 (4)	0.5535 (4)	0.8494 (7)	0.044 (3)	0.152 (8)	0.084 (5)	0.023 (4)	0.029 (3)	0.003 (4)
C_{22}	0.1496 (3)	0.7404 (2)	0.7296 (4)	0.048 (2)	0.048 (2)	0.051 (2)	−0.001 (2)	0.012 (2)	0.002 (2)
C_{23}	0.2006 (5)	0.8488 (3)	0.6818 (6)	0.073 (4)	0.061 (4)	0.093 (5)	−0.012 (3)	0.023 (4)	0.027 (3)
C_{24}	0.0807 (5)	0.8392 (3)	0.7872 (8)	0.087 (5)	0.052 (4)	0.115 (6)	0.009 (3)	0.037 (4)	−0.015 (4)
C_{25}	0.3766 (7)	0.3207 (5)	0.513 (1)	0.102 (8)	0.128 (8)	0.22 (1)	−0.023 (6)	0.011 (9)	−0.002 (9)
C_{26}	0.434 (1)	0.2999 (6)	0.632 (1)	0.14 (1)	0.22 (1)	0.14 (1)	−0.02 (1)	0.028 (9)	0.011 (8)
C_{27}	0.5272 (9)	0.2859 (6)	0.652 (1)	0.12 (1)	0.19 (1)	0.18 (1)	−0.016 (9)	0.010 (9)	0.018 (9)
C_{28}	0.5656 (7)	0.2908 (7)	0.560 (1)	0.125 (9)	0.115 (7)	0.18 (1)	−0.003 (6)	0.026 (9)	−0.001 (7)
C_{29}	0.510 (1)	0.3117 (5)	0.443 (1)	0.17 (1)	0.106 (7)	0.128 (8)	−0.028 (7)	0.016 (8)	−0.014 (6)
C_{30}	0.417 (1)	0.3246 (5)	0.421 (1)	0.14 (1)	0.123 (8)	0.16 (1)	−0.029 (8)	−0.020 (8)	0.028 (7)

	x	y	z	U, Å^2		x	y	z	U, Å^2
HC_5	0.255 (4)	0.324 (3)	0.858 (5)	0.07	H_3C_{18}	−0.385 (6)	0.457 (4)	0.593 (8)	0.12
HC_6	0.215 (5)	0.236 (3)	0.724 (6)	0.08	H_1C_{20}	0.543 (5)	0.651 (4)	0.014 (7)	0.11
HC_8	0.052 (4)	0.350 (3)	0.487 (5)	0.07	H_2C_{20}	0.567 (6)	0.590 (4)	0.072 (7)	0.11
HC_9	0.089 (4)	0.434 (2)	0.626 (5)	0.05	H_3C_{20}	0.485 (5)	0.619 (4)	0.078 (8)	0.11
H_1C_{10}	0.100 (7)	0.233 (4)	0.433 (8)	0.12	H_1C_{21}	0.527 (6)	0.579 (4)	0.806 (9)	0.12
H_2C_{10}	0.051 (6)	0.216 (5)	0.48 (1)	0.12	H_2C_{21}	0.501 (6)	0.521 (4)	0.792 (7)	0.12
H_3C_{10}	0.133 (6)	0.187 (4)	0.527 (8)	0.12	H_3C_{21}	0.573 (5)	0.523 (4)	0.901 (7)	0.12
HC_{13}	−0.062 (4)	0.523 (2)	0.635 (5)	0.06	H_1C_{23}	0.198 (5)	0.831 (3)	0.610 (6)	0.09
HC_{14}	−0.206 (4)	0.508 (3)	0.517 (5)	0.07	H_2C_{23}	0.260 (5)	0.852 (3)	0.718 (6)	0.09
HC_{16}	−0.300 (4)	0.531 (2)	0.802 (5)	0.06	H_3C_{23}	0.174 (5)	0.889 (3)	0.656 (7)	0.09
HC_{17}	−0.145 (4)	0.548 (2)	0.919 (5)	0.05	H_1C_{24}	0.048 (5)	0.809 (4)	0.795 (7)	0.10
H_1C_{18}	−0.392 (7)	0.490 (5)	0.495 (8)	0.12	H_2C_{24}	0.046 (6)	0.862 (4)	0.750 (8)	0.10
H_2C_{18}	−0.420 (6)	0.522 (4)	0.586 (7)	0.12	H_3C_{24}	0.121 (5)	0.865 (3)	0.864 (7)	0.10

fractometer controlled by a PDP-81 computer, using graphite-monochromated Mo Kα radiation.

Intensity data were collected by use of the θ–2θ scan technique with a scan range of 1.6° and a scan rate of 2°/min. Stationary background counts (20 s) were recorded at each end of the scan. Attenuators were used whenever the scan count exceeded 7000 counts/s. The intensities of three standard reflections were monitored throughout data collection at intervals of 75 measurements and showed no appreciable decomposition of the sample. A standard deviation was assigned to each measured intensity by using the expression

$$\sigma(I) = |C + (t_c/t_b)^2 (B_1 + B_2) + (pI)^2|^{1/2}$$

where C is the scan count, B_1 and B_2 are background counts, t_c and t_b are respectively scan and background times, and p is an empirical coefficient of the net count I.[27] The factor p was given a value of 0.05. A total of 7724 independent reflections were recorded in the range $6° < 2\theta < 60°$; 3372 of these had $\sigma(I)/I$ less than 0.33 and were retained. No absorption corrections were applied in view of the small crystal dimensions and linear absorption coefficient.

Structure Solution and Refinement. The molybdenum and four sulfur atom positions were readily located in a three-dimensional Patterson map. A Fourier map computed with these revealed the positions of all other atoms and a benzene molecule of solvation.

In all structure factor calculations, the atomic scattering factors tabulated by Moore for neutral atoms by using Pepinsky's development were used.[28] The effects of anomalous dispersion were included for molybdenum and sulfur atoms; the values of $\Delta f'$ and $\Delta f''$ are those listed in the ref 29. Atomic coordinates and individual anisotropic thermal parameters were refined by full-matrix least squares using the program SFLS-5.[30] In all least-squares computations, the function

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Table II. Geometrical Data for $OMo(S_2CNMe_2)_2DTA \cdot C_6H_6$

(a) Bond Lengths (Å)

(i) Metal Environment

Mo-O	1.686 (2)	Mo-S_4	2.525 (1)
Mo-S_1	2.514 (1)	Mo-C_1	2.122 (4)
Mo-S_2	2.429 (1)	Mo-C_2	2.119 (4)
Mo-S_3	2.696 (1)	C_1-C_2	1.267 (6)

(ii) Dithiocarbamato Ligands

S_1-C_{22}	1.719 (5)	S_3-C_{18}	1.694 (5)
S_2-C_{22}	1.731 (5)	S_4-C_{19}	1.719 (4)
C_{22}-N_2	1.307 (6)	C_{19}-N_1	1.327 (5)
N_2-C_{23}	1.469 (6)	N_1-C_{20}	1.464 (8)
N_2-C_{24}	1.470 (10)	N_1-C_{21}	1.466 (10)

(iii) DTA Ligand

C_1-C_{11}	1.475 (6)	C_2-C_3	1.472 (6)
C_{11}-C_9	1.218 (5)	C_3-O_2	1.215 (4)
C_{11}-C_{12}	1.479 (5)	C_3-C_4	1.481 (6)
C_{12}-C_{13}	1.380 (6)	C_4-C_5	1.387 (7)
C_{13}-C_{14}	1.385 (6)	C_5-C_6	1.372 (8)
C_{14}-C_{15}	1.383 (8)	C_6-C_7	1.367 (7)
C_{15}-C_{16}	1.385 (7)	C_7-C_8	1.386 (7)
C_{16}-C_{17}	1.375 (6)	C_8-C_9	1.368 (7)
C_{17}-C_{12}	1.385 (7)	C_9-C_4	1.388 (5)
C_{15}-C_{18}	1.510 (7)	C_7-C_{10}	1.505 (9)

(iv) Average C-C in C_6H_6: 1.39 ± 0.03

(b) Selected Bond Angles (Deg)

O-Mo-C_1	101.2 (2)	S_1-Mo-S_4	82.6 (1)
O-Mo-C_2	101.2 (2)	S_1-Mo-S_3	81.3 (1)
C_1-Mo-C_2	34.8 (1)	S_2-Mo-S_3	86.0 (1)
O-Mo-S_1	93.0 (1)	S_4-Mo-S_3	67.3 (1)
O-Mo-S_2	108.7 (2)	C_1-Mo-S_3	91.5 (1)
O-Mo-S_3	161.7 (2)	C_2-Mo-S_3	82.8 (1)
O-Mo-S_4	94.9 (1)	C_1-Mo-S_2	81.3 (1)
S_1-Mo-S_2	71.0 (1)	C_2-Mo-S_4	85.5 (1)
Mo-C_1-C_{11}	138.0 (1)	Mo-C_2-C_3	137.5 (1)
C_2-C_1-C_{11}	149.3 (4)	C_1-C_2-C_3	149.7 (4)

minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors. The weight w was taken as $1/\sigma^2(F_o)$. The refinement converges to a discrepancy factor $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ equal to 0.048 and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ equal to 0.060. Introduction of the hydrogen atoms at this stage and further refinement yields $R_1 = 0.039$ and $R_2 = 0.046$. The standard deviation of a unit weight observation is 1.09. A final Fourier map showed important residual peaks still persisted between bonded atoms (as much as 0.6 e/Å^3). No other important residuals were observed. Final positional and thermal parameters are assembled in Table I. A listing of observed and computed structure factors is available.[31] Geometrical data determined herein are listed in Tables II and III. The figure was drawn by using C. K. Johnson's ORTEP.[32]

Results

Preparations. We have extended our previous report[6] of the reaction of $OMo(S_2CNMe_2)_2$ with DMAC to give the 1:1 complex $OMo(S_2CNMe_2)_2(DMAC)$ to include the analogous *N,N*-diethyldithiocarbamato complex and three additional activated acetylenes (eq 2). We also find that $OMo(S_2CNR_2)_2$ will bind acetylene itself,[15] a known substrate of nitrogenase,[33] by observation of visible spectral changes of solutions of $OMo(S_2CNR_2)_2$ on exposure to acetylene atmospheres. These visible spectral changes are reversible, and on replacement of the acetylene atmosphere by argon, the original spectrum of $OMo(S_2CNR_2)_2$ is produced. This equilibrium has prevented us from isolating a pure sample of the 1:1 acetylene complex, which has, however, been characterized spectroscopically (see Table IV). Similar binding of phenylacetylene and diphenylacetylene is also observed.

$$OMo(S_2CNR_2)_2 + Ac \rightarrow OMo(S_2CNR_2)_2(Ac) \quad (2)$$

$$R = Me, Et$$

$$Ac = MeO_2CC{\equiv}CCO_2Me \quad (DMAC)$$
$$= HC{\equiv}CCO_2Me \quad (MP)$$
$$= F_3CC{\equiv}CCF_3 \quad (HFB)$$
$$= MeC_6H_5COC{\equiv}CCOC_6H_5Me \quad (DTA)$$

Infrared Spectra. Important bands in the infrared spectra of the complexes $OMo(S_2CNR_2)_2(Ac)$ are found in Table IV. The spectra contain medium intensity bands at 1790–1900 cm^{-1}, which are assigned to the carbon–carbon stretch of the coordinated acetylene and strong bands at ~930 cm^{-1}, which are assigned to the Mo=O stretch. For the MP complexes, the carbon–hydrogen stretching frequency of the coordinated acetylene is observed at 3090 cm^{-1}.

NMR Spectra. The ambient-temperature NMR spectra (Table IV) of the adducts $OMo(S_2CNMe_2)_2(Ac)$ in $CDCl_3$ all contain resonances of varying broadness at ~3.4 ppm assigned to the dithiocarbamate (dtc) methyl groups. Similarly, the spectra of $OMo(S_2CNEt_2)_2(Ac)$ contain varyingly broad triplets at ~1.3 ppm (methyl) and broad multiplets at ~3.8 ppm (methylene) due to the dithiocarbamate ethyl groups. The shape of these dtc resonances is temperature dependent (vide infra), while the sharpest signals are exhibited by the acetylene complex; those of the MP adducts are only slightly broader. The DMAC and DTA complexes show significant broadening and partial resolution of these dtc resonances, while the HFB complex shows distinct separation of the methyl resonance of both ligand types into two broad signals with a relative intensity of 3:1. In addition, the spectra of $OMo(S_2CNR_2)_2(DTA)$ contain a single resonance at ~2.4 ppm, which is assigned to the protons of the *p*-methyl group of coordinated DTA, and an A_2B_2 pattern centered at ~7.5 ppm due to the phenyl protons of DTA. The spectra of $OMo(S_2CNR_2)_2(DMAC)$ contain a single resonance at ~4.0 ppm assigned to the protons of the ester methyl group of DMAC, which for R = Et overlaps with the resonance of the methylene protons of the dithiocarbamate ethyl groups. The spectra of $OMo(S_2CNR_2)_2(MP)$ have resonances at ~3.9 and ~8.8 ppm due to the acetylene methyl protons (which overlap with the methylene resonances for R = Et) and terminal protons, respectively. A single resonance is observed for the terminal acetylenic protons of $OMo(S_2CNEt_2)_2(C_2H_2)$ at 8.73 ppm. The ^{19}F spectrum of $OMo(S_2CNMe_2)(HFB)$ shows two equivalent CF_3 resonances at 53.7 and 54.9 ppm relative to $CFCl_3$ (as an external reference) in CH_2Cl_2 solution. The observation of two CF_3 resonances is indicative of stereochemical rigidity of the acetylene group on the NMR time scale at +35 °C and of asymmetry in the molecule as a whole. The integrated intensities of all resonances support the proposed formulation of the complexes. Although overlap of the acetylenic methyl ester resonances and those of the methylene protons of the ethyl dithiocarbamates always occurs, integration over this whole region supports the 1:1 nature of the complexes.

Variable-Temperature NMR Spectrometry. The complexes $OMo(S_2CNR_2)_2(Ac)$ (Ac = HFB, DMAC, and MP) hydrolyze rapidly (vide infra), while the complexes with Ac = DTA are very stable hydrolytically. Thus, the complexes containing this last acetylene were selected for the initial variable-temperature NMR study.

As a deuteriochloroform solution of $OMo(S_2CNMe_2)_2(DTA)$ is warmed above the ambient probe temperature (~34 °C), the only noticeable change occurs with the two broad, poorly resolved methyl resonances of the dithiocarbamate

(31) See supplementary material.
(32) C. K. Johnson, Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(33) R. Scholhorn and R. H. Burris, *Proc. Natl. Acad. Sci. U.S.A.*, **58**, 213 (1967); M. J. Dilworth, *Biochim. Biophys. Acta*, **127**, 285 (1966).

Table III. Least-Squares Planes and Some Selected Angles

plane	atoms defining the plane	eq: $Ax + By + Cz - D = 0$ A	B	C	D	selected distances from the plane, Å
1	S_1, S_2, S_4, C_{11}, C_2	−0.3618	−0.2721	−0.8901	−10.7825	Mo 0.500 (1)
2	Mo, C_1, C_2	−0.3349	−0.3813	−0.8617	−11.3031	O_1 1.656 (4), O_2 −1.096 (4), O_3 −1.157 (4), C_3 −0.027 (6), C_{11} −0.065 (6)
3	C_1, C_{11}, C_{12}, O_3	0.0489	0.9302	−0.3639	6.7169	
4	C_2, C_3, C_4, O_2	0.8576	0.3464	−0.3802	−0.6071	
5	C_{12}–C_{18}	−0.0812	0.9672	−0.2406	8.7498	
6	C_4–C_{10}	0.9049	0.2315	−0.3571	−1.2943	
7	MoO line	0.2078	0.2559	0.9477		

plane	angle, deg	plane	angle, deg	plane	angle, deg	plane	angle, deg
2–3	93.3	3–5	10.5	2–5	97.7	5–6	76.3
2–4	95.3	4–6	7.3	2–6	94.8	2–7	100.3

Table IV. Infrared and ^{1}H NMR Spectra of the Complexes $OMo(S_2CNR_2)_2(Ac)$

compd	IR[a,b] ν(Mo=O)	ν(C=C)	ν(C=O)	NMR[c] δ(AcR)	δ(AcH)	δ(NCH_3)	δ(NC_2H_5)
$OMo(S_2CNMe_2)_2$(DMAC)	940	1870	1720	3.97 (s)		3.2 (u), 3.5 (u)	
$OMo(S_2CNEt_2)_2$(DMAC)	925	1850	1715	3.87 (s)			1.34 (u, t), ~3.8 (u, m)
$OMo(S_2CNMe_2)_2$(MP)	920	1795	1700	3.92 (s, 3)	8.78 (s, 1)	3.40 (s, 12)	
$OMo(S_2CNEt_2)_2$(MP)	925	1790	1700	3.93 (s)	8.88 (s, 1)		1.30 (u, t, 12), 3.85 (u, q)
$OMo(S_2CNMe_2)_2$(HFB)	940	1850		53.7 (s, 1), 54.9 (s, 1)[d]		3.18 (s, 1), 3.51 (s, 3)	
$OMo(S_2CNEt_2)_2$(HFB)	950	1855					1.13 (t), 1.38 (t), ~3.9 (u, m)
$OMo(S_2CNMe_2)_2$(DTA)	920	1815	1645	7.52 (m, 4), 2.37 (s, 3)		3.08 (u), 3.22 (u)	
$OMo(S_2CNEt_2)_2$(DTA)	935	1835	1660	7.60 (m, 4), 2.38 (s, 3)			~1.2 (u, t, 6), ~3.8 (u, m, 4)
$OMo(S_2CNEt_2)_2(C_2H_2)$	935[e]	1684[e]			8.73 (s)[f]		~1.32 (t, 6),[f] ~3.86 (q, 4)

[a] KBr pellets. [b] Frequencies in cm^{-1}. [c] Ppm downfield from Me_4Si in deuteriochloroform solution at 35 °C. Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; u, poorly or unresolved. AcR refers to the methyl resonances of DMAC and MP or both the center of the phenyl A_2B_2 pattern and the para methyl protons of DTA or the ^{19}F resonances of the CF_3 groups of HFB, AcH is the terminal proton resonance of MP and C_2H_2, NCH_3 lists the methyl dithiocarbamate resonances, and NC_2H_5 refers to the ethyl dithiocarbamate resonances. Integrated intensities are in parentheses also. [d] Ppm from $CFCl_3$ (external reference) in CH_2Cl_2 solution. [e] CH_2Cl_2 solution. [f] CD_2Cl_2 solution.

ligands at δ ~3.4. At +40 °C, they coalesce completely. As the temperature is further increased, a single resonance grows in until, at +62 °C, a sharp singlet at δ 3.26 is observed with an integrated intensity twice that of the methyl resonance of DTA at δ 2.37. The new resonance obviously accounts for all four methyl groups of the dithiocarbamate. On cooling of the solution to +14 °C, the spectrum consists of three sharp singlets for the dithiocarbamate methyl groups at δ 3.40, 3.25, and 3.01 with intensities 2:1:1. No change is observed for the A_2B_2 pattern of the phenyl protons nor for the methyl protons of the DTA ligand in this temperature range. On cooling of the solution to −50 °C, still no broadening of the DTA resonances is apparent and no further change in the dithiocarbamate resonances was observed. The ambient-temperature spectrum at the end of the variable temperature study shows that no decomposition had occurred under these conditions.

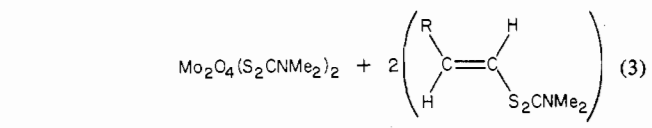
A similar study of $OMo(S_2CNEt_2)_2$(DTA) indicates that, on warming of the deuteriochloroform solution to +60 °C, the broad, poorly resolved methyl and methylene proton resonances of the dithiocarbamate ligands are the only signals to change. The methyl proton resonance sharpens to a single triplet at δ 1.21 and the methylene resonance to a single, sharp quartet at δ 3.76. Integration of these signals gives 6:4:3 relative intensities for (dtc methyl):(dtc methylene):(DTA methyl). Cooling results in the differentiation of both dithiocarbamate signals with a coalescence temperature of +27 °C. At +14 °C, three poorly resolved, overlapping methyl triplets and two poorly resolved, overlapping quartets are visible. At −2 °C, these methyl and methylene resonances are fully resolved into four sharp overlapping triplets centered at δ 1.33, 1.30, 1.18, and 1.00 and four overlapping quartets centered at δ 3.93, 3.88, 3.80, and 3.50. Further cooling to −50 °C produces no other changes in the spectrum. At no temperature did the DTA methyl proton singlet and the phenyl proton A_2B_2 pattern broaden or change in any way. The complex did not decompose or undergo any irreversible change during this study as judged by its ambient-temperature spectrum at the end of the run.

When a $CDCl_3$ solution of the complex $OMo(S_2CNMe_2)_2$(DMAC) is warmed to +50 °C, the broad weaker resonance of the dithiocarbamate methyl protons at δ 3.2 broadens further and coalesces with the stronger dtc signal originally at δ 3.5. This single resonance (at δ 3.45) then continues to sharpen even at the maximum temperature of +60 °C used in this study. At +25 °C, the two dithiocarbamate signals (at δ 3.2 and 3.5) integrate as 1:3. Cooling to +19 °C produces splitting in the more intense δ 3.5 signal as a shoulder at δ 3.57 appears. All three signals at δ 3.57, 3.50, and 3.20 sharpen to their maximum at +8 °C and integrate as 1:2:1, respectively. No other changes occur in these signals on further cooling. However, on cooling of the solution below +13 °C, the singlet at δ 3.97 due to the methyl protons of the methoxycarbonyl group of the acetylene broadens significantly until at −3 °C, a shoulder becomes obvious. Further cooling to −42 °C gives two equally intense singlets at δ 3.97 and 4.00. All changes are cleanly reversed on warming to ambient temperature.

Equilibrium Measurements. Complex formation between $OMo(S_2CNR_2)_2$ and C_2H_2, HC≡CPh, PhC≡CPh, MP, and DMAC are reversible as judged by visible spectral changes at 490 nm on addition of acetylene to a dichloromethane solution of $OMo(S_2CNR_2)_2$. The equilibrium constants measured vary over a range of three orders of magnitude from ~20 000 M^{-1} for DMAC to ~20 M^{-1} for C_2H_2. Strict observance of eq 1 indicates the formation of 1:1 adducts, which was confirmed by the isolation of eight such adducts. No attempt was made to test the reversibility of these reactions involving HFB, but reactivity studies (vide infra) provide some

indication that this adduct may not dissociate.

Reactivity of Adducts with Water. In air, $OMo(S_2CNMe_2)_2(MP)$ undergoes an oxygen-sensitive hydrolysis according to eq 3. Both products are isolated in essentially



$$2OMo(S_2CNMe_2)_2(RC_2H) + \tfrac{1}{2}O_2 + H_2O \rightarrow Mo_2O_4(S_2CNMe_2)_2 + 2\begin{pmatrix} R & & H \\ & C{=}C & \\ H & & S_2CNMe_2 \end{pmatrix} \quad (3)$$

quantitative yield. The same molybdenum-containing product is also obtained for the very rapid hydrolyses with Ac = DMAC and HFB, but no corresponding trans (or cis) olefins are observed in these cases. The fate of the acetylene moiety in these reactions is unknown.

When these hydrolyses are attempted anaerobically in acetone–water with Ac = MP and R = Me or Et, the major metal-containing product is slightly impure $OMo(S_2CNR_2)_2$ (50–70% yield) with *trans*-$(R_2NCS_2)HC{=}CH(CO_2Me)$ being formed in 52% yield. Similar experiments in ethanol-free chloroform gives similar yields of the trans olefin, but instead of the oxomolybdenum(IV) complex, equivalent yields of the appropriate oxomolybdenum(V) dimer, $Mo_2O_4(S_2CNR_2)_2$ (as produced aerobically), are isolated. The adduct with Ac = DMAC gives no olefins in either solvent system, and the metal-containing fractions are mixtures of products still containing ester groups together with some $Mo_2O_4(S_2CNMe_2)_2$.

With Secondary Amines. The complexes $OMo(S_2CNR_2)_2(Ac)$ (R = Me, Et; Ac = MP, DMAC, DTA) react with secondary amines as in eq 4. The stereochemistry of

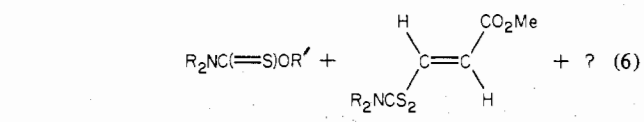
$$OMo(S_2CNR_2)_2(RC_2R) + R'_2NH \rightarrow OMo(S_2CNR_2)_2 + R(R'_2N)C{=}C(H)R \quad (4)$$

the olefinic products corresponds to cis addition of the amine to the coordinated acetylene. In contrast, no reaction takes place between the HFB adduct and secondary amines under these same conditions.

With Alcohols. Reactions of the HFB and DMAC adducts with alcohol proceed as in eq 5 No molybdenum-containing

$$OMo(S_2CNR_2)_2(Ac) + R'OH \rightarrow R_2NC(=S)OR' \quad (5)$$
$$Ac = HFB, DMAC$$

product could be identified in these reaction mixtures. The reaction of the MP adduct with methanol (eq 6) is more



$$OMo(S_2CNR_2)_2(HC{\equiv}CCO_2Me) + R'OH \rightarrow R_2NC(=S)OR' + \begin{matrix} H & & CO_2Me \\ & C{=}C & \\ R_2NCS_2 & & H \end{matrix} + ? \quad (6)$$

complicated because not only are the dithiocarbamate ligands incorporated into thiourethane (as in eq 4) but they also add across to the acetylene to form an olefin (as in eq 3). No molybdenum-containing product(s) could be isolated from these reaction mixtures.

No reaction occurs between the DTA adducts and alcohols, consistent with their very low susceptibility to hydrolysis.

Structure of $OMo(S_2CNMe_2)_2(DTA)$. The geometry of the complex and numbering of main atoms are shown in Figure 1. The environment of the metal is a deformed pentagonal bipyramid with an apex defined by the oxygen atom O_1. The other apex is define by sulfur atom S_3. The O–Mo–S_3 angle (161.7 (2)°) deviates considerably from 180°, probably due to the short bite of the dithiocarbamate ligand. The atoms defining the plane are indicated by open shaded ellipsoids. It is readily seen that the carbon–carbon multiple bond (1.27 Å) sits in the equatorial plane of the bipyramid and lies perpendicular to the Mo–O bond (1.69 Å). The molybdenum carbon distance is a short 2.12 Å. As usual, the molybdenum atom

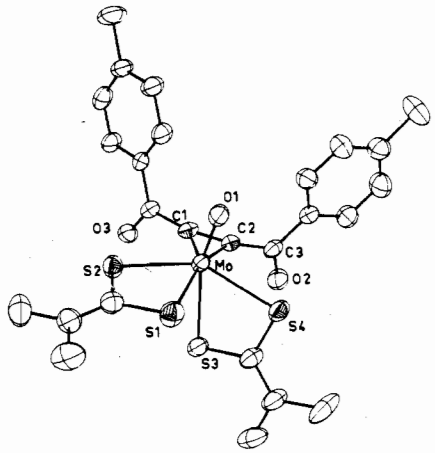


Figure 1. Perspective view of $OMo(S_2CNMe_2)_2DTA$ and numbering of main atoms. See Table III for bond lengths and selected bond angles.

is displaced above the plane by about 0.5 Å. The geometry of the acetylene ligand is similar to that usually observed,[34] the two substituents are bent away from the metal and the acetylenic carbons can be regarded as having sp^2 character. The average angle to the head carbon of the substituents is 149.5 (2)°. Selected bond lengths and angles are collected in Table II.

Interestingly, both carbonyl groups of DTA lie away from the metal oxo group and below the plane of the bipyramid. The mean planes containing one acetylenic carbon, the vicinal carbonyl group and the head carbon of the toluoyl group make an angle of 59.8 (5)°. This plane is not copolanar with the aromatic rings but slightly twisted by 9.6 ± 1.6°. The mean planes of the aromatic rings make an angle of 76.3° with respect to one another. The angles between the MoC_1C_2 plane and the various above-mentioned planes are on the order of 95 ± 2° (see Table III).

The structure of the related compound $OMo(S_2CNEt_2)_2(PhC{\equiv}Ph)$ has also recently been determined by X-ray techniques.[35] The basic geometry around the molybdenum atom is virtually identical with that found for $OMo(S_2CNEt_2)_2(DTA)$, but a disorder problem has prevented the satisfactory refinement of this structure.

Discussion

Previously,[6] the reaction of $OMo(S_2CNMe_2)_2$ with DMAC was reported to give the 1:1 adduct $OMo(S_2CNMe_2)_2(DMAC)$ and, on the basis of spectral data, was postulated to involve oxidative addition to form a Mo(VI) species. A similar reaction occurs not only with other similarly activated acetylenes but also with phenyl-substituted acetylenes and the parent compound, acetylene itself.[12,15] Virtually all the reactions are equilibria. The latter group of acetylenes bind much more weakly than the activated acetylenes, so much so that pure adducts are not easily isolated. A recent report,[12] however, describes the successful isolation of $OMo(S_2CNR_2)_2(Ac)$ (Ac = PhC_2Ph, PhC_2H), although pure $OMo(S_2CNR_2)_2(C_2H_2)$ is still known only in solution. The activated acetylenes associate more strongly with $OMo(S_2CNR_2)_2$ as reflected by their considerably larger equilibrium constants. This is very likely the result of the increased electron back-donation from metal d orbitals of molybdenum(IV) into the acetylenic π^* orbitals due to the electron-withdrawing effect of carboxylate or trifluoromethyl groups.

The infrared spectra of these complexes show the carbon–carbon stretch of the coordinated acetylenes to be ~350 cm^{-1}

(34) S. Otsuka and A. Nakamura, *Adv. Organomet. Chem.*, **14**, 245 (1976), and references therein.
(35) R. A. D. Wentworth and E. A. Maatta, private communication.

lower than that of the free acetylenes, reflecting a significant weakening of the triple bond. The frequency of the Mo=O stretch in the adduct is ~30 cm^{-1} lower than that of $OMo(S_2CNR_2)_2$ and is consistent with an effective increase in the oxidation state and coordination number of molybdenum. The Mo=O stretch in the heptacoordinate Mo(VI) complex $OMoCl_2(S_2CNR_2)_2$, for example, appears[36] at 945 cm^{-1}. The frequencies of the carbon–carbon and molybdenum–oxygen stretches in $OMo(S_2CNR_2)_2(Ac)$ allow them to be simplistically described as complexes of Mo(VI) formed by oxidative addition of the acetylenic bond to Mo(IV). The observation of a carbon–carbon stretch contrasts with its absence in the IR spectra of the related complexes $Mo(CO)_n(C_2R_2)_{2-n}(S_2CNR'_2)_2$ (R = H, Ph; n = 0, 1).[1,44] These observations are discussed below in the context of the molybdenum–acetylene bond order in these two types of complexes.

The structure of $OMo(S_2CNMe_2)_2(DTA)$ also conforms to this description. It has the the carbon–carbon multiple bond in the equatorial plane of a pentagonal bipyramid and located perpendicular to the axial metal–oxygen bond, which is a common feature of alkene or alkyne complexes of molybdenum and tungsten. This arrangement was previously observed in $OMo(S_2CNPr_2)_2TCNE$,[37] $CpMoO(SC_6F_5)(CF_3C_2CF_3)$,[38] and $CpWO(\sigma\text{-}C_6H_5)(H_5C_6C_2C_6H_5)$.[39] For the complex to reach an 18-electron configuration, the acetylene must donate two electrons to the metal and a metal–oxygen triple bond has to be (reasonably) assumed. The usual molybdenum–carbon bond length is on the order of 2.38 Å.[40] The observed values (2.12 Å) thus look rather short, even if one allows for the sp^2 character of the chelated acetylenic carbons. They are even shorter than those found in the analogous TCNE complex where an average of 2.285 Å was found.[37] The geometrical features of the molecule give some indications regarding the origin of this shortening. The Mo–O bond length in the complex (1.686 (2) Å) is longer than in $OMo(S_2CNPr_2)_2$ (1.66 Å) and is approximately the same as in *cis*-dioxobis(dithiocarbamato)molybdenum(VI) (1.695 (5) Å).[41,42] The Mo–O bond order of the complex should then be less than 3 (~2.5).[43] Similarly, the O–Mo–O angle in the dioxo complex (105.7 (1)°) is very close to the angle between the Mo–O bond direction and the MoCC plane (101.3 (3)°). An argument similar to that invoked for the dioxo complex[43] can thus be used to account for the observed geometry of the acetylene complex, namely, some competition between an oxygen pπ orbital and a π-bonding orbital of the acetylene for donation to an empty dπ metal orbital.

The present complex can be regarded as having C_s virtual symmetry. If the axes are oriented as in Figure 2, with the Mo–O bond along the z axis and the symmetry plane perpendicular to the x axis, the s, p_y, p_z, d_{z^2}, $d_{x^2-y^2}$, and d_{yz} metal orbitals will have a′ representation. The acetylenic bond is located perpendicular to the molecular plane, so that the two π-bonding orbitals have a′ symmetry and the two π-antibonding orbitals a″ symmetry. The oxygen pπ orbitals will

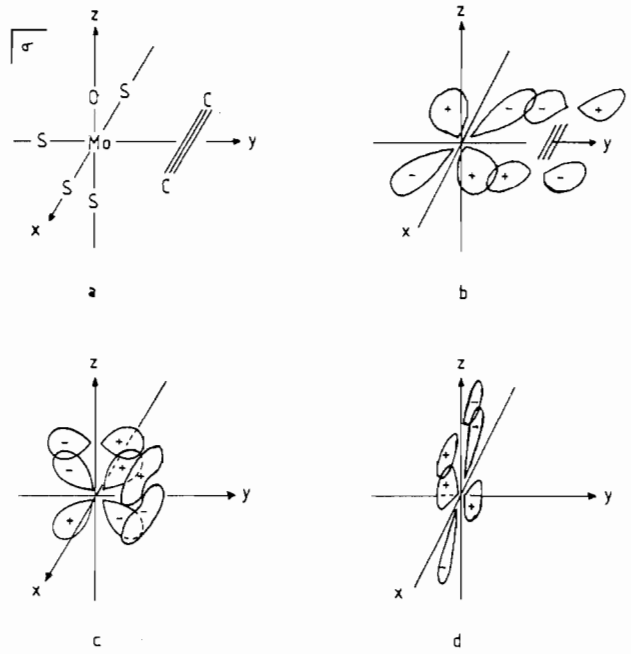


Figure 2. Schematic representation of the overlap between the metal dπ and ligand orbitals: (a) molecular coordinates used; (b) overlap between filled metal d_{xy} and vacant acetylene π^*_{xy}; (c) overlap of vacant metal d_{yz} with both the filled acetylene π_{xz} and the filled oxygen $2p_y$; (d) overlap between vacant metal d_{xz} and filled oxygen $2p_x$.

have a′ + a″ representation. It is therefore possible for the oxygen atom to interact with the d_{xz} orbital to form a π bond, and the filled d_{xy} orbital can be used for back-bonding to a π^* acetylene orbital. The second oxygen pπ orbital and the acetylene π orbitals have the same symmetry as the remaining d_{yz} orbital. Consequently, both ligands can donate electrons into the d_{yz} orbital. Compared with the $OMo(S_2CNR_2)_2$ starting material,[41] where the second oxygen pπ orbital has no competition for this metal d_{yz} orbital, a substantial increase in the molybdenum–oxygen distance should, and does, result (1.66 to 1.69 Å). This competition thus weakens the Mo–O bond and strengthens the metal–acetylene bond. The competition between the oxygen and acetylene ligands for the same orbitals would also explain the deviation of the O–Mo–CC angle from 90° and, at least in part, the shorter Mo–C bond lengths. These considerations support the structural comparison with *cis*-$MoO_2(dtc)_2$ and imply that the metal–acetylene bond order is larger than 1 and the metal–oxygen bond order is ~2.5 in this and similar oxoacetylene complexes.

A comparison with the structural parameters of the related complexes, $W(CO)(C_2H_2)(S_2CNR_2)_2$[1] and $Mo(C_5H_5)X(SC_6F_5)(F_3CC_2CF_3)$ (X = O, CO),[38] shows that the acetylene C–C bond lengths vary only slightly (1.28 ± 0.02 Å). In contrast, a significant difference exists in the Mo–C bond lengths to acetylene for the carbonyl complexes (2.03 ± 0.2 Å) compared with the oxo complexes (2.11 ± 0.02 Å). This difference, together with other spectral measurements, was used as the basis for suggesting a Mo–acetylene bond order of close to 2 for the carbonyl complexes and about 1 for the oxo complexes.[1] The present determination supports this contention.

The NMR spectra $OMo(S_2CNR_2)_2(RC_2H)$ are also consistent with this hypothesis. If the resonance of the terminal protons in these compounds at ~8.8 ppm is compared to that observed for $(C_5H_5)_2Mo(C_2H_2)$ at 7.68 ppm,[45] where acetylene must be a formal two-π-electron donor (a bond order of 1)

(36) W. E. Newton, D. C. Bravard, and J. W. McDonald, *Inorg. Nucl. Chem. Lett.*, **11**, 553 (1975); J. Dirand, L. Ricard, and R. Weiss, *J. Chem. Soc., Dalton Trans.*, 278 (1976).
(37) L. Ricard and R. Weiss, *Inorg. Nucl. Chem. Lett.*, **10**, 217 (1974).
(38) J. A. K. Howard, R. F. D. Stanfield, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 246 (1976).
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(40) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 120 (1971).
(41) L. Ricard, J. Estienne, P. Karagianidis, P. Toledano, J. Fischer, A. Mitschler, and R. Weiss, *J. Coord. Chem.*, **3**, 277 (1974).
(42) F. A. Cotton and R. M. Wing, *Inorg. Chem.* **4**, 867 (1965).
(43) F. A. Cotton in "Proceedings of the 1st Climax International Conference on the Chemistry and Uses of Molybdenum", P. C. H. Mitchell, Ed., Climax Molybdenum Co. Ltd., London, 1973, p 6.
(44) J. W. McDonald, W. E. Newton, C. T. C. Creedy, and J. L. Corbin, *J. Organomet. Chem.*, **92**, C25 (1975).
(45) K. L. Tang Wong, J. L. Thomas, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **96**, 3694 (1974).

to the 16-electron $(C_5H_5)_2Mo$ core, it is obvious that the increased deshielding in our compounds comes from an increase in π-electron donation from acetylene to metal resulting in a bond order of somewhat greater than one. However, these resonances are still not as far downfield as those reported for $Mo(C_2H_2)_2(S_2CNEt_2)_2$ (δ 10.15)[44] and $M(CO)(C_2H_2)(S_2CNEt_2)_2$ (δ 12.3 for M = Mo[1,44] and δ 13.1 for M = W[1]). In these last compounds, the metal–acetylene bond order can be described as 2.5 (each acetylene acting as a formal three-π-electron donor) and 3 (a formal donation of all four π-electrons by acetylene to metal), respectively.

The two resonances observed at low temperature for $OMo(S_2CNR'_2)_2(C_2R_2)$ at δ 8.74 and 8.81 for R = H[12,15] and at δ 3.97 and 4.00 for R = CO_2CH_3, in addition to the two ^{19}F resonances observed at ambient temperature for R = CF_3, are all consistent with the cis arrangement of oxo and acetylenic ligands in solution. Coalescence of these signals at elevated temperatures could be interpreted as indicative of a fluxional process involving the acetylenes, which interconverts and, thus, averages the two environments of the terminal groups of the acetylene. Spinning around the metal–acetylene bond could occur and might explain[12] the observation with C_2H_2,[12,15] but we were unable to confirm this process by using bulkier substituents. These acetylenes should have a higher barrier to rotation and should stop spinning at higher temperatures relative to C_2H_2. However, the DTA complex, for example, shows no inequivalence of the DTA signals from +60 to −49 °C. In this case, the continued equivalnce of these signals could be due to the significant distance between the protons being monitored and the acetylenic bond, resulting in a chemical shift difference too small to observe at 60 MHz. Similarly, the small chemical shift differences observed between the two methoxycarbonyl methyl resonances on cooling the DMAC complex to −15 °C could make the observation of coalescence difficult at 60 MHz, assuming it was occurring. This small inequivalence could, however, be due simply to the different temperature dependencies of the two chemical shifts. At this time, we prefer the last interpretation of these observations and suggest that these larger acetylenes are not spinning around the metal–acetylene bond.

The resonances of the alkyl groups of the dithiocarbamates (S_2CNR_2) undergo coalescence at or above ambient temperature which indicates a fluxional nature. In all the compounds studied, the single NMR signal of these alkyl groups at higher temperatures splits first into two with a 3:1 ratio, followed by a further split to give three signals in a 2:1:1 ratio for R = methyl or four signals in a 1:1:1:1 ratio for R = ethyl on cooling. For $OMo(S_2CNMe_2)_2$(DMAC), the 1:2:1 pattern of the dtc methyl resonances is frozen out at +13 °C, which is before any noticeable change occurs in the methoxycarbonyl methyl proton resonance of the acetylene. For $OMo(S_2CNR_2)_2$(DTA) (R = Me, Et), no observable change occurs in the DTA proton resonances in the temperature range studied, while the protons of the dtc groups are frozen out at −2 °C (R = Et) and +14 °C (R = Me). Although not rigorous, these data suggest that only those mechanisms for the interconversion of the dtc alkyl resonances which are independent of the acetylene need be considered in the further discussion. Data on related systems suggest that mechanisms involving metal–ligand bond cleavage are not likely,[46] although the strong trans effect of the oxo group could cause rupture of an Mo–S bond aiding the interconversion. On the basis of the determined structure, simple rotation about the C–N bond would interchange the two alkyl groups in the equatorial plane, the "equatorial–equatorial" pair, with one another and also the "axial–equatorial" pair with each other to give two resonances but would not interconvert all four alkyl groups to give a single resonance as observed. Thus, a metal-centered interchange of the dithiocarbamate ligands must occur either alone or (more likely) in addition to C–N bond rotation to scramble all the alkyl groups. If C–N bond rotation is frozen out at the somewhat higher temperature, then the metal-centered interconversion, which equilibrates the "axial" and "equatorial" sites, could allow differentiation of the one axial site from the three equatorial sites, in keeping with our observations. Further cooling then freezes out this dithiocarbamate interchange to give four equally intense resonances for the alkyl groups. We observe four such resonances for R = Et and three in a ratio of 2:1:1 (with accidental degeneracy) for R = Me. If, however, the metal-centered interconversion was stopped before C–N bond rotation, then the equatorial–equatorial pair of methyl groups will give rise to one signal and the axial–equatorial pair to a second signal in a 1:1 intensity ratio. Although this pattern may occur but remain undetected in our experiments due to small differences in chemical shift, we prefer the former explanation based on a comparison with previously published studies with dithiocarbamate complexes.[46] Our data are insufficient to comment further on the mechanism(s) of these processes, but there can be no doubt that the similarity of these spectra indicates similar structures for all $OMo(S_2CNR_2)_2(Ac)$ complexes and that the stereochemistry determined in the solid state for $OMo(S_2CNMe_2)_2$(DTA) is conserved in solution.

The adducts $OMo(S_2CNR_2)_2(Ac)$ (Ac = MP, DMAC, HFB, DTA) have varying reactivities toward water, secondary amines, and alcohols. Even with just water their reactivities vary. In fact, the adduct with Ac = DTA does not hydrolyze under any of the conditions tried. Further complicating factors arise in that the course of the hydrolyses depends upon both the solvent used and whether the conditions are aerobic or anaerobic. The oxygen-sensitive hydrolysis of $OMo(S_2CNMe_2)_2(MeCO_2C_2H)$ gives the molybdenum(V) dimer,[10] $Mo_2O_4(S_2CNMe_2)_2$, and *trans*-$MeCO_2(H)C{=}C(H)(S_2CNMe_2)$ quantitatively. Previously,[47] it was suggested that a dismutation reaction of the type postulated by Mitchell and Scarle[48] might be occurring, but our more careful study reveals this to be untrue. The same molybdenum-containing product occurred for the DMAC and HFB complexes, but no products involving the acetylenic moiety were identified. Anaerobic hydrolysis of $OMo(S_2CNR_2)_2(Ac)$ with Ac = MP in acetone–water gave the molybdenum(IV) compound, $OMo(S_2CNR_2)_2$, while an ethanol-free chloroform–water mixture gave $Mo_2O_4(S_2CNR_2)_2$, both in about 50% yields. Both solvent systems gave ~50% yields of *trans*-$MeCO_2(H)C{=}C(H)S_2CNR_2$. In contrast, with Ac = DMAC, a very small amount of $Mo_2O_4(S_2CNR_2)_2$ was formed as the only recognizable product.

Except for Ac = HFB, reaction with a secondary amine (R'_2NH) strips the acetylene (C_2R_2) from these complexes as the olefin, $R(R'_2N)C{=}C(H)R$, and liberates the $OMo(S_2CNR''_2)_2$ starting material. All reactions correspond to cis addition of the amine to the acetylene. The same stereochemistry is associated with amine addition to the free acetylenes.[23] As these 1:1 complexes are known to be in equilibrium with $OMo(S_2CNR_2)_2$ and free acetylene, this reaction may, in fact, proceed by way of scavenging free acetylene from the solution until only $OMo(S_2CNR_2)_2$ and olefin remain. In any case, this reaction provides a clean, simple method for

(46) See, for example: D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, **13**, 2045 (1974); E. O. Bishiop, G. Butler, J. Chatt, J. R. Dilworth, G. J. Leigh, D. Orchard, and M. W. Bishop, *J. Chem. Soc., Dalton Trans.*, 1654 (1978).

(47) L. Ricard, C. Martin, R. Wiest, and R. Weiss, *Inorg. Chem.*, **14**, 2300 (1975).

(48) P. C. H. Mitchell and R. D. Scarle, *J. Chem. Soc., Dalton Trans.*, 110 (1975).

reconversion of acetylene complexes to the starting oxomolybdenum(IV) complexes, a reaction which might be useful in synthesis. The surprising lack of reaction exhibited by Ac = HFB contrasts strikingly with its most rapid hydrolysis and, if the above speculation concerning the mechanism is correct, indicates that the HFB adducts do *not* dissociate in solution.

The thiourethane product formed by reaction of the HFB and DMAC adducts with alcohol apparently comes from attack on the positively charged α-carbon of the dithiocarbamate ligand. These observations suggest that the hydrolysis reactions might take a similar course for the HFB and DMAC complexes, where no olefins were formed. This reactivity is very similar to that observed[49] for the reaction of the alkylxanthate complexes $Mo_2O_3(S_2COR)_4$ with alcohols (eq 7), where the organic products were identified as the *O,O*-dialkylthiocarbonates. *No* formation of thiourethane was

$$Mo_2O_3(S_2COR)_4 + 2R'OH \rightarrow ROC(=S)OR' + Mo_2O_2S_2(S_2COR)_2 + H_2O \quad (7)$$

observed from reaction of $Mo_2O_3(S_2CNEt_2)_4$ with alcohol. The fate of the molybdenum in these reaction mixtures is unknown. The reaction of the MP adduct with alcohol not only forms the thiourethane as for the DMAC and HFB adducts but also adds dtcH across the acetylene (as for the hydrolysis of the MP adducts) forming the olefinic product. No reaction occurred between the DTA complex and alcohols, which is perhaps cosistent with the stability of this complex to hydrolysis.

The variability of the reactivity of these acetylenic complexes toward the same reagent is striking, the nature of the acetylene having a very significant effect. The binding of acetylene also radically alters the susceptibility of the dithiocarbamate ligands to attack by water and alcohol as evidenced by a comparison with $MoO_2(S_2CNR_2)_2$, $OMo(S_2CNR_2)_2$, and $Mo_2O_3(S_2CNR_2)_4$ which are stable toward these reagents. These reactions are not simple and in many cases, no molybdenum-containing products could be isolated and/or identified. They show that marked changes of reactivity patterns with changes in coordination occur and these may be particularly significant for the understanding of the role of molybdenum in enzymes, where apparently small changes in the environment of molybdenum can drastically alter its catalytic capability and substrate selectivity.[3,50,51]

Acknowledgment. We are grateful to R. A. D. Wentworth and E. A. Maatta for informing us of their experimental results before publication and to E. I. Stiefel and G. D. Watt for continuing helpful discussions.

Registry No. $OMo(S_2CNMe_2)_2(DMAC)$, 39584-77-5; $OMo(S_2CNEt_2)_2(DMAC)$, 55723-31-4; $OMo(S_2CNMe_2)_2(MP)$, 73367-33-6; $OMo(S_2CNEt_2)_2(MP)$, 73367-34-7; $OMo(S_2CNMe_2)_2(HFB)$, 73367-35-8; $OMo(S_2CNEt_2)_2(HFB)$, 73367-36-9; $OMo(S_2CNMe_2)_2(DTA)\cdot C_6H_6$, 73367-38-1; $OMo(S_2CNEt_2)_2(DTA)$, 73367-39-2; $OMo(S_2CNEt_2)_2(C_2H_2)$, 66060-13-7; $OMo(S_2CNMe_2)_2$, 39587-09-2; $OMo(S_2CNEt_2)_2$, 25395-92-0; $Mo_2O_4(S_2CNMe_2)_2$, 50860-30-5; *trans*-$(Me_2NCS_2)CH{=}CH(CO_2Me)$, 73377-27-2; *cis*-$(Me_2NCS_2)CH{=}CH(CO_2Me)$, 25924-87-2; Me_2NCS_2Na, 128-04-1; MP, 922-67-8; $(Me_2NCS_2)(CO_2Me)C{=}C(H)(CO_2Me)$, 73377-28-3; DMAC, 762-42-5; Me_2NH, 124-40-3; Et_2NH, 109-89-7; methanol, 67-56-1; water, 7732-18-5.

Supplementary Material Available: A listing of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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Formation of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$, a Complex with a Bridging Imido Ligand, and Its Reactions with Acids

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Received September 18, 1979

The nature of the reaction between $MoO(S_2P(OEt)_2)_2$ and HN_3 is discussed. The decomposition of a purple intermediate, thought to be $Mo_2O_2(NH)(S_2P(OEt)_2)_4$, results in the formation of $Mo_2O_3(NH)(S_2P(OEt)_2)_2$. The structure of the latter includes bridging oxo and imido ligands. The reaction of this complex with HCl results in the protonation of the imido ligand (substantiated by ^{15}N labeling) and the formation of $Mo_2O_2(NH_2)Cl(S_2P(OEt)_2)_2$. Similarly, the reaction with $HS_2P(OEt)_2$ results in the formation of $Mo_2O_3(NH_2)(S_2P(OEt)_2)_3$. The site of protonation was again substantiated by ^{15}N labeling. The contrasting behaviors of terminal and bridging imido ligands as well as bridging oxo ligands to protonation are compared.

Introduction

Several recent studies have focused on the reactions of dithiocarbamate complexes of oxomolybdenum(IV) with small, easily reduced compounds.[1,2] Of primary interest for present purposes is the oxidation of $MoO(S_2CNR_2)_2$ by HN_3 with the latter distributed between acidic aqueous and organic phases.[2] The products of this reaction are $MoO_2(S_2CNR_2)_2$, N_2, and NH_3. These results were interpreted in terms of an initial abstraction of the NH ligand to give $MoO(NH)(S_2CNR_2)_2$ and N_2, followed by hydrolysis of the intermediate to yield the remainder of the products. Subsequently, we have been able to demonstrate the abstraction of NR ligands from various

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0020-1669/80/1319-2006$01.00/0