

**Preparation and Characterization of
Bis(dialkyldithiocarbamato)[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]molybdenum(III)
Complexes Produced by the Oxidative Decarbonylation of
[HB(3,5-Me₂C₃N₂H)₃]Mo(CO)₃⁻ by Tetraalkylthiuram Disulfides. Crystal Structure of
[HB(3,5-Me₂C₃N₂H)₃]Mo(η²-S₂CNEt₂)(η¹-S₂CNEt₂)**

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The reactions of Et₄N[[HB(Me₂pz)₃]Mo(CO)₃] [HB(Me₂pz)₃⁻ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate anion] and tetraalkylthiuram disulfides in refluxing acetonitrile produce the yellow or orange, air-sensitive compounds [HB(Me₂pz)₃]Mo(η²-S₂CNR₂)(η¹-S₂CNR₂) (1, R = Me; 2, R = Et). The compounds are monomeric, paramagnetic (μ_{eff}: 1, 3.93 μ_B; 2, 3.84 μ_B) and exhibit infrared bands characteristic of both mono- and bidentate dithiocarbamate ligands. Complex 2 crystallizes in triclinic space group P1̄ with a = 10.162 (4) Å, b = 11.089 (4) Å, c = 31.10 (1) Å, α = 88.49 (3)°, β = 86.34 (3)°, γ = 68.37 (3)°, V = 3251 (3) Å³, and Z = 4. The structure was solved by Patterson and Fourier methods, followed by least-squares refinement, using 5547 reflections, to a conventional R value of 0.043 (R_w = 0.049). The complex possesses a distorted octahedral fac-N₃-fac-S₃ coordination sphere composed of tridentate HB(Me₂pz)₃⁻, bidentate S₂CNEt₂⁻, and monodentate S₂CNEt₂⁻ ligands. Structural comparison of the two dithiocarbamate ligands indicates considerable thioureide character in the η¹-ligand framework.

Introduction

Our investigation of the high-valent molybdenum chemistry of hydrotris(3,5-dimethyl-1-pyrazolyl)borate, HB(Me₂pz)₃⁻, is aimed at further understanding the structure and function of the mononuclear molybdenum active sites of oxo-type molybdoenzymes. Exploiting the "steric pocket" of this ligand to prevent dimerization reactions has, for example, permitted the preparation of a unique and extensive range of EPR-active monomeric Mo(V) complexes of the type [HB(Me₂pz)₃]MoOXY (X, Y = Cl⁻, NCS⁻, N₃⁻, OR⁻, SR⁻, and the dianions of HZCH₂CH₂ZH (Z = O, S), o-HOC₆H₄OH, o-HSC₆H₄OH, o-H₂NC₆H₄OH, o-H₂NC₆H₄SH, and o-HSC₆H₄SH).¹ The reversible electrochemical reduction of these Mo(V) complexes has encouraged our recent efforts to extend this chemistry to biologically relevant oxo- and sulfido-Mo(IV) species containing S-donor coligands. Toward this end, we investigated the reaction of [[HB(Me₂pz)₃]Mo(CO)₃]⁻ and tetraalkylthiuram disulfides as a possible route to Mo(II) species that could be air-oxidized to oxo-Mo(IV) complexes. Although [HB(Me₂pz)₃]MoO(S₂CNR₂) complexes may be prepared in such a manner,² the predominant products are monomeric Mo(III) complexes of the type [HB(Me₂pz)₃]Mo(η²-S₂CNR₂)(η¹-S₂CNR₂) (R = Me (1), Et (2)). The preparation and properties of these complexes and the molecular structure of 2, the first structurally characterized example of monodentate dithiocarbamate coordination in molybdenum chemistry, are the subject of this report. A preliminary account of this work has been published.³

Experimental Section

Materials and Methods. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate and Et₄N[[HB(Me₂pz)₃]Mo(CO)₃] were prepared by methods described by Trofimenko.^{4,5} The tetraalkylthiuram disulfides were purchased from Aldrich Chemical Co. The disulfides and Et₄N[[HB(Me₂pz)₃]Mo(CO)₃] were recrystallized from acetonitrile before use. The solvents employed were dried and deoxygenated, and all reactions and solution measurements were performed under an atmosphere of dinitrogen by using standard Schlenk and glovebox techniques. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer as KBr disks. The solution magnetic susceptibilities were measured by the Evans NMR method⁶ using a Bruker WM250 FT-NMR spectrometer; the data

were treated according to Live and Chan,⁷ and the molar susceptibilities were corrected for diamagnetism with use of the appropriate Pascal constants.⁸ The electronic spectra were recorded on an IBM 9420 spectrophotometer using quartz cells. Cyclic voltammograms at a platinum working electrode were recorded on an IBM EC/225 voltammetric analyzer using 10⁻³ M solutions of the complexes in 0.1 M Bu₄NBF₄/dimethylformamide. The experiments used an Ag/AgCl reference electrode (+0.19 V vs. SCE) and a platinum-wire auxiliary electrode. Microanalyses were performed by Atlantic Microlab Inc.

Preparation of Complexes. [HB(Me₂pz)₃]Mo(η²-S₂CNMe₂)(η¹-S₂CNMe₂) (1). A mixture of Et₄N[[HB(Me₂pz)₃]Mo(CO)₃] (1.0 g, 1.65 mmol) and tetramethylthiuram disulfide (0.62 g, 2.6 mmol) in acetonitrile (20 mL) was refluxed for 2 h. Upon cooling, the mixture was filtered in air, and the yellow crystals obtained were washed with acetonitrile (5 mL) and dried under vacuum. The yield was 0.4 g (37%). The compound was sometimes contaminated by small crystals of Mo-(S₂CNMe₂)₄, which were removed by recrystallization, under anaerobic conditions, from dichloromethane solutions by the addition of methanol.

Anal. Calcd for C₂₁H₃₄BMoN₈S₄: C, 39.8; H, 5.4; N, 17.5; S, 20.2. Found: C, 39.3; H, 5.4; N, 17.5; S, 19.8. Magnetic moment, CHCl₃ solution: μ_{eff} = 3.93 μ_B (300 K). Infrared spectrum: 2927 m, 2550 m, 1540 s, 1520 m, 1505 w, 1448 m, 1418 m, 1375 m, 1250 m, 1205 s, 1075 m, 1043 m, 982 s, 900 m, 855 m, 810 m, 780 m, 695 m, 640 m cm⁻¹. Electronic spectrum, CH₂Cl₂: λ 400 nm, ε 2700 (sh); λ 350 nm, ε 7100 (sh). Electrochemistry: irreversible reduction at -1.58 V.

[HB(Me₂pz)₃]Mo(η²-S₂CNEt₂)(η¹-S₂CNEt₂) (2). A mixture of Et₄N[[HB(Me₂pz)₃]Mo(CO)₃] (1.0 g, 1.65 mmol) and tetraethylthiuram disulfide (0.76 g, 2.56 mmol) in acetonitrile (20 mL) was refluxed for 3 h. Upon cooling, the mixture was filtered in air, and the orange crystals obtained were washed with acetonitrile (10 mL) and dried under vacuum. The yield was 0.6 g (53%). The compound may be recrystallized, under anaerobic conditions, from dichloromethane solution by the addition of methanol.

Anal. Calcd for C₂₅H₄₂BMoN₈S₄: C, 43.5; H, 6.1; N, 16.3; S, 18.6. Found: C, 43.3; H, 6.2; N, 16.3; S, 18.5. Magnetic moment, CHCl₃ solution: μ_{eff} = 3.84 μ_B (300 K). Infrared spectrum: 2975 m, 2927 m, 2540 m, 1540 s, 1504 s, 1475 w, 1448 s, 1418 s, 1370 s, 1352 s, 1300 m, 1254 s, 1207 s, 1150 m, 1125 m, 1070 m, 1045 m, 1005 m, 987 m, weak bands at 914, 850, 832, 813, 780, 692, 644, 569, 470, 363 cm⁻¹. Electronic spectrum, CH₂Cl₂: λ 400 nm, ε 1100 (sh); λ 350 nm, ε 4000 (sh). Electrochemistry: irreversible reduction at -1.73 V.

Crystal Structure Determination. Orange crystals of 2 were grown under anaerobic conditions by the slow diffusion of methanol into a dichloromethane solution of the compound. A plate-shaped crystal was mounted inside a capillary. Crystal data for 2, together with details of the X-ray diffraction experiment, are reported in Table I. Cell constants

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Table I. Experimental Details of the Crystal Structure Determination for $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\eta^2\text{-S}_2\text{CNEt}_2)(\eta^1\text{-S}_2\text{CNEt}_2)$

A. Crystal Data			
chem formula	$\text{C}_{25}\text{H}_{42}\text{BMoN}_8\text{S}_4$	$a, \text{\AA}$	10.162 (4)
fw	689.66	$b, \text{\AA}$	11.089 (4)
cryst dims, mm	$0.52 \times 0.25 \times 0.10$	$c, \text{\AA}$	31.100 (10)
peak width at half-height, deg	0.30	α, deg	88.49 (3)
cryst color	orange	β, deg	86.34 (3)
Mo $K\alpha$ radiation	0.71073	γ, deg	68.37 (3)
$\lambda, \text{\AA}$		$V, \text{\AA}^3$	3251 (3)
temp, °C	$23 \pm (1)$	Z	4
space group	$P\bar{1}$	$\rho_{\text{calc}} (\rho_{\text{meas}})$, g cm^{-3}	1.41 (1.38)
		μ, cm^{-1}	6.6
B. Intensity Measurements			
instrument	Syntax (Nicolet) P2 ₁ with modified software		
monochromator	graphite cryst, incident beam		
scan type	θ - 2θ		
scan rate, deg min ⁻¹	2.5–12.5		
scan width, deg	$K\alpha_1 - 1.1$ to $K\alpha_2 + 1.2$		
max 2θ , deg	45		
portion of sphere colld	$\pm h, \pm k, l$		
no. of reflns measd	8322 total, 5547 unique		
corren	Lorentz-polarization, reflcn averaging (agreement on $I = 2.2\%$ and on $F_o = 1.6\%$), analytical abs (0.791–0.958; av 0.937)		
C. Structure Solution and Refinement			
solution	Patterson method		
hydrogen atoms	included as fixed contributors to the structure factor		
refinement	full matrix least-squares		
minimization function	$\sum w(F_o - F_c)^2$		
least-squares wts	$4F_o^2/(\sigma^2(I) + (pF_o)^2)$; $p = 0.03$		
anomalous dispersion	all non-hydrogen atoms		
no. of reflns included	5547 with $F_o^2 > 3\sigma(F_o)^2$		
no. of params refined	703		
unwtd agreement factor	$\sum F_o - F_c / \sum F_o = 0.043$		
wtd agreement factor	$(\sum w(F_o - F_c)^2 / \sum wF_o^2)^{1/2} = 0.049$		
esd of observn of unit wt	1.63		
convergence, largest shift	0.20		
high peak in final diff map, e \AA^{-3}	0.55		

and an orientation matrix for data collection were obtained from least-squares refinement, using setting angles of 20 reflections in the range $20^\circ < 2\theta < 30^\circ$. Attempts to reduce the cell to one with only one molecule per asymmetric unit were unsuccessful. Three intense reflections were recollected every 100 reflections and showed no change in intensity throughout data collection. Lorentz and polarization corrections were applied to the raw data. An analytical absorption correction was made, but no decay correction was necessary.

The positions of the two Mo atoms were determined from the Patterson map. The remaining non-hydrogen atoms were located in successive difference Fourier syntheses. Hydrogen atoms were included in the structure factor calculation at idealized positions and were not refined. Scattering factors were taken from Cromer and Waber.⁹ Anomalous dispersion effects were included in F_o ; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.¹⁰ In the final cycles of refinement the non-hydrogen atoms were refined anisotropically. The largest peak in the final difference map was located near one of the Mo atoms. For space group $P\bar{1}$ and $Z = 4$, there are two molecules per asymmetric unit; parameters between atoms in different molecules show no unusual correlations. All correlation coefficients greater than 0.25 related thermal parameters B_{11} – B_{12} or B_{22} – B_{12} on the same atom. All calculations were performed on a PDP-11/34 computer using SDP-PLUS.¹¹ The final atomic coordinates for all non-hydrogen atoms may be found in Table II.¹²

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Selected bond distances and angles are given in Table III. The remaining bond distances and angles, anisotropic thermal parameters, calculated hydrogen atom positions, and structure factors (observed and calculated) have been included as supplementary material.

Results and Discussion

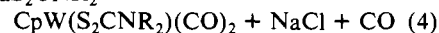
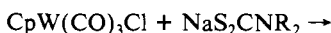
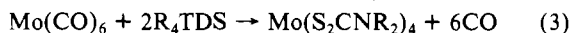
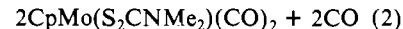
Syntheses and Properties. The complexes $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\eta^2\text{-S}_2\text{CNR}_2)(\eta^1\text{-S}_2\text{CNR}_2)$ ($R = \text{Me}$ (1), Et (2)) are produced by the anaerobic reaction of the appropriate tetraalkylthiuram disulfide, $\text{R}_2\text{NC}(\text{S})\text{SSC}(\text{S})\text{NR}_2$ (R_4TDS), with $\{\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\text{CO})_3\}^-$ in refluxing acetonitrile (eq 1). Solvent $\{\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\text{CO})_3\}^- + 1.5\text{R}_4\text{TDS} \rightarrow$



choice appears to be important to the success of the reaction. The relatively high boiling point of acetonitrile and the precipitation of the complexes from this solvent favor eq 1. The complexes are yellow (1) or orange (2) and are sparingly soluble in most organic solvents with the exception of CH_2Cl_2 , in which they are very soluble. As dry solids, the compounds may be handled in air for several hours, but in solution, decomposition is soon evident.

A three-electron oxidation of the molybdenum center clearly accompanies product formation. The mechanism of the reactions may involve Mo(II) intermediates such as $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\text{S}_2\text{CNR}_2)(\text{CO})$, which are further oxidized to the products by R_4TDS . The formation of such intermediates is supported by the isolation of $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoO}(\text{S}_2\text{CNR}_2)$ from the reaction mother liquors upon their exposure to air.²

The synthesis of group 6¹³ metal dithiocarbamate complexes by thermal routes invariably leads to bidentate coordination, e.g., the reactions shown in eq 2–4^{14–16} ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). Recently, $[\text{CpMo}(\text{CO})_3]_2 + \text{Me}_4\text{TDS} \rightarrow$



however, the first authentic example of monodentate dithiocarbamate coordination in group 6 chemistry, $\text{CpW}(\eta^1\text{-S}_2\text{CNMe}_2)(\text{CO})_3$, was prepared by a photochemical method.^{17,18} This complex readily loses a carbonyl ligand to form the bidentate dithiocarbamate complex, $\text{CpW}(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})_2$. In contrast to the above example, 1 and 2 are formed by a thermal route. Here, monodentate dithiocarbamate coordination is a consequence of the steric bulk of the $\text{HB}(\text{Me}_2\text{pz})_3^-$ ligand, which is known to restrict the coordination number of molybdenum to 6 in monomeric oxo–Mo(V),¹ oxo– and sulfido–Mo(IV),² and electron-deficient nitrosyl complexes, $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\text{NO})\text{XY}^{19}$ (X and Y are monoanions). The formation of the Mo(III) complexes also reflects the thermodynamic stability of the $\{\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}\}^{2+}$ core, a conclusion previously drawn from the isolation and redox properties of $\{\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{MoCl}_3\}^-$ and $\{\{\text{HB}(\text{pz})_3\}\text{MoCl}_2(\text{pyrazole})\}^-$ [$\text{HB}(\text{pz})_3^- = \text{hydrotris}(\text{pyrazolyl})\text{borate anion}$].²⁰ The large negative reduction potentials and the absence of oxidation processes in the cyclic voltammograms of 1 and 2 are consistent with this conclusion.

- (12) The complete atom-labeling scheme used for this structure determination is shown in Figure 1. In the tables, this scheme is further qualified by an additional digit, immediately following the element symbol, which refers to the independent molecule (1 or 2) to which the atom belongs.
 (13) The periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18.
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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, ^a Å ²	atom	x	y	z	B, ^a Å ²
Mo1	0.91582 (5)	0.01776 (5)	0.37639 (2)	2.39 (1)	C134	1.1501 (7)	0.0878 (7)	0.4495 (3)	4.8 (2)
Mo2	0.33125 (5)	0.48764 (5)	0.12949 (2)	2.35 (1)	C135	1.1910 (8)	-0.3684 (8)	0.4905 (3)	5.3 (2)
S11	0.7482 (2)	0.1516 (2)	0.32266 (6)	3.26 (4)	C141	0.7223 (6)	0.2834 (6)	0.3554 (2)	3.4 (2)
S12	0.8174 (2)	0.2496 (2)	0.39980 (6)	3.64 (4)	C142	0.5558 (8)	0.4282 (7)	0.3060 (3)	4.5 (2)
S13	1.1043 (2)	0.0722 (2)	0.33542 (7)	3.89 (4)	C143	0.4095 (8)	0.4267 (8)	0.3137 (3)	5.4 (2)
S14	1.3000 (2)	-0.2034 (2)	0.34931 (8)	4.65 (5)	C144	0.6119 (8)	0.5118 (7)	0.3731 (3)	5.3 (2)
S21	0.5208 (2)	0.3600 (2)	0.17772 (6)	3.54 (4)	C145	0.507 (1)	0.5249 (9)	0.4104 (3)	7.2 (3)
S22	0.4021 (2)	0.2512 (2)	0.11372 (6)	3.40 (4)	C151	1.2706 (6)	-0.0540 (6)	0.3306 (3)	3.7 (2)
S23	0.1626 (2)	0.4599 (2)	0.18610 (6)	3.43 (4)	C152	1.3579 (8)	0.1080 (7)	0.2956 (3)	5.6 (2)
S24	-0.0413 (2)	0.7251 (2)	0.16400 (7)	3.54 (4)	C153	1.318 (1)	0.1342 (8)	0.2506 (4)	7.7 (3)
N111	0.7547 (5)	-0.0382 (5)	0.4150 (2)	3.1 (1)	C154	1.520 (1)	-0.1340 (9)	0.2931 (4)	8.4 (3)
N112	0.8039 (5)	-0.1634 (5)	0.4318 (2)	3.1 (1)	C155	1.600 (1)	-0.139 (1)	0.3271 (5)	11.5 (4)
N121	0.9661 (5)	-0.1697 (5)	0.3479 (2)	2.8 (1)	C211	0.6049 (6)	0.4626 (7)	0.0600 (3)	4.3 (2)
N122	0.9873 (5)	-0.2760 (5)	0.3747 (2)	3.0 (1)	C212	0.6365 (7)	0.5448 (7)	0.0309 (3)	5.0 (2)
N131	1.0449 (5)	-0.0705 (4)	0.4297 (2)	2.6 (1)	C213	0.5216 (7)	0.6579 (7)	0.0300 (3)	4.8 (2)
N132	1.0565 (5)	-0.1943 (5)	0.4412 (2)	2.9 (1)	C214	0.6975 (7)	0.3313 (8)	0.0718 (3)	5.5 (2)
N141	0.6356 (5)	0.4021 (5)	0.3451 (2)	3.6 (1)	C215	0.5023 (9)	0.7802 (8)	0.0062 (3)	6.5 (2)
N151	1.3725 (6)	-0.0231 (6)	0.3093 (3)	6.1 (2)	C221	0.2946 (6)	0.7398 (6)	0.1868 (2)	3.1 (2)
N211	0.4727 (5)	0.5242 (5)	0.0778 (2)	3.3 (1)	C222	0.2545 (7)	0.8732 (6)	0.1798 (3)	3.9 (2)
N212	0.4214 (5)	0.6444 (5)	0.0588 (2)	3.6 (1)	C223	0.2351 (7)	0.8935 (6)	0.1370 (3)	3.9 (2)
N221	0.3004 (5)	0.6835 (5)	0.1491 (2)	2.8 (1)	C224	0.3286 (7)	0.6664 (7)	0.2270 (2)	4.1 (2)
N222	0.2636 (5)	0.7783 (5)	0.1176 (2)	3.2 (1)	C225	0.1879 (9)	1.0194 (7)	0.1127 (3)	5.8 (2)
N231	0.1750 (5)	0.5624 (4)	0.0822 (2)	2.6 (1)	C231	0.0707 (6)	0.5297 (6)	0.0686 (2)	3.1 (2)
N232	0.1612 (5)	0.6799 (4)	0.0637 (2)	3.0 (1)	C232	-0.0105 (6)	0.6260 (6)	0.0419 (2)	3.5 (2)
N241	0.6053 (5)	0.1042 (5)	0.1635 (2)	3.7 (1)	C233	0.0467 (7)	0.7193 (6)	0.0391 (2)	3.2 (2)
N251	-0.1143 (5)	0.5346 (5)	0.1960 (2)	3.7 (1)	C234	0.0497 (7)	0.4075 (6)	0.0822 (3)	4.2 (2)
C111	0.6165 (7)	0.0135 (7)	0.4271 (2)	3.7 (2)	C235	-0.0016 (8)	0.8458 (7)	0.0164 (3)	5.2 (2)
C112	0.5762 (7)	-0.0771 (7)	0.4509 (3)	4.8 (2)	C241	0.5207 (6)	0.2225 (6)	0.1526 (2)	3.2 (2)
C113	0.6957 (7)	-0.1864 (6)	0.4528 (2)	3.8 (2)	C242	0.7081 (7)	0.0829 (7)	0.1963 (3)	5.0 (2)
C114	0.5207 (7)	0.1469 (8)	0.4158 (3)	5.4 (2)	C243	0.8471 (9)	0.0869 (8)	0.1788 (3)	6.2 (2)
C115	0.7133 (8)	-0.3121 (7)	0.4753 (3)	5.6 (2)	C244	0.6008 (9)	-0.0102 (7)	0.1416 (3)	5.4 (2)
C121	0.9903 (6)	-0.2138 (6)	0.3074 (2)	3.4 (2)	C245	0.681 (1)	-0.0390 (9)	0.0991 (3)	7.5 (3)
C122	1.0273 (7)	-0.3475 (6)	0.3074 (2)	3.9 (2)	C251	-0.0095 (6)	0.5742 (6)	0.1826 (2)	2.7 (1)
C123	1.0249 (6)	-0.3838 (6)	0.3497 (2)	3.4 (2)	C252	-0.0940 (7)	0.4014 (7)	0.2093 (3)	5.0 (2)
C124	0.9783 (8)	-0.1254 (7)	0.2703 (3)	4.6 (2)	C253	-0.0764 (9)	0.3826 (8)	0.2573 (3)	6.8 (3)
C125	1.0544 (9)	-0.5147 (7)	0.3689 (3)	5.9 (2)	C254	-0.2620 (7)	0.6236 (7)	0.1958 (3)	5.1 (2)
C131	1.1343 (6)	-0.0389 (6)	0.4528 (2)	3.5 (2)	C255	-0.3241 (8)	0.6278 (8)	0.1526 (3)	6.7 (3)
C132	1.2011 (7)	-0.1427 (7)	0.4790 (3)	4.2 (2)	B1	0.9596 (8)	-0.2543 (7)	0.4232 (3)	3.4 (2)
C133	1.1524 (7)	-0.2383 (7)	0.4714 (2)	3.8 (2)	B2	0.2710 (8)	0.7430 (7)	0.0709 (3)	3.6 (2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $8\pi^2(U_{11} + U_{22} + U_{33})/3$.

Table III. Selected Bond Distances (Å) and Interbond Angles (deg) for [HB(Me₂p_z)₃]Mo(η²-S₂CNEt₂)(η¹-S₂CNEt₂)^a

	mol 1		mol 2	
Mo-S1	2.503 (2)	2.492 (2)	S1-C41	1.733 (6)
Mo-S2	2.500 (2)	2.503 (2)	S2-C41	1.690 (6)
Mo-S3	2.481 (2)	2.471 (2)	C41-N41	1.331 (7)
Mo-N11	2.228 (4)	2.217 (4)	S3-C51	1.753 (5)
Mo-N21	2.150 (4)	2.175 (4)	S4-C51	1.667 (6)
Mo-N31	2.162 (4)	2.153 (4)	C51-N51	1.338 (7)

	mol 1		mol 2	
S1-Mo-S2	70.56 (5)	70.82 (5)	S3-Mo-N11	177.2 (1)
S1-Mo-S3	87.33 (5)	86.04 (5)	S3-Mo-N21	96.4 (1)
S2-Mo-S3	86.32 (5)	87.22 (5)	S3-Mo-N31	94.6 (1)
S1-Mo-N11	95.4 (1)	96.9 (1)	N11-Mo-N21	82.7 (2)
S1-Mo-N21	98.4 (1)	100.1 (1)	N11-Mo-N31	82.7 (2)
S1-Mo-N31	170.5 (1)	169.0 (1)	Mo-S1-C41	86.6 (2)
N21-Mo-N31	90.5 (2)	90.8 (2)	Mo-S2-C41	87.7 (2)
S2-Mo-N11	95.0 (1)	95.5 (1)	S1-C41-S2	115.1 (3)
S2-Mo-N21	168.6 (1)	170.7 (1)	Mo-S3-C51	115.3 (2)
S2-Mo-N31	100.3 (1)	98.2 (1)	S3-C51-S4	123.1 (3)

^a mol 1 and mol 2 refer to molecules 1 and 2, respectively.

The infrared spectra of the complexes exhibit bands due to HB(Me₂p_z)₃⁻ ($\nu(\text{BH})$ 2540 cm⁻¹), bidentate S₂CNR₂⁻ (e.g., for 2 $\nu(\text{CN})$ 1504 cm⁻¹ and $\nu(\text{CS})$ 987 cm⁻¹) and monodentate S₂CNR₂⁻ (e.g., for 2 $\nu(\text{CN})$ 1475 cm⁻¹ and $\nu(\text{CS})$ 987 and 1005 cm⁻¹) ligands. No bands due to carbonyl, acetonitrile, or terminal oxo ligands are present. The complexes are paramagnetic with solution (CHCl₃) magnetic moments of 3.93 and 3.84 μ_{B} for 1 and 2, respectively. This is consistent with a $S = 3/2$ (d^3) ground state and a monomeric Mo(III) formulation. The electronic spectra exhibit slight shoulders on otherwise continuum absorptions into the UV region. The formulation of the complexes as six-

coordinate Mo(III) monomers, [HB(Me₂p_z)₃]Mo(η²-S₂CNR₂)(η¹-S₂CNR₂), was confirmed by the X-ray crystal structure of 2.

Description of the Structure. The unit cell of 2 contains two independent molecules of nearly identical structures, and unless otherwise stated, the following discussion refers to both molecules. An ORTEP view of molecule 2 is shown in Figure 1. The discrete monomeric complex possesses a distorted octahedral coordination sphere composed of monodentate and bidentate dithiocarbamate ligands and a facially tridentate HB(Me₂p_z)₃⁻ ligand. The most notable coordination sphere distortion is a trigonal elongation,

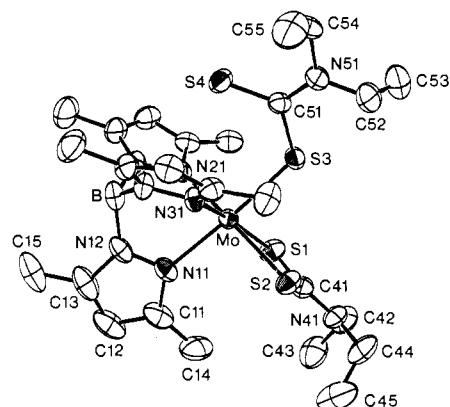


Figure 1. Molecular structure of molecule 2 of $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\eta^2\text{-S}_2\text{CNET}_2)(\eta^1\text{-S}_2\text{CNET}_2)$ showing the atom-labeling scheme.¹² The numbering of atoms in the pyrazole rings containing N21 and N31 parallels that shown for the ring containing N11. Thermal ellipsoids are plotted at the 50% probability level, and hydrogen atoms are not included.

which is reflected in the average N–Mo–S, S–Mo–S, and N–Mo–N bond angles of 96.6, 81.4, and 86.0°, respectively. Further distortion from this simplified view is produced by differing S1–Mo–S2, S1–Mo–S3, and S2–Mo–S3 bond angles; the relatively small S1–Mo–S2 angle is dictated by the bidentate coordination of the ligand containing S1 and S2. There is also an opening of the N21–Mo–N31 bond angle compared to those of N11–Mo–N21 and N11–Mo–N31, a likely consequence of the steric interactions of S4 with N21 and N31 and their respective pyrazolyl rings. The Mo–S bond lengths are almost identical although Mo–S3 is the shortest of the three. The Mo–N11 bond trans to the Mo–S3 bond is slightly longer than the Mo–N21 and Mo–N31 bonds. In oxo- and sulfido–Mo(IV) complexes of $\text{HB}(\text{Me}_2\text{pz})_3^-$, where the terminal chalcogenides exert a marked trans influence, the trans Mo–N bond is up to 0.28 Å longer than the other Mo–N bonds.² The slight lengthening observed in **2** suggests that there is little or no trans influence associated with the monodentate ligand.

The most remarkable feature of the structure is the monodentate dithiocarbamate ligand coordinated to Mo through S3, trans to the Mo–N11 bond. Both sulfur atoms of the monodentate ligand lie roughly in the pseudomirror plane defined by Mo, C41, N41, and the N11-containing pyrazolyl ring. (maximum displacement 0.08 Å for S4 of molecule 2). The presence of the methyl group on the $\text{HB}(\text{Me}_2\text{pz})_3^-$ ligand prevents the monodentate ligand from taking another orientation. The uncoordinated sulfur atom, S4, is located in the center of the S3–N21–N31-coordinated face 3.83 Å from the Mo atom, a distance larger than the sum of the van der Waals radii of Mo and S.²¹ The S4–N and S4–S3 distances are near the sums of the van der Waals radii for the atoms involved.²² The positioning of S4 results in the opening of the Mo–S3–C51 bond angle to 113.0 (2)°, a value much larger than the corresponding angle of the bidentate ligand (ca. 87.3°). The S3–C51–S4 bond angle is also ca. 8° larger than the S1–C41–S2 angle of the bidentate ligand. However, other structural features of the monodentate ligand are indicative of considerable thioureide character. The S3–C51 bond length of 1.749 (5) Å is only slightly longer than the S–C bonds of the bidentate ligand (1.732 (6) Å), while the S4–C51 bonds (ca. 1.67 Å) are longer than a normal C=S bond (1.61 Å²²). The short C51–N51 bond length (1.33 (1) Å) and its equality with the analogous bond of the bidentate ligand are also indicative of extensive π -bonding in the S₂CN portion of the monodentate ligand.²² Moreover, the monodentate ligand is nearly planar with an average (molecules 1 and 2) dihedral angle of ca. 7.8° between the planes defined

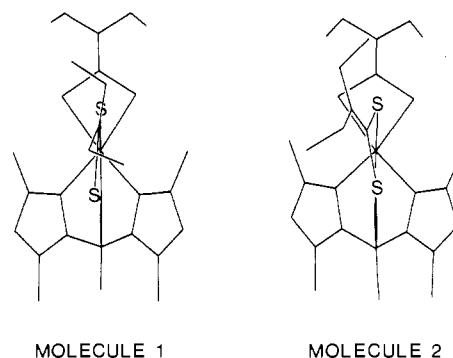


Figure 2. Identical views of molecules 1 and 2 showing the structural difference associated with the orientation of the monodentate ligands. Only the sulfur atoms of the monodentate ligands are identified.

by S3, C51, and S4 and by N51, C52, and C54. The thioureide character of the monodentate ligand is supported by the presence of an almost metrically identical bidentate ligand in the *same* molecule.

Unless noted above, the bond lengths and angles within the bidentate dithiocarbamate²³ and $\text{HB}(\text{Me}_2\text{pz})_3^-$ ligands²⁴ are comparable to values found elsewhere. The planarity of the bidentate ligand is reflected in a dihedral angle of ca. 1.2° between the S1, C41, and S2 and the N41, C44, and C42 planes. The ethyl substituents are syn with respect to the ligand plane.

The primary feature that distinguishes molecules 1 and 2 is the orientation of the monodentate ligand with respect to the pseudomirror plane. This structural difference is highlighted in Figure 2. In molecule 1, the dithiocarbamate ligand plane, defined by S3, S4, C51, N51, C52, and C54, lies close to the pseudomirror plane, the dihedral angle between these planes being only 8.9°. In molecule 2, the dithiocarbamate ligand plane makes an angle of 27.4° with the pseudomirror plane. The origin of this structural feature is the bending of S₂CNC₂ plane away from the plane of Mo, S3, and S4. In the case of molecule 2 this bending is quite striking, the C51, N51, C52, and C54 atoms being displaced by 0.40, 1.03, 1.50, and 1.37 Å, respectively, from this plane. Analogous values for molecule 1 (0.05, 0.07, 0.25, and 0.2 Å) reflect the less severe distortion of this molecule. If the two molecules are superimposed, the positions of N151 and N251 are separated by ca. 0.9 Å, with correspondingly larger differences in the positions of the ethyl group carbon atoms.

Despite the rich chemistry shared by molybdenum and dithiocarbamate ligands, **2** is the first structurally characterized example of monodentate dithiocarbamate coordination in molybdenum chemistry. Indeed, it is only the second example of this coordination mode known for any group 3 to group 7 transition metal. With the exception of $\text{CpW}(\eta^1\text{-S}_2\text{CNMe}_2)(\text{CO})_3$,^{17,18} all transition-metal examples of monodentate dithiocarbamate coordination are restricted to groups 8–11.²⁵ Interestingly, the structural parameters of the monodentate ligand in **2** closely resemble those found for the monodentate ligand in $\text{CpW}(\eta^1\text{-S}_2\text{CNMe}_2)(\text{CO})_3$. Moreover, Abrahamson et al.^{17,18} have pointed out that the monodentate ligand in $\text{CpW}(\eta^1\text{-S}_2\text{CNMe}_2)(\text{CO})_3$ (similarly for **2**) is quite distinct from those previously characterized structurally.²⁵ In particular, the metal to “uncoordinated”

(21) Assuming the van der Waals radius of molybdenum is not appreciably larger than that deduced for tungsten in ref 18, the sum of the van der Waals radii for Mo and S approximates 3.8 Å.

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(25) Monodentate dithiocarbamate ligands have been structurally characterized in the following cases. (a) $\text{Ru}(\text{S}_2\text{CNET}_2)_3(\text{NO})$: Domenicano, A.; Vacicago, A.; Zambonelli, L.; Loader, P. L.; Vanzani, L. M. *J. Chem. Soc., Chem. Commun.* **1966**, 476–477. (b) $\text{Au}(\text{S}_2\text{CNET}_2)_3$: Noordik, J. H. *Cryst. Struct. Commun.* **1973**, *2*, 81–84. (c) $\text{Pt}(\text{S}_2\text{CN-}i\text{-Bu}_2)_2(\text{PMe}_2\text{Ph})_2$: Lin, I. J. B.; Chen, H. W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 394–401. (d) $\text{Pt}(\text{S}_2\text{CN-}i\text{-Bu}_2)_2(\text{C}_6\text{H}_5)_2$: Christidis, P. C.; Rentzepis, P. J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *35B*, 2543–2547. (e) $\text{Pt}(\text{S}_2\text{CNET}_2)_2(\text{PPh}_3)_2$: Fackler, J. P., Jr.; Thompson, L. D.; Lin, I. J. B.; Stephenson, T. A.; Gould, R. O.; Alison, J. M. C.; Fraser, A. J. *F. Inorg. Chem.* **1982**, *21*, 2397–2403.

sulfur distances in $\text{CpW}(\eta^1\text{-S}_2\text{CNMe}_2)(\text{CO})_3$ (3.905 (1) Å and **2** are considerably longer than those observed previously (3.097^{25b} to 3.633 Å^{25a}). The shorter distances appear to reflect some bonding interaction in the late-transition-metal " η^1 -dithiocarbamate" complexes. Steric interactions involving S4 and the N21- and N31-containing pyrazolyl rings clearly dictate the Mo-S4 distance in **2**.

Concluding Remarks

The anaerobic reaction of $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\text{CO})_3^-$ and tetraalkylthiuram disulfides in refluxing acetonitrile results in the formation of η^1 -dithiocarbamate-Mo(III) complexes, $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\eta^2\text{-S}_2\text{CNR}_2)(\eta^1\text{-S}_2\text{CNR}_2)$. The complexes are postulated to form via the oxidation of Mo(II) intermediates, the monodentate ligation of the dithiocarbamate being dictated by the steric demands of the $\text{HB}(\text{Me}_2\text{pz})_3^-$ ligand. Oxidative addition of tetraalkylthiuram disulfides to other molybdenum complexes containing bulky *fac*-tridentate ligands, e.g., $(\text{Me}_3[9]\text{aneN}_3)$ -

$\text{Mo}(\text{CO})_3$,²⁶ may provide a general route to six-coordinate η^1 - S_2CNR_2^- complexes.

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Registry No. **1**, 102512-75-4; **2**, 102512-76-5; $\text{Et}_4\text{N}[\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\text{CO})_3]$, 22357-70-6; tetramethylthiuram disulfide, 137-26-8; tetraethylthiuram disulfide, 97-77-8.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and calculated hydrogen atom positions (6 pages); a table of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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Biological Analogues. A Structural Model for the Binding Site of Blue Copper Proteins

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A quadridentate chelate containing the ligands of the binding site of blue copper proteins has been synthesized. The chelate contains two imidazole, one thioether, and one mercaptan ligand, which can adopt a tetrahedral geometry about a metal ion. The mercaptan sulfur atom is sterically hindered in order to slow the rate of disulfide formation when copper(II) is coordinated. The ligand, when coordinated to cobalt(II), produces a spectacular blue complex, which, from physical data, is undoubtedly a tetrahedral species. Further, the electronic absorption spectrum of this complex is an excellent reproduction of the spectra observed for the cobalt(II)-substituted proteins plastocyanin and azurin. Although deep blue-green solutions are formed when the ligand is allowed to form a copper(II) complex, the copper is rapidly reduced in solutions even at low temperatures. A stable copper(II) complex could be isolated as a solid. Copper(II), however, does not form a tetrahedral monomer to any detectable extent; instead, tetragonal coordination oligomers appear to be the major species. The copper(I) complex also deposits as oligomers.

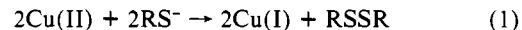
The design and synthesis of low molecular weight facsimiles of the copper binding site of blue proteins represents a challenge of considerable complexity. It is now known that the metal binding site of the plant protein plastocyanin consists of a copper atom coordinated to one mercaptide, one thioether, and two imidazole ligands in a highly distorted tetrahedral array with an exceptionally long copper-thioether bond.¹ A similar structure obtains for the related protein azurin,^{2,3} but this does not appear to be the case for another spectroscopically similar blue protein, stellacyanin, which is devoid of methionine.⁴ A number of attempts have been made to replicate some of the structural and electronic⁵ features of these proteins,⁶⁻¹¹ but none has involved the use of a single ligand

or a combination of ligands that incorporates all of the features of the blue binding site. These studies, however, have served to illustrate the difficulties of designing a stable system with all of the necessary characteristics.

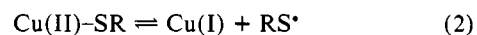
This paper describes a partially successful attempt at incorporating all of the donor ligands about a tetrahedral metal center by means of a quadridentate chelate.

1. Strategy

It has proved especially difficult to form stable copper(II)-mercaptide complexes because of the extremely rapid reduction of the metal and the irreversible formation of the corresponding disulfide (eq 1). There are a number of possible mechanisms



for this metal reduction, but we assume a radical coupling scheme after a one-electron reductive elimination of the copper(II)-mercaptide bond (eq 2 and 3). The reductive elimination (eq



2) is a reversible reaction, but the overall system is driven to completion by the formation of disulfide (eq 3). Clearly, the

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