Synthesis and Structure of a Molybdenum Dimer Illustrating dπ Orbital Participation in π Donation, π Acceptance, and Metal–Metal Bond Formation

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Abstract: The synthesis of a series of molybdenum dimers with bridging sulfur and alkyne ligands has been realized from monomeric $Mo(R^1C{\equiv}CR^2)_2(S_2CNR_2)_2$ reagents (R^1 = H, R^2 = Ph; R^1 = CH_3, R^2 = Ph; R^1 = H, R^2 = *n*-Bu; R^1 = R^2 = Et). The molecular structure of the dimeric 3-hexyne derivative $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(S_2CNMe_2)_3(SCNMe_2)$ has been determined by a single-crystal X-ray diffraction study. The crystals were found to be monoclinic of space group $P2_1/c$ with a = 12.105 (3) Å, b = 16.998 (4) Å, c = 17.998 (5) Å, and β = 94.57 (2)°. The structure was refined to R = 0.044 and R_w = 0.038 using 3649 reflections with $I > 3\sigma(I)$. The unsymmetrical dimer can be viewed as a conlateral bioctahedron with one sulfur atom bridge and one alkyne bridge linking the two metal centers. The coordination sphere of one molybdenum is completed by two chelating dithiocarbamate ligands while the second molybdenum binds one chelating dithiocarbamate and one thiocarboxamido ligand through both the sulfur and the carbon, in the terminal positions. The formation of a bridging sulfur ligand and a thiocarboxamido ligand ($SCNR_2$) from one of the original dithiocarbamates (S_2CNR_2) corresponds to oxidative addition of one C–S bond to the molybdenum(II) centers. The Mo–C bond length of 2.056 (6) Å and the low-field carbon-13 chemical shift of this thiocarboxamido carbon (263.7 ppm) reflect considerable carbene character. Infrared ν(CN) frequencies and spin saturation transfer experiments probing C–N bond rotation processes are consistent with enhanced C–N multiple-bond character in the η^2-$SCNR_2$ ligand compared to the S_2CNR_2 ligands. Proton NMR spectra of the dimeric products indicate the presence of at least two isomers for symmetrical alkyne derivatives (RC≡CR) and at least four isomers for unsymmetrical alkyne derivatives (RC≡CR′) in solution. The Mo–Mo distance of 2.647 (1) Å observed in the 3-hexyne-bridged dimer suggests an attractive metal–metal interaction. A qualitative molecular orbital description has been formulated which accounts for the diamagnetism of these dimers and the observed structural parameters. The two nests of three dπ orbitals remaining on the metals following formation of six σ bonds to each center are used to generate Mo–Mo σ and σ* orbitals, two alkyne π*-stabilized molecular orbitals, one combination destabilized by π donation from a filled bridging sulfur atom p orbital, and one dπ combination destabilized by π donation from terminal dithiocarbamate sulfur atoms. The orientation of the dπ orbital combination available for π donation from chelating terminal ligands limits this interaction to only two of the seven terminal sulfurs, and the structure reveals an average Mo–S_t distance of 2.44 Å to these two atoms while the remaining five Mo–S_t distances average 2.57 Å.

A number of organometallic six-coordinate d^4 complexes with both π-acid and π-base ligands in the coordination sphere now exist. These complexes are exceptions to the effective atomic number rule when only ligand σ donation is considered in the electron-counting formalism. Representative compounds of this type that have been isolated include $M(CO)_2(S_2CNR_2)_2$ (M = Mo,[1] W[2]), $M(CO)(RC{\equiv}CR)(S_2CNR'_2)_2$ (M = Mo,[3] W[4]), $Mo(CO)_2(py)_2(OR)_2$,[5] $Mo(CO)_2(PR_3)_2X_2$,[6] $Mo(CNR)_4(SR)_2$,[7] $(\pi\text{-}C_5H_5)M(CO)(RC{\equiv}CR)X$ (M = Mo, W),[8] $(\pi\text{-}C_5H_5)M(CO)(RC{\equiv}CR)(SR')$ (M = Mo, W),[9] $(\pi\text{-}C_5H_5)M(RC{\equiv}CR)_2X$ (M = Mo, W),[10] $(\pi\text{-}C_5H_5)W(CO)(RC{\equiv}CR)Me$,[11] $[(\pi\text{-}C_5H_5)M(CO)(RC{\equiv}CR)_2]^+$ (M = Mo, W),[12] and $[(\pi\text{-}C_5H_5)Mo(dppe)(RC{\equiv}CR)]^+$.[13] The electrophilicity of these formal 16-electron complexes is less than anticipated for unsaturated intermediates and differs dramatically from the reactivity of comparable species such as $(\pi\text{-}C_5H_5)M(CO)_3^+$ (M = Mo, W)[14] and $(\pi\text{-}C_5H_5)W(CO)_2R$.[15] Spectral, structural, and theoretical[16] analyses of this class of compounds have been presented.

The synthesis and characterization of bis(alkyne)bis(dithiocarbamato)molybdenum(II) complexes, $Mo(R^1C{\equiv}CR^2)_2(S_2CNR_2)_2$, have been reported for a series of terminal and internal aryl- and alkylalkynes.[17] The first members of this class of compounds were prepared by McDonald and co-workers, who noted that an effective donation of 3 electrons/alkyne would allow these complexes to attain the inert gas configuration.[18] Simple molecular orbital considerations are compatible with this model; these formal 16-electron complexes are stabilized by ligand π donation from a linear combination of the two filled alkyne $\pi_\perp$ orbitals into the lone vacant dπ orbital that dominates the lowest unoccupied orbital (LUMO).[19]

The reactivity patterns of 16-electron organometallic molybdenum(II) complexes stabilized by ligand π donation are not easily predicted. In order to provide experimental information concerning the chemical behavior of $Mo(RC{\equiv}CR)_2(dtc)_2$ (dtc = $^-S_2CNR'_2$) in the presence of Lewis bases, we have carried out reactions of these monomers with phosphorus nucleophiles. No phosphine adducts have been observed, but PEt_3 and $P(OMe)_3$ have been shown to promote formation of molybdenum dimers as represented

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in the net reaction (1), where dtca is a thiocarboxamido ligand ($^-SCNR_2$).

$$2Mo(RC_2R)_2(dtc)_2 \xrightarrow[\Delta]{PR_3} Mo_2(\mu\text{-}S)(\mu\text{-}C_2R_2)(dtc)_3(dtca) + 3RC_2R \quad (1)$$

We report here syntheses and spectral properties of a series of these dimers in addition to the crystal structure of one member of this class, $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(S_2CNMe_2)_3(SCNMe_2)$. Although the low symmetry of the dimer and the presence of bridging ligands complicate the bonding picture in these molecules, it is possible to generate a satisfying qualitative molecular orbital description. A model based on utilization of the three $d\pi$ orbitals of each six-coordinate metal center in metal–metal bond formation, π acceptance, and π donation is compatible with the gross geometry and diamagnetism and also accounts for discrepancies observed in terminal Mo–S distances to different dithiocarbamate sulfur atoms.

Experimental Section

Materials and Methods. All syntheses were performed under a dry oxygen-free atmosphere by using standard vacuum line techniques. Solvents were degassed prior to use. Molybdenum hexacarbonyl, chlorine gas, sodium dialkyldithiocarbamates, alkynes, phosphines, and phosphites were obtained from commercial sources and used without further purification. $Mo(CO)_4Cl_2$,[20] $Mo(CO)_2(S_2CNR_2)_2$,[1] and $Mo(R^1C_2R^2)_2(S_2CNR_2)_2$[17] were prepared as described previously. Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer and calibrated with a polystyrene standard. ^1H NMR and ^{13}C NMR spectra were recorded on a WM Bruker 250 spectrometer. Chemical shifts are reported as parts per million downfield of Me_4Si. NMR sample temperatures were measured via a thermocouple located near the probe. Elemental analyses were performed by Galbraith Laboratories of Knoxville, TN.

Syntheses. $Mo_2(\mu\text{-}S)(\mu\text{-}R^1C_2R^2)(S_2CNR_2)_3(SCNR_2)$ (R = Me (a), Et (b); R^1 = H, R^2 = Ph (1); R^1 = CH_3, R^2 = Ph (2a). 1. In a representative reaction, $Mo(HC_2Ph)_2(S_2CNMe_2)_2$ (1.00 g, 1.85 mmol) was dissolved in 25 mL of toluene. Triethylphosphine (0.273 mL, 0.219 g, 1.85 mmol) was added and the solution brought to reflux. The bright orange solution quickly turned dark greenish brown. After 1.5 h the heating bath was removed and the solution volume reduced in vacuo. Chromatography on an alumina column with toluene as an eluent brought off a small orange band consisting of unreacted starting material. An unidentified violet band was eluted next. The product was then eluted with CH_2Cl_2/toluene (1:1) as a green band. Solvent was removed from the solution in vacuo. An ice water cold finger was attached, and the dry product was heated (50 °C) under vacuum for 2 h to remove residual $SPEt_3$ as clear needles (mp 93–94 °C). The dimer was recrystallized from toluene/hexane to produce emerald green crystals in 25% yield. The products are air stable both as solids and in solution.

2. $Mo(HC_2Ph)_2(S_2CNMe_2)_2$ (1.00 g, 1.85 mmol) was dissolved in 25 mL of toluene. $P(OMe)_3$ (0.22 mL, 0.23 g, 1.85 mmol) was added and the solution brought to reflux. The solution color slowly changed from bright orange to dark green. After being heated for 1.5 h, the solution was allowed to cool and the product was isolated as described above. These dimeric complexes crystallized with half solvent molecule/dimer as determined by elemental analysis. Both ^1H and ^{13}C NMR signals due to phenyl groups and dithiocarbamate alkyl groups were observed, but these data are not listed explicitly below.

1a: ^1H NMR ($CDCl_3$) δ 8.23 and 8.02 (s, 1 H, ≡CH, geometric isomers in the ratio 3:2, respectively); ^{13}C NMR ($CDCl_3$) (the average chemical shift of the four isomers observed for each carbon is reported) δ 260.29 (av) ($SCNMe_2$), 208.92, 205.36, and 202.82 (S_2CNMe_2), 135.13 (HC≡); peaks due to the substituted acetylenic carbon occur in the range 130–150 ppm; IR (KBr) ν(C=N) of $SCNMe_2$, 1550 cm^{-1} (w), ν(C=N) of S_2CNMe_2, 1516 cm^{-1} (s). Anal. Calcd for $Mo_2S_8N_4C_{20}H_{30}\cdot 0.5C_6H_6$: C, 33.94 H, 4.09. Found: C, 33.32; H, 4.20.

1b: ^1H NMR ($CDCl_3$) δ 8.23 and 7.89 (s, 1 H, ≡CH, geometric isomers in the ratio 1:2, respectively); ^{13}C NMR ($CDCl_3$) δ 259.77 ($SCNMe_2$), 207.64, 204.68, and 200.80 (S_2CNMe_2), 140–150 (several peaks, ≡CR); IR (KBr) ν(C=N) of $SCNEt_2$, 1525 cm^{-1} (m), ν(C=N) of S_2CNEt_2, 1490 cm^{-1} (s). Anal. Calcd for $Mo_2S_8N_4C_{28}H_{46}\cdot 0.5C_6H_6$: Mo, 20.73; S, 27.67; N, 6.05; C, 40.22; H, 5.32. Found: Mo, 20.28; S, 27.11; N, 6.05; C, 40.59; H, 5.64.

2a: ^{13}C NMR ($CDCl_3$) δ 262.43 (average chemical shift of three isomers, $SCNMe_2$), 210.21, 206.17, and 204.40 (each chemical shift is the average of three isomers, S_2CNMe_2), 141–156 (range of 6 peaks due to ≡CMe and ≡CPh). IR (KBr) ν(C=N) of $SCNMe_2$, 1550 cm^{-1} (w); ν(C=N) of S_2CNMe_2 1512 cm^{-1} (s). Anal. Calcd for $Mo_2S_8N_4C_{21}H_{32}\cdot 0.5C_7H_8$: C, 35.23; H, 4.35. Found: C, 34.96; 4.99.

$Mo_2(\mu\text{-}S)(\mu\text{-}R^1C_2R^2)(S_2CNMe_2)_3(SCNMe_2)$ (R^1 = H, R^2 = n-Bu (3a); R^1 = R^2 = C_2H_5 (4a)). In a representative reaction, $Mo(3\text{-hexyne})_2(S_2CNMe_2)_2$ (1.55 g, 3.10 mmol) was dissolved in 25 mL of benzene. Triethylphosphine (4.6 mL, 0.366 g, 3.10 mmol) was added, and the solution was heated to reflux. The bright orange solution slowly turned dark green. After 1 h the solution was allowed to cool and the solvent was removed in vacuo. Chromatography on an alumina column with toluene first eluted a small orange band of starting material. An unidentified dark violet band eluted next. The product was eluted with toluene/CH_2Cl_2 (1:1) as a green band. The solvent was removed in vacuo. An ice water cold finger was attached, and the product was heated (50 °C) under vacuum for 2 h to remove residual $SPEt_3$. The product was recrystallized from benzene/heptane as emerald green crystals (30% yield). The products are air stable as solids and in solution. Again routine NMR data for the alkyl groups has been omitted from the listing.

3a: ^1H NMR ($CDCl_3$) δ 8.02, 7.73, 7.22, and 7.10 (s, 1 H, ≡CH, geometric isomers in the ratio of 4:1:2:3, respectively); ^{13}C NMR ($CDCl_3$) δ 262.19 (average chemical shift of three isomers, $SCNMe_2$), 208.96, 205.43, and 202.38 (each chemical shift is the average of three isomers, S_2CNMe_2), 143–167 (range of five observed peaks due to ≡CH and ≡CC_4H_9); IR (KBr) ν(C=N) of $SCNMe_2$, 1548 cm^{-1} (m), ν(C=N) of S_2CNMe_2, 1514 cm^{-1} (s). Anal. Calcd for $Mo_2S_8N_4C_{18}H_{34}\cdot 0.5C_7H_8$: C, 32.24; H, 4.35. Found: C, 31.86; H, 4.97.

4a: ^1H NMR (toluene-d_8) δ 3.89, 3.31, and 3.18 (q, 2 H, ≡CCH_2, one quartet was not observed), 2.73 and 1.78 (s, 3 H, $SCNMe_2$), 2.68, 2.67, 2.64, 2.47, 2.43, and 2.31 (s, 3 H, S_2CNMe_2), 1.98 (t, 12 H, ≡CCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 263.72 ($SCNMe_2$), 209.75, 206.15, and 203.00 (S_2CNMe_2), 148.99 and 143.84 (≡CCH_2CH_3), 47.38, 46.79 (major isomer), 45.94, and 45.78 (major isomer) ($SCNMe_2$), 39.53, 39.36, 39.07, and 38.90 (S_2CNMe_2), 28.22, 27.84, 26.74 (major isomer), and 26.20 (major isomer) (≡CCH_2CH_3), 16.49 and 14.85 (major isomer) (≡CCH_2CH_3); IR (KBr) ν(C=N) of $SCNMe_2$, 1545 cm^{-1} (m), ν(C=N) of S_2CNMe_2, 1508 cm^{-1} (s). Anal. Calcd for $Mo_2S_8N_4C_{18}H_{34}\cdot 0.5CDCl_3$: C, 27.26; H, 4.34. Found: C, 27.71; H, 4.49.

Single-Crystal Data Collection. Dark emerald green prismatic crystals of $Mo_2(\mu\text{-}S)(\mu\text{-3-hexyne})(dmtc)_3(dmtca)$ were grown from a benzene/heptane solution. A single crystal of approximate dimensions 0.30 mm × 0.30 mm × 0.30 mm was selected, mounted on a glass fiber, and coated with epoxy cement. Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer.[21] Twenty-five reflections located in the region 30° < 2θ < 34° were centered, and angular data were refined by least-squares calculations. A monoclinic lattice system was indicated

Table I. Crystallographic Data and Collection Parameters for $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(S_2CNMe_2)_3(SCNMe_2)\cdot C_6H_6$

space group	$P2_1/c$
a, Å	12.105 (3)
b, Å	16.998 (4)
c, Å	17.507 (5)
β, deg	94.57 (2)
vol, Å^3	3591 (3)
d(calcd), g/cm^3	1.541
Z	4
fw	833.01 g/mol
μ, cm^{-1} (abs coeff)	11.51
radiatn	Mo Kα, λ = 0.710 73 Å
monochromator	graphite crystal
takeoff angle	2.6°
scan range	2° < 2θ < 50°
data collected	$\pm h,+k,+l$
scan width, deg	1.0 + (0.35 tan θ)
bkgd scan width	25% of full peak width on each side
no of unique data	6306
no of data, $I > 3\sigma(I)$	3659
no of variables	313
$R_{unweighted}$	0.044
$R_{weighted}$	0.038
esd (error in an observn of unit weight)	1.79

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(21) Programs utilized during solution and refinement were from the Enraf-Nonius structure determination package.

with cell constants as listed in Table I.

Diffraction data were collected in the quadrant ($\pm h,+k,+l$) under conditions noted in Table I. Three reflections chosen as intensity standards were monitored every 5 h and showed no significant (<1.5%) decay. The crystal was checked for recentering after every 300 reflections (recentering was necessary only when the scattering vectors varied by more than 0.15°). Psi scans with nine reflections having $80° < \chi < 90°$ were performed to provide an empirical correction for absorption. A total of 6306 unique reflections were collected in the region $2° < 2\theta < 50°$. Only the 3659 reflections having $I > 3\sigma(I)$[22] were used in the solution and refinement of the structure. The data were corrected for Lorentz-polarization effects and absorption during the final stages of refinement.

Solution and Refinement of the Structure. Inspection of the data showed systematic absences ($0k0$, $k \neq 2n$, and $h0l$, $l \neq 2n$) suggesting the space group $P2_1/c$, which was subsequently confirmed by successful structure determination. The positions of the two metal atoms, Mo(1) and Mo(2), were located from a three-dimensional Patterson function.

Fourier and difference Fourier calculations following refinement of the metal atom positions yielded all eight sulfur positions. The remaining nonhydrogen atoms of the dimer were obtained following least-squares refinement[23] and Fourier calculations. Anisotropic refinement of these 32 atoms produced unweighted and weighted residuals of 0.067 and 0.122, respectively.[24] A difference Fourier calculation at this point revealed six peaks indicative of one molecule of benzene/asymmetric unit. Hydrogen positions for the ligands and for the benzene solvate molecule were calculated by using a C–H distance of 0.95 Å and isotropic thermal parameters set at 5.0 and 15.0, respectively. Full-matrix least-squares refinement using anisotropic thermal parameters for the nonhydrogen atoms of the dimer and isotropic thermal parameters for the carbon atoms of the benzene molecule converged with R factors of $R_1 = 0.044$ and $R_2 = 0.038$.[25] The final Fourier difference map showed no peak ≥ 0.5 e/Å^3.

Results and Discussion

Syntheses. The conversion of monomeric $Mo(R^1C_2R^2)_2(dtc)_2$ complexes (dtc = $^-S_2CNR_2$) to dimeric compounds with sulfur- and alkyne-bridging ligands occurs in refluxing aromatic solvents in the presence of one equivalent of PEt_3. No phosphine is present in the isolated products which have been characterized. Note that no dimerization (and only a small amount of decomposition) of the monomeric reagent is observed when $Mo(RC{\equiv}CR)_2(dtc)_2$ compounds are heated in the same manner in the absence of phosphine or phosphite reagents.

The identity of the dimeric material has been determined by a single-crystal X-ray structure of the product isolated from the reaction of bis(3-hexyne)bis(*N,N*-dimethyldithiocarbamato)molybdenum. Spectral properties of all the dimeric products herein reported are indicative of similar formulations when one considers potential isomers that could be formed in these systems. These dimers can be represented as $(dtc)_2Mo(\mu\text{-}S)(\mu\text{-}RC{\equiv}CR)Mo(dtc)(dtca)$ where the newly formed thiocarboxamido ligand (dtca = $^-SCNR_2$) binds to the molybdenum through both the sulfur and the adjacent carbon atom.

This condensation reaction is general for internal and terminal aryl- and alkyl-substituted alkyne complexes. Reactions of alkylacetylene complexes (1-hexyne and 3-hexyne) with PEt_3 proceed to completion in 1 h in refluxing benzene while reactions of arylalkyne complexes (phenylacetylene and 1-phenylpropyne) are more sluggish and require 1.5 h in refluxing toluene to reach completion. Column chromatography on alumina leads to isolation of dimeric products as a green band that is contaminated with triethylphosphine sulfide. The volatile $SPEt_3$ can be sublimed away from the molybdenum products as 50 °C under vacuum. Yields are low (20–30%) but reproducible.

The net reaction can be described as dimerization accompanied by oxidative addition of one C–S bond of a dithiocarbamate ligand to the two metal centers. If the alkyne ligands are considered to be neutral donor ligands in both the reagents and products the oxidation corresponds to a change from Mo(II) in the monomer to Mo(III) in the dimer. The thiocarboxamido is counted as a bidentate, monoanionic ligand in this scheme. Formal oxidative addition of a dithiocarbamate C–S bond to Mo(II) has been observed previously in the isolation of a sulfur-bridged dimer of Mo(IV) containing thiocarboxamido ligands prepared according to eq 2.[26] Another reaction that may be germane to our results

$$Mo_2(O_2CCH_3)_4 + 4Na(dtc) \rightarrow NaO_2CCH_3 + Mo_2(\mu\text{-}S)_2(dtc)_2(dtca)_2 \quad (2)$$

is the partial conversion of $[Os_2(\mu\text{-}S_3CNR_2)_2(S_2CNR_2)_3]^+$ to $[Os_2(\mu\text{-}S_2CNR_2)_2(S_2CNR_2)_3]^+$ by sulfur abstraction from the trithiocarbamate ligands with PR_3 or $P(OMe)_3$ reagents.[27] Formation of the $Mo_2(\mu\text{-}S)(\mu\text{-}RC{\equiv}CR)(dtc)_3(dtca)$ dimers from $Mo(RC{\equiv}CR)_2(dtc)_2$ monomers occurs only in the presence of phosphine reagents, but neither PEt_3 nor $SPEt_3$ appears in the stoichiometric equation for conversion of monomers to dimers. Thus the phosphine appears to serve as an initiator for dimerization. Retention of four sulfur atoms/metal in the dimeric product indicates that $SPEt_3$ is formed in a secondary pathway that does not lead to the dimeric products characterized in this work. At this point speculation concerning the mechanism of the dimerization, the oxidative addition route or the role of the phosphine is unwarranted.

Description of the Structure of $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(S_2CNMe_2)_3(SCNMe_2)$. The molecular structure of the dimer formed from bis(3-hexyne)bis(dithiocarbamato)molybde-

Table II. Final Atomic Positional Parameters for $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(dmtc)_3(dmtca)\cdot C_6H_6$

atom	x	y	z
Mo(1)	0.23665 (5)	0.28133 (4)	0.05992 (4)
Mo(2)	0.25493 (5)	0.13135 (4)	0.09968 (4)
S(1)	0.2320 (2)	0.1768 (1)	−0.0221 (1)
S(2)	0.1847 (2)	0.3652 (1)	−0.0612 (1)
S(3)	0.0488 (2)	0.3317 (1)	0.0612 (1)
S(4)	0.3029 (2)	0.4138 (1)	0.1220 (1)
S(5)	0.4342 (2)	0.3130 (1)	0.0341 (1)
S(6)	0.2955 (2)	−0.0018 (1)	0.0382 (1)
S(7)	0.4409 (2)	0.0852 (1)	0.1439 (1)
S(8)	0.1769 (2)	0.0451 (1)	0.2036 (1)
N(1)	−0.0265 (5)	0.4123 (4)	−0.0619 (3)
N(2)	0.5126 (5)	0.4471 (3)	0.0949 (3)
N(3)	0.4884 (5)	−0.0601 (3)	0.0982 (3)
N(4)	0.0029 (5)	0.0752 (4)	0.1032 (4)
C(1)	0.0594 (5)	0.3754 (4)	−0.0273 (4)
C(2)	−0.1323 (6)	0.4191 (4)	−0.0298 (5)
C(3)	−0.0181 (7)	0.4466 (5)	−0.1378 (5)
C(4)	0.4265 (6)	0.3980 (4)	0.0855 (4)
C(5)	0.6183 (7)	0.4323 (5)	0.0647 (5)
C(6)	0.5077 (8)	0.5186 (5)	0.1387 (5)
C(7)	0.4175 (5)	−0.0013 (4)	0.0929 (4)
C(8)	0.4659 (7)	−0.1328 (4)	0.0565 (5)
C(9)	0.5906 (7)	−0.0557 (5)	0.1460 (4)
C(10)	0.1063 (6)	0.0839 (4)	0.1259 (4)
C(11)	−0.0445 (6)	0.1127 (5)	0.0349 (5)
C(12)	−0.0737 (7)	0.0251 (6)	0.1423 (5)
C(13)	0.3881 (7)	0.2097 (4)	0.3022 (4)
C(14)	0.4012 (6)	0.2480 (4)	0.2244 (4)
C(15)	0.3038 (5)	0.2319 (4)	0.1680 (4)
C(16)	0.1963 (5)	0.2349 (4)	0.1660 (4)
C(17)	0.1072 (6)	0.2443 (4)	0.2209 (4)
C(18)	0.1136 (6)	0.3225 (5)	0.2625 (4)
C(19)	0.709 (1)	0.1882 (7)	0.2730 (7)
C(20)	0.721 (1)	0.1935 (7)	0.2002 (7)
C(21)	0.794 (1)	0.3164 (8)	0.2291 (8)
C(22)	0.770 (1)	0.2611 (8)	0.1747 (8)
C(23)	0.782 (1)	0.3116 (8)	0.3048 (8)
C(24)	0.743 (1)	0.2415 (9)	0.3284 (9)

(22) $I = S(C + RB)$ and $\sigma(I) = [2S^2(C + R^2B) + (\rho I)^2]^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan count time to background count time, B = total background count, and $\rho = 0.01$ is a correction factor.

(23) The function minimized was $\sum w(|F_o| - |F_c|)^2$.

(24) $R_{\text{unweighted}} = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_{\text{weighted}} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(25) Scattering factors were taken from: Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.

(26) Ricard, L.; Estienne, J.; Weiss, R. *Inorg. Chem.* **1973**, *12*, 2182–2186.

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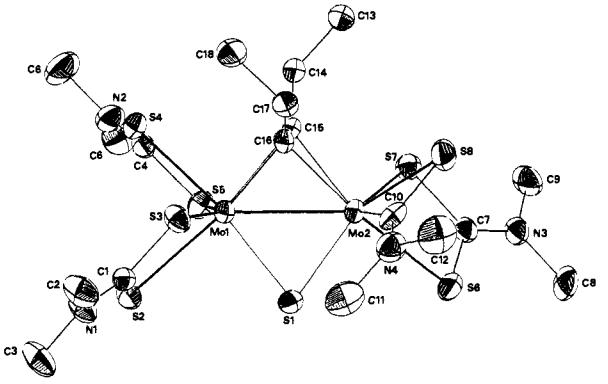
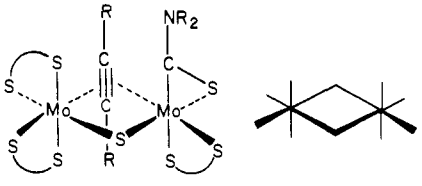


Figure 1. The molecular structure of $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(dmtc)_3(dmtca)$ illustrating the atomic numbering scheme with the thermal ellipsoids at 30% probability.

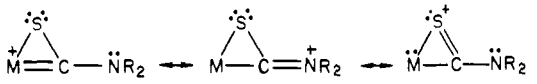
Table III. Selected Bond Distances (Å) in $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(dmtc)_3(dmtca)\cdot C_6H_6$

Mo(1)-Mo(2)	2.647 (1)	Mo(2)-C(10)	2.056 (6)
Mo(1)-C(15)	2.171 (5)	C(15)-C(16)	1.300 (7)
Mo(1)-C(16)	2.111 (5)	S(2)-C(1)	1.681 (5)
Mo(2)-C(15)	2.142 (5)	S(3)-C(1)	1.732 (5)
Mo(2)-C(16)	2.255 (5)	C(1)-N(1)	1.319 (6)
Mo(1)-S(1)	2.282 (1)	S(4)-C(4)	1.695 (6)
Mo(2)-S(1)	2.264 (2)	S(5)-C(4)	1.709 (6)
Mo(1)-S(2)	2.590 (1)	C(4)-N(2)	1.337 (6)
Mo(1)-S(3)	2.431 (2)	S(6)-C(7)	1.697 (6)
Mo(1)-S(4)	2.599 (2)	S(7)-C(7)	1.730 (5)
Mo(1)-S(5)	2.526 (2)	C(7)-N(3)	1.315 (6)
Mo(2)-S(6)	2.569 (2)	S(8)-C(10)	1.681 (6)
Mo(2)-S(7)	2.450 (2)	C(10)-N(4)	1.293 (7)
Mo(2)-S(8)	2.573 (2)		

num(II) is depicted in Figure 1 where the atomic numbering scheme is defined. Atomic positional parameters are listed in Table II, and intramolecular bond distances and angles are reported in Tables III and IV, respectively. The molecule contains two metal centers linked by two distinct bridging ligands: the 3-hexyne ligand, and one sulfur atom. The coordination sphere of each molybdenum is completed by two chelating ligands. Two terminal dithiocarbamate ligands are bound to Mo(1) while Mo(2) has one dithiocarbamate and one thiocarboxamido occupying the four terminal positions. If one veiws the alkyne as filling one coordination site of each metal, the geometry at Mo(1) is roughly octahedral while the local geometry of Mo(2) is at best described as a severely distorted octahedron. The dithiocarbamate bite produces S–Mo–S angles of 68–70° for each of these chelates while the thiocarboxamido C–S distance of 1.68 Å yields an acute C(10)–Mo(2)–S(8) angle near 41° which accounts in large part for the degree of distortion at Mo(2) relative to an octahedral model. If each metal is considered to be six-coordinate, the observed structure is transparently related to an idealized conlateral bioctahedron.



The thiocarboxamido ligand is bound to Mo(2) through both the carbon atom and the sulfur atom. The observed Mo(2)–C(10) distance of 2.06 Å is substantially shorter than typical molybdenum alkyl carbon bond lengths.[28] Similar Mo–C distances (2.07 Å) were found for the terminal thiocarboxamido ligands in the $Mo_2(\mu\text{-}S)_2(dtc)_2(dtca)_2$ structure.[26] As discussed by Weiss and co-workers the short metal–carbon distances in these structures suggest multiple bond character reminiscent of metal–carbene bonding. In valence bond terms an important resonance form for a bound thiocarboxamido is a heteroatom-stabilized carbene with the α-sulfur atom anchored to the metal center.



The planar thiocarboxamido exhibits C–S (1.68 Å, S–CNR_2) and C–N (1.29 Å, SC–NR_2) bond lengths that are nearly identical with those found in the $Mo(\mu\text{-}S)_2(dtc)_2(dtca)_2$ dimer.[26] The surprising retention of Mo–S, C–S, and C–N bond lengths similar to those of dithiocarbamato ligands in the newly formed thiocarboxamido was noted by Weiss and applies equally well here. It seems that oxidative cleavage of one of the original S_2CNR_2 C–S bonds and formation of a Mo–C bond in its place leaves the remaining $SCNR_2$ fragment geometry largely unchanged from the parent S_2CNR_2 moiety. The minimal rearrangement of the $SCNR_2$ fragment upon literally excising one sulfur from the MoS_2CNR_2 unit suggests that the metal forms a covalent bond to the carbon center *and* provides some lone pair π-electron density to the three-coordinate carbon in a manner comparable to that of the displaced sulfur in the precursor ligand.

The three dithiocarbamates exhibit normal intraligand distances and angles.[29] An informative feature of this structure is the existence of two categories of Mo–S bond lengths to terminal dithiocarbamate ligands. Four Mo–S(dtc) bonds are longer than 2.50 Å (average 2.57 Å) and two are shorter than 2.50 Å (average 2.44 Å). The trans influence cannot satisfactorily explain this difference of more than 0.1 Å since the short Mo–S(dtc) on Mo(1) is trans to one of the long Mo–S(dtc) distances. Note that delocalization of dithiocarbamate π-electron density into vacant metal $d\pi$ orbitals has been invoked to account for the stability of electron-deficient compounds such as $Mo(CO)_2(S_2CNR_2)_2$.[19] Indeed the shorter M–S(dtc) distances in $Mo(CO)_2(dtc)_2$ (2.46 Å average)[30a] compared to $W(CO)_3(dtc)_2$ (2.53-Å average)[30b] are compatible with more multiple M–S bond character in the formal 16-electron complex. The role of these chelating single-faced π-donor dithiocarbamates in the dimer reported herein is uniquely compatible with the observed shortening of the Mo(1)–S(3) and Mo(2)–S(7) bonds as elucidated in the bonding section.

The bridging sulfur is tightly bound to both metals and the Mo–S_{br} distances (2.26, 2.28 Å) are similar to those in other sulfur-bridged molybdenum dimers.[31] The alkyne bridge exhibits a carbon–carbon distance of 1.30 Å and a cis-bent structure with C—C≡C angles near 138° in accord with representative values for dinuclear complexes with perpendicular bridged alkyne ligands.[32] The average Mo–C bond length of 2.17 Å to the alkyne bridge is more than 0.1 Å longer than comparable distances reported for $Mo_2(\mu\text{-}C_2H_2)(\mu\text{-}OR)_2(OR)_4(py)_2$ (R = isopropyl).[33] The alkyne bridge in $Mo_2(\mu\text{-}S)(\mu\text{-}EtC_2Et)(dtc)_3(dtca)$ is twisted 10.9° from a rigorously perpendicular orientation relative to the Mo–Mo vector.

A Mo–Mo separation of 2.647 Å in this dimer suggests an attractive metal–metal interaction. The question of metal-metal bond order will be addressed below. Molybdenum–molybdenum distances in selected dimers are presented in Table V for comparative purposes.

(28) (a) Churchill, M. R. *Perspect. Struct. Chem.* **1971**, *3*, 91–164. (b) Bennett, M. J.; Mason, R. *Proc. Chem. Soc.* **1963**, 273–274.

(29) (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301–469. (b) Willemse, J.; Cras, J. A.; Steggarda, J. J.; Keijzers, C. P. *Struct. Bonding (Berlin)* **1976**, *28*, 83–126.

(30) (a) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6568–6569. (b) *Inorg. Chem.* **1980**, *19*, 1753–1759.

(31) (a) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–223. (b) Vergamini, P. J.; Vahrenkamp, H.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6327–6329. (c) Chisholm, M. H.; Corning, J. F.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 286–289.

(32) (a) Sly, W. G. *J. Am. Chem. Soc.* **1959**, *81*, 18–20. (b) Bailey, W. I.; Collins, D. M.; Cotton, F. A. *J. Organomet. Chem.* **1977**, *135*, C53–C56. (c) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354–2356.

(33) Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1981**, *103*, 4245–4246.

Table IV. Selected Bond Angles (deg) in $Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(dmtc)_3(dmtca)\cdot C_6H_6$

Mo(1)-S(1)-Mo(2)	71.23 (4)	S(1)-Mo(1)-S(4)	158.24 (5)	C(15)-Mo(2)-C(10)	113.33 (21)
Mo(1)-C(15)-Mo(2)	75.73 (17)	S(1)-Mo(1)-S(5)	91.70 (5)	S(2)-Mo(1)-S(3)	69.35 (5)
Mo(1)-C(16)-Mo(2)	74.57 (17)	S(1)-Mo(2)-S(6)	85.37 (5)	S(2)-Mo(1)-S(4)	84.96 (5)
S(1)-Mo(1)-C(15)	103.16 (13)	S(1)-Mo(2)-S(7)	116.56 (6)	S(2)-Mo(1)-S(5)	84.73 (5)
S(1)-Mo(1)-C(16)	105.49 (14)	S(1)-Mo(2)-S(8)	146.68 (6)	S(3)-Mo(1)-S(4)	87.06 (5)
S(1)-Mo(2)-C(15)	105.19 (14)	S(1)-Mo(2)-C(10)	107.49 (18)	S(3)-Mo(1)-S(5)	145.66 (5)
S(1)-Mo(2)-C(16)	101.45 (13)	C(15)-Mo(1)-S(2)	167.74 (14)	S(4)-Mo(1)-S(5)	67.99 (5)
C(15)-C(16)-C(17)	138.77 (53)	C(15)-Mo(1)-S(3)	114.45 (15)	S(6)-Mo(2)-S(7)	69.44 (5)
C(14)-C(15)-C(16)	138.07 (54)	C(15)-Mo(1)-S(4)	83.64 (13)	S(6)-Mo(2)-S(8)	83.65 (5)
Mo(2)-C(10)-N(4)	145.03 (51)	C(15)-Mo(1)-S(5)	86.82 (15)	S(6)-Mo(2)-C(10)	86.96 (16)
Mo(2)-C(10)-S(8)	86.42 (27)	C(15)-Mo(2)-S(6)	151.99 (16)	S(7)-Mo(2)-S(8)	88.52 (6)
S(1)-Mo(1)-S(2)	85.48 (5)	C(15)-Mo(2)-S(7)	82.72 (15)	S(7)-Mo(2)-C(10)	126.97 (18)
S(1)-Mo(1)-S(3)	107.68 (6)	C(15)-Mo(2)-S(8)	99.18 (15)	S(8)-Mo(2)-C(10)	40.69 (18)

Table V. Representative Structural Parameters for Related Molybdenum Dimers

complex	Mo-Mo[a]	Mo-S_{br}	Mo-S_{br}'	Mo-C_{br}[b]	Mo-C_{br}'	C≡C	ref
$Mo_2(\mu\text{-}S)(\mu\text{-}EtC{\equiv}CEt)(dtc)_3(dtca)$	2.65	2.26	2.28	2.13	2.21	1.30	this work
$Mo_2(\mu\text{-}HC{\equiv}CH)(\mu\text{-}O\text{-}i\text{-}Pr)_2(O\text{-}i\text{-}Pr)_4(py)_2$	2.55			2.08	2.09	1.37	33
$Mo_2(\mu\text{-}EtC{\equiv}CEt)(\pi\text{-}C_5H_5)_2(CO)_4$	2.98			2.17	2.24	1.34	*c*
$Mo_2(\mu\text{-}S)_2(dtc)_2(dtca)_2$	2.71	2.24	2.34				26
$Mo_2(\mu\text{-}S)_2(\pi\text{-}C_5H_5)_2O_2$	2.89	2.32	2.32				*d*
$Mo_2(\mu\text{-}S)_2(dtc)_4S_2$	2.80	2.31	2.31				*e*
$Mo_2(\mu\text{-}S)_2(S\text{-}t\text{-}Bu)_4(HNMe_2)_2$	2.73	2.24	2.33				31c

[a] All distances are in Å. [b] Each Mo-C distance listed is the average of the two nonadjacent Mo-C distances to the alkyne bridge. [c] Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* 1978, *100*, 5764. [d] Stevenson, D. L.; Dahl, L. F. *J. Am. Chem. Soc.* 1967, *89*, 3721. [e] Spivack, B.; Dori, Z.; Stiefel, E. I. *Inorg. Nucl. Chem. Lett.* 1975, *11*, 501.

Infrared Spectra. Infrared spectra of the dimeric products are compatible with the proposed formulations. In addition to absorptions anticipated for bidentate dithiocarbamate ligands an additional absorption is observed in the 1525-1550-cm^{-1} region as a moderately intense shoulder on the high-energy side of the intense dithiocarbamate C–N stretching absorption. Two plausible assignments merit consideration: C–C stretch of the bridging alkyne or C–N stretch of the thiocarboxamido ligand. Alkyne-bridged transition-metal dimers often show C–C stretching absorptions in the 1400–1600-cm^{-1} region.[34] Normally this band is broad and weak and shifts on the order of a hundred wave numbers between terminal (lower energy) and internal (higher energy) alkyne derivatives. No such frequency shift is observed in the absorption near 1540 cm^{-1} as a function of alkyne. Rather the 3-hexyne and 1-phenylpropyne derivatives exhibit a broad, weak infrared absorption at 1611 and 1594 cm^{-1}, respectively. If these are assigned as the C–C stretch of these bound alkynes, then a decrease of roughly one hundred wavenumbers for terminal alkyne derivatives would bury the bound triple bond stretch under the intense dithiocarbamate S_2CNR_2 C–N absorption near 1500 cm^{-1}. These considerations are consistent with assigning the 1525–1550-cm^{-1} absorptions to the unique thiocarboxamido $SCNR_2$ C–N stretch. This assignment is in accord with a frequency of 1573 cm^{-1} reported for the $SCNR_2$ C–N stretching mode in $(\pi\text{-}C_5H_5)Mo(CO)_2(SCNMe_2)$.[35]

^{1}H NMR Spectra. The ^{1}H NMR spectrum of $Mo_2(\mu\text{-}S)(\mu\text{-}HC{\equiv}C\text{-}n\text{-}Bu)(dmtc)_3(dmtca)$ exhibits four singlets with different intensities in the range of 7–8 ppm. The chemical shift of acetylenic protons for group 6 metal alkyne complexes is known to vary substantially in response to the metal environment and the metal-alkyne bonding interaction.[36] In the acetylene-bridged $Mo_2(\mu\text{-}C_2H_2)(\mu\text{-}OR)_2(OR)_4(py)_2$ complex the acetylenic proton resonance is located at 7.26 ppm.[33] The 1-hexyne-bridged molybdenum dimer synthesized in this work provides a particularly informative NMR spectrum since only the acetylenic proton will exhibit a low field chemical shift. The observed four singlets (δ 8.02, 7.73, 7.22 and 7.10 with intensity ratios of approximately 4:1:2:3) in the region appropriate for metal-bound ≡CH units in analytically pure samples of $Mo_2(\mu\text{-}S)(\mu\text{-}HC{\equiv}C\text{-}n\text{-}Bu)(dmtc)_3(dmtca)$ indicate the presence of at least four distinct isomers. On the basis of the structure of the 3-hexyne-bridged dimer, several isomeric possibilities warrant consideration. One probable isomer pair for unsymmetrically substituted alkynes arises from the orientation of the alkyne substituents relative to the metal ligand skeleton (case I in Figure 2). A second pair of isomers giving rise to two NMR distinct terminal alkyne proton environments could result from the chirality of the two metal moieties. The $Mo(dtc)_2(S)$(alkyne) octahedral fragment depicted in case I can accordingly be labeled Δ, and generation of this unit as a Λ fragment from the racemic reagent compels one to draw diastereomeric isomers as depicted in case II. Other isomers could result from exchanging the bridging alkyne and sulfur positions relative to the terminal molybdenum octahedral remnants. When coupled with alkyne orientation and chelate-generated chirality, a total of four more isomers are produced. Given the observed solid-state structure and the unique compatibility of the molecular

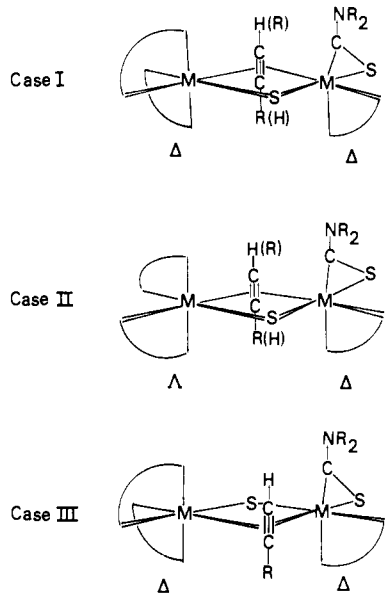


Figure 2. Schematic representations of plausible geometric isomers for unsymmetrical alkyne derivatives of the type $Mo_2(\mu\text{-}S)(\mu\text{-}HC{\equiv}CR)(dtc)_3(dtca)$. The chirality of each of the idealized $Mo(chelate)_2(S)$(alkyne) fragments is indicated for each isomer depicted.

(34) Iwashita, Y. *Inorg. Chem.* **1970**, *9*, 1178–1182.
(35) Treichel, P. M.; Dean, W. K. *J. Chem. Soc., Chem. Commun.* **1972**, 804–805.
(36) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248–1253.

orbital description with location of the thiocarboxamido plane roughly *cis* to the bridging alkyne position, it is clear that the four isomers represented by cases I and II are to be preferred since they offer minimum disruption of the total bonding scheme. Since only four isomers are observed by NMR spectroscopy the additional geometries represented by case III are not required to account for the data. Examination of the ^{1}H NMR spectrum of $Mo_2(\mu\text{-S})(\mu\text{-HC}{\equiv}\text{CPh})(\text{dmtc})_3(\text{dmtca})$ shows only two singlets separated from the phenyl region that can be assigned to terminal alkyne protons of different isomers. Additional acetylenic proton signals that may be present could be masked by the phenyl resonances.

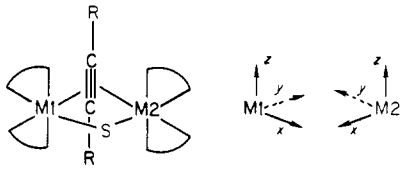
Some spectral simplification results when symmetrical alkyne derivatives are utilized. Only two isomers are evident in the $Mo_2(\mu\text{-S})(\mu\text{-EtC}{\equiv}\text{CEt})(\text{dmtc})_3(\text{dmtca})$ ^{1}H NMR and the second isomer constitutes less than 10% of the material. The spectral featues of this complex are as expected except for an unusually high-field methyl singlet at 1.78 ppm. The remaining seven methyl singlets of the chelating terminal ligands are clustered near 2.5 ppm (ranging from 2.31 to 2.73 ppm). The substantial chemical shift difference of one N-bound alkyl group prompted us to examine the structure for a unique methyl environment, and we tentatively assign the 1.78-ppm signal to the thiocarboxamido methyl group that lies over the metal–metal bond axis (C(11) in Figure 1). Anomalous anisotropic chemical shifts have been reported previously for alkyl nuclei proximal to metal–metal triple[37] and quadruple[38] bonds in molybdenum dimers. A related anisotropic effect could provide an explanation for the anomalous chemical shift of the C(11) methyl protons in this dimer.

A spin saturation transfer experiment[39] was performed to probe high-temperature methyl-exchange processes in $Mo_2(\mu\text{-S})(\mu\text{-EtC}{\equiv}\text{CEt})(\text{dmtc})_3(\text{dmtca})$. At 80 °C in toluene-$d_8$ six of the eight signals exhibited pairwise exchange with one another. Selective saturation of each of the three singlets between 2.31 and 2.47 ppm caused an intensity decrease in a unique mate among the three methyl signals clustered between 2.64 and 2.68 ppm. Only the peaks at 2.73 and 1.78 ppm failed to respond to saturation of any of the remaining seven methyl resonances. The infrared ν(CN) data, the observed C–N distances, the location of one thiocarboxamido methyl group in the vicinity of the Mo–Mo axis, and the higher barrier to rotation of the C–N bond responsible for the methyl signals at 1.78 and 2.73 ppm as implied from the spin saturation transfer experiment merge to support assignment of these signals as due to the thiocarboxamido methyl groups. The conclusion that the dithiocarbamate ligands have slightly less multiple bond character in the C–N linkage than the thiocarboxamido ligand is supported not only by these pieces of evidence but also by literature precedent.[40]

^{13}C NMR Spectra. The most conspicuous feature of the $^{13}C\{^1H\}$ spectrum of $Mo_2(\mu\text{-S})(\text{EtC}{\equiv}\text{CEt})(\text{dmtc})_3(\text{dmtca})$ is a low-field singlet at 263.7 ppm with intensity comparable to signals assigned to the three central dithiocarbamate carbons in the region between 203 and 210 ppm.[41] The downfield signal can confidently be assigned to the thiocarboxamido metal-bound carbon in accord with previous carbon-13 results for $Fe(CO)_2(\text{dmtc})(\text{dmtca})$ where the dmtca central carbon exhibited a shift of 246.0 ppm.[42] The chemical shift of the dmtca carbon presumably reflects carbene character in the thiocarboxamido carbon–metal bond given the low-field resonances, often below 300 ppm, typical of metal–carbene complexes.[43]

The alkyne carbons attributable to the major isomer are evident as singlets at 149.0 and 143.8 ppm. The dithiocarbamate methyl groups can be assigned to the singlets near 39 ppm that span a range of only 0.6 ppm, thus leaving the signals near 46 ppm, spanning 1.5 ppm, as thiocarboxamido methyl groups. The relationship of the two dtca methyl groups to the Mo–Mo axis can again be invoked to rationalize the chemical shift difference between these two alkyl carbons. The two alkyne ethyl carbons appear well above all of the N-bound carbon-13 methyl resonances. The presence of a second isomer, as detected in ^{1}H spectra, is evident only in the more intense ^{13}C signals due to signal-to-noise limitations.

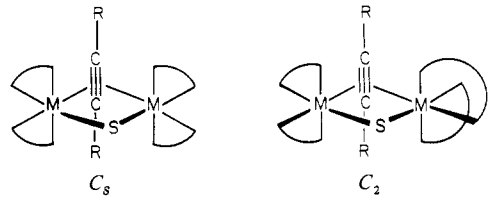
Qualitative Molecular Orbital Description. A qualitative understanding of the bonding scheme in this set of dimeric molecules can be initiated most simply by considering an idealized conlateral bioctahedral model bridged by one alkyne and one sulfur atom. For discussion purposes consider all four terminal chelating ligands to be dithiocarbamates in anticipation of ultimately replacing one of these with a thiocarboxamido to produce the actual dimeric unit. An axis system can be imposed on each of the octahedral components as shown.



If one views the bridging alkyne as providing one σ-electron pair to each metal center from the filled alkyne π orbitals an octahedral two above three orbital pattern serves as a point of departure for each six-coordinate metal center.

Following the common practice of considering acetylene to be a neutral ligand for purposes of assigning oxidation states a d^3 configuration results for each Mo(III) center with the S^{2-}, dtc^-, and $dtca^-$ ligands yielding a neutral $Mo_2(\mu\text{-S})(\mu\text{-RC}_2\text{H})(\text{dtc})_3(\text{dtca})$ molecule. Since assigning oxidation states is only a formalism, one could also consider acetylene to be a tetraanion, $\text{H}\ddot{\text{C}}{-}\ddot{\text{C}}\text{H}^{4-}$, leaving each metal as 5^+ (d^1); we will return to this alternative assignment, probably less appealing to most chemists, after the bonding description has been more fully developed. A third option might be to count the bridging alkyne as a dianion, $\text{H}\ddot{\text{C}}{=}\ddot{\text{C}}\text{H}^{2-}$, as is expedient for parallel bridging alkynes resembling dimetallated olefins,[44] but chemical intuition militates against this conceptualization in the present case. A lucid and extensive treatment of parallel and perpendicular, dianionic and neutral, alkyne bridge–metal bonding interactions has been published.[44]

Once the octahedral σ-bonding framework has been established, the three $d\pi$ orbitals of each metal and ligand π-type orbitals remain to be considered. A total of six electrons are available for occupation of $d\pi$-based MO's. Although the point group of the isolated dimers is C_1, the models built with four equivalent chelating ligands can be classified as C_2 or C_s depending on the relationship between the two $M(\text{dtc})_2$ ends of the molecule. In



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either of these two point groups a division into symmetric and antisymmetric representations aids in the MO analysis. Linear combinations of each related pair of metal $d\pi$ orbitals lead directly to the following molecular orbital features. The two d_{xy} orbitals are directed along the metal–metal axis such that the symmetric and antisymmetric combinations of these two orbitals correspond to metal–metal σ and σ^* MO's, respectively. The two d_{yz}-based combinations are directed toward the alkyne bridge, and utilization of the two vacant acetylene π^* orbitals, in accord with the Dewar–Chatt–Duncanson bonding model for olefin–metal bonding,[45] can be realized by back-donation from two filled d_{yz} $d\pi$ combinations. Both d_{yz}-based metal orbital combinations find an antibonding mate in the two alkyne π^* orbitals. At this point the diamagnetism and the metal–metal distance of 2.65 Å can be attributed to a metal–metal bond of order 1 and selective stabilization of the filled d_{yz} orbitals on each metal by the bridging alkyne π^* system.

Having distributed all of the $d\pi$ metal electrons into orbitals with bonding character we are left with two d_{xz} combinations that remain vacant. In light of previous studies involving vacant metal $d\pi$ orbitals,[19] an effort to identify ligands with π-electron density available for donation into these $d\pi$ orbitals was undertaken. Clearly the bridging sulfur can fill this role. For simplification consider sp^2 hybridization at the sulfur with two Mo–S bonds and one lone pair consuming the three sp^2 hybrid orbitals. The remaining lone pair in the unique sulfur p orbital is then available for π donation. Symmetry restrictions indicate that of the two d_{xz}-derived orbitals only the symmetric combination will be of the correct symmetry to form bonding and antibonding MO's when interactions with the bridging sulfur $p\pi$ are turned on. Obviously the d_{xz} symmetric combination takes on antibonding character and remains vacant while stabilizing the sulfur lone pair. The short Mo–S(1) bond lengths of 2.26 and 2.28 Å are compatible with this description invoking some degree of π bonding. Examples of metal–sulfur bonding geometries reflecting sulfur-to-metal π donation are common.[46]

At this point only the antisymmetric d_{xz} combination has not been incorporated into a bonding scheme of some sort, and hence it remains as a nonbonding orbital at the level of this crude description. It is here that the principle of maximum orbital utilization proves fruitful. *Nature attempts to avoid nonbonding orbitals.* Since no d electrons remain the antisymmetric d_{xz} combination can only serve as an acceptor orbital, and we now turn to the dithiocarbamate ligands in search of ligand π-electron density. The delocalized π-system present in the planar S_2CNR_2 unit can indeed provide electron density to appropriate $d\pi$ orbitals, but the chelate orientation alone dictates the location of the perpendicular sulfur $p\pi$ orbitals. Inspection of the model dimer reveals that only *two* of the eight terminal sulfur atoms, namely, S_3 and S_7, are correctly oriented to realize $p\pi$ overlap with the vacant d_{xz} orbital combination. The surrogate thiocarboxamido, S_5–S_6, is π innocent with respect to the d_{xz} orbitals, so the identity of the two unique π-donor sulfur atoms in the terminal positions transfers directly to the actual thiocarboxamido dimer. Inspection of the observed Mo–S distances provides strong support for this qualitative bonding picture since in fact S_3 and S_7 do exhibit bond lengths substantially shorter (~0.1 Å) than the remaining five Mo–S terminal bond lengths.

Incorporation of the thiocarboxamido ligand does not alter any of the gross bonding features derived above. The metal-bound carbon atom is only three-coordinate and hence, as is true in general for metal carbenes, a filled $d\pi$ orbital should be available to assist the nitrogen and sulfur lone-pair electrons in stabilizing this carbon center. Indeed the observed location of the $SCNR_2^-$ ligand places the vacant carbon $p\pi$ orbital in position to overlap with the d_{yz} orbital on Mo(2) that will be occupied on the basis of the analysis presented.

As alluded to above one can formally recognize π acceptance by the alkyne π^* orbitals by assigning oxidation states consistent with the involvement of four electron pairs and eight orbitals in the dimolybdenum alkyne bridge unit. A tetrahedrane analogy then applies with each carbon four-coordinate in a $C_2H_2^{4-}$ formulation. As when olefin bonding to a metal is depicted as a metallocyclopropane, this emphasizes the limiting case. Here the Mo^{5+} centers that result are left with d^1 configurations to form a metal–metal σ bond; this is of course consistent with a neutral acetylene plus back-bonding analysis. A thorough MO study of dinuclear bridging acetylene complexes has been presented that provides a much more general approach to related systems of interest.[44] The conclusions we reach agree with those of Hoffman, Hoffmann, and Fisel concerning the electronic structure of alkyne bridged dimers. Of particular interest were their calculations performed on two group 6 derivatives: analogues of $Mo_2(\mu\text{-}R'C{\equiv}CR')(\mu\text{-}OR)_2(OR)_4(py)_2$,[33] a confacial bioctahedral d^3–d^3 dimer, and $W_2(\mu\text{-}MeC{\equiv}CMe)(\mu\text{-}Br)Br(CO)_5(Ph_2AsCH_2AsPh_2)$,[47] a conlateral bioctahedral d^5–d^5 dimer.

The role of $d\pi$ orbitals in back-bonding to π-acid ligands has been enunciated as a key feature of metal–carbonyl and metal–olefin bonding. The chemical utility of ligand π donation has received less attention in recent years but may be of equal importance in many metal complexes. In this dimer system a simple conceptual bonding approach originating with two octahedral fragments enables one to focus on the nest of three $d\pi$ orbitals at each metal center. The resulting classification of these orbitals as metal–metal bonding, π accepting, or π donating produces an internally consistent MO description that nicely accounts for two uniquely short terminal Mo–S bonds observed in the crystal structure.

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Registry No. 1a (isomer 1), 84927-19-5; **1a** (isomer 2), 84985-67-1; **1a** (isomer 3), 84985-68-2; **1a** (isomer 4), 84985-69-3; **1b**, 84927-20-8; **2a**, 84927-21-9; **3a** (isomer 1), 84927-22-0; **3a** (isomer 2), 84985-70-6; **3a** (isomer 3), 84985-71-7; **3a** (isomer 4), 84985-72-8; **4a** (isomer 1), 84927-24-2; **4a** (isomer 2), 84985-73-9; $Mo(HC_2Ph)_2(S_2CNMe_2)_2$, 81476-37-1; $Mo(EtC_2Et)_2(S_2CNMe_2)_2$, 81476-39-3; $P(OmE)_3$, 121-45-9; PEt_3, 554-70-1; Mo, 7439-98-7.

Supplementary Material Available: Three figures [^1H NMR spectrum of $Mo_2(\mu\text{-}S)(\mu\text{-}HC_2\text{-}n\text{-}Bu)(dmtc)_3(dmtca)$ and ^1H and ^{13}C NMR spectra of $Mo_2(\mu\text{-}S)(\mu\text{-}EtC_2Et)(dmtc)_3(dmtca)$] and Tables VI–IX of thermal parameters, distances, angles, and observed and calculated structure factors, respectively (33 pages). Ordering information is given on any current masthead page.

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