trans configuration of the two thiocyanate ligands, but the broadness of the IR absorbance, as well as the small (but real) displacement of the Raman absorbance maximum from the position of the IR absorbance, leads to the not unexpected conclusion that ideal D_{2h} symmetry does not obtain, presumably due (in part) to the nonlinearity of the NCS ligand.

The structural inferences summarized above would seem to be important with respect to devising synthetic strategies involving Ru complexes that are intended for use as model compounds in a variety of physicochemical studies. In particular, the use of such complexes in the study of electron-transport processes in model systems having biological significance is being actively pursued in these laboratories. A clearer understanding of the stereochemistry of these materials would appear to be crucial in the pursuit of such studies.

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Note Added in Proof. After the completion of this study, it proved possible to grow diffraction-suitable single crystals from both CH_3CN and $(CH_3)_2SO$ solutions. In the presence of mother liquor, these crystals contain one molecule of solvent per metal atom and adopt a configuration in which the two SCN ligands are cis to each other. The details of these crystallographic studies are to be published.[23]

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Structures of Three Novel Polynuclear Oxo- and Sulfidomolybdenum Complexes Containing the Hydrotris(3,5-dimethyl-1-pyrazolyl)borate Ligand

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The complexes $[\{HB(Me_2pz)_3\}MoS(\mu\text{-}S)_2MoO(\mu\text{-}OH)]_2$ (**1**), $[\{HB(Me_2pz)_3\}MoO]_2(\mu\text{-}O)(\mu\text{-}S_2)$ (**2**), and $\{HB(Me_2pz)_3\}MoS(\mu\text{-}S)_2MoS(S_2CNEt_2)$ (**3**) have been isolated and characterized by X-ray crystallography. $\mathbf{1}\cdot 3C_2H_4Cl_2$ crystallizes in the triclinic space group $C\bar{1}$ with $a = 18.421$ (3) Å, $b = 10.547$ (3) Å, $c = 15.575$ (4) Å, $\alpha = 90.07$ (2)°, $\beta = 104.76$ (2)°, $\gamma = 90.53$ (2)°, and $Z = 2$. Each linear tetranuclear complex possesses $\bar{1}$ symmetry. $\mathbf{2}\cdot{}^1/_2C_6H_6$ crystallizes in monoclinic space group $P2_1/n$ with $a = 15.126$ (1) Å, $b = 14.364$ (2) Å, $c = 20.145$ (2) Å, $\beta = 105.835$ (7)°, and $Z = 4$. Complex **2** contains a rare mode of cis end-on disulfide bridge in which each molybdenum is coordinated to a different sulfur atom of the S_2^{2-} ligand. $\mathbf{3}\cdot{}^2/_3CH_2Cl_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.103$ (3) Å, $b = 16.107$ (4) Å, $c = 26.404$ (7) Å, $\alpha = 79.82$ (2)°, $\beta = 82.00$ (2)°, $\gamma = 85.51$ (2)°, and $Z = 6$. This binuclear complex contains both a six-coordinate molybdenum atom with an N_3S_3 coordination sphere and a five-coordinate molybdenum atom having only sulfur donor ligands. There are five different types of molybdenum–sulfur bonds in **3**.

Introduction

Recently, we have used the bulky tridentate ligand hydrotris(3,5-dimethyl-1-pyrazolyl)borate, $HB(Me_2pz)_3^-$, to prepare an extensive series of mononuclear six-coordinate oxo- and sulfidomolybdenum complexes with *fac* stereochemistries.[2-5] The 3-methyl groups of the ligand project beyond the metal atom and severely restrict the access of other ligands to the metal atom of the $[\{HB(3,5\text{-}Me_2pz)_3\}MoE]^{n+}$ (E = O, S; n = 1, 2) fragments. With a cone angle[6] of 225°,[7] $HB(Me_2pz)_3^-$ occupies over half the coordination sphere and thereby inhibits formation of dinuclear and polynuclear complexes with short molybdenum–molybdenum distances. However, we have now isolated three novel polynuclear complexes containing the $[\{HB(3,5\text{-}Me_2pz)_3\}MoE]^{2+}$ fragment. These complexes are produced in low yield, but their structural features include relatively unfamiliar bridging ligands for oxomolybdenum(V), namely μ-OH and μ-S_2, and an unusual linear tetranuclear complex.[8]

Experimental Section

Materials and Methods. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate was prepared by literature methods.[9] All reactions were performed under an atmosphere of pure dinitrogen with use of dried and deoxygenated solvents. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer as KBr disks. ^1H NMR spectra were recorded on a Bruker WM250 spectrometer with chemical shifts referenced to internal TMS.

Preparation of Compounds. $\mathbf{[\{HB(Me_2pz)_3\}MoS(\mu\text{-}S)_2MoO(\mu\text{-}OH)]_2}$ **(1).** This compound was isolated as a byproduct of the preparation of $[\{HB(Me_2pz)_3\}Mo(CO)_2]_2S$.[10] During the final step in the synthesis, chromatography on silica gel with dichloromethane as the eluant, the main product $[\{HB(Me_2pz)_3\}Mo(CO)_2]_2S$ eluted as a green fraction, followed by yellow and then red fractions. Partial evaporation of the red fraction and addition of dry ether gave red-brown microcrystals of the product (25 mg) as the ether solvate. Anal. Calcd for $C_{38}H_{64}B_2Mo_4N_{12}O_6S_6$: C, 33.00; H, 4.67; N, 12.16. Found: C, 32.19;

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Table I. Details of Structure Determinations

	1	2	3
	Crystal Data		
color	red-brown	purple	burgundy
size, mm		0.40 × 0.30 × 0.20	0.30 × 0.15 × 0.05
ω-scan width, deg		0.30	0.30
radiation		Mo Kα (0.710 73 Å)	
temp, °C		23 ± 1	
space group, crystl class	$C\bar{1}$, triclinic	$P2_1/n$, monoclinic	$P\bar{1}$, triclinic
cell params			
a, Å	18.421 (3)	15.126 (1)	12.103 (3)
b, Å	10.547 (3)	14.364 (2)	16.107 (4)
c, Å	15.575 (4)	20.145 (2)	26.404 (7)
α, deg	90.07 (2)	90.0	79.82 (2)
β, deg	104.76 (2)	105.835 (7)	82.00 (2)
γ, deg	90.53 (2)	90.0	85.51 (2)
cell vol, Å^3	2926	4211	5009
Z	2	4	6
ρ_{calcd}, ρ_{measd}, g cm^{-3}	1.74, 1.74	1.48	1.66, 1.61
μ, cm^{-1}	13.5	7.23	11.2
	Intensity Measurements		
scantype	θ/2θ	θ/2θ	ω
scan rate, deg min^{-1}	1.4–15	2.0–12.0	2.5–12.5
scan wdith, deg	2.0 + (Kα_2 − Kα_1)	2.2 + (Kα_2 − Kα_1)	0.7
2θ_{max}, deg	35.0	45.0	45.0
rflns collected	±h,±k,l	±h,k,l	±h,±k,l
no. of rflns (total, unique)	3913, 2627	5990, 5530	13 077, 12 708
corrections	Lp, decay, abs	Lp	Lp
rfln av (R_{int}), %	2.3	2.8	4.1
	Solution and Refinement		
no. of rflns (F_o^2 > 3σ(F_o^2))^a	1550	3717	6218
least-squares wts		$4F_o^2/(\sigma^2(F_o^2))$	
p		0.03	
no. of params	188	487	577
R^b	0.060	0.035	0.069
$R_w{}^c$	0.079	0.042	0.080
GOF^d	3.51	1.21	1.64
$(\Delta/\sigma)_{max}$	0.05	0.1	0.33
$\delta\rho_{max}$, e Å^{-3}	0.83	0.35	1.36

[a] $\sigma^2(F_o^2) = (\sigma^2(I) + (pF_o^2)^2)$. [b] $R = (\sum||F_o| - |F_c||/\sum|F_o|)$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [d] $\mathrm{GOF} = [(\sum w(|F_o| - |F_c|)^2)/(N_o - N_v)]^{1/2}$.

Table II. Positional Parameters for $[\{HB(Me_2pz)_3\}MoS(\mu\text{-}S)_2MoO(\mu\text{-}OH)]_2\cdot 3C_2H_4Cl_2$[a]

atom	x	y	z	B_{eq}, Å^2
Mo1	0.95314 (7)	0.1045 (1)	0.91996 (9)	1.78 (4)
Mo2	0.82028 (7)	0.1687 (1)	0.79171 (9)	1.68 (3)
S1	0.8616 (2)	0.3412 (4)	0.7511 (3)	2.8 (1)
S2	0.8460 (2)	0.1884 (4)	0.9457 (3)	2.1 (1)
S3	0.9099 (2)	0.0201 (4)	0.7805 (3)	2.4 (1)
O1	1.0115 (5)	0.224 (1)	0.9116 (7)	3.4 (3)
O2	0.9775 (5)	0.054 (1)	1.0544 (6)	2.5 (3)
N11	0.7129 (6)	0.266 (1)	0.7880 (8)	2.3 (3)*
N12	0.6459 (6)	0.223 (1)	0.7303 (8)	2.0 (3)*
N21	0.7677 (6)	0.115 (1)	0.6491 (8)	1.8 (3)*
N22	0.6908 (6)	0.090 (1)	0.6212 (8)	1.9 (3)*
N31	0.7422 (6)	−0.006 (1)	0.8079 (8)	2.1 (3)*
N32	0.6676 (6)	−0.005 (1)	0.7584 (8)	2.0 (3)*
C11	0.7512 (9)	0.459 (2)	0.885 (1)	3.5 (4)*
C12	0.6970 (8)	0.378 (2)	0.820 (1)	2.7 (4)*
C13	0.6217 (9)	0.408 (2)	0.784 (1)	3.2 (4)*
C14	0.5922 (8)	0.309 (2)	0.726 (1)	2.5 (4)*
C15	0.513 (1)	0.294 (2)	0.671 (1)	5.6 (5)*
C21	0.8743 (9)	0.135 (2)	0.577 (1)	3.5 (4)*
C22	0.7935 (8)	0.111 (2)	0.576 (1)	2.3 (4)*
C23	0.7357 (9)	0.079 (2)	0.505 (1)	2.8 (4)*
C24	0.6745 (8)	0.067 (1)	0.534 (1)	2.0 (3)*
C25	0.596 (1)	0.032 (2)	0.481 (1)	4.1 (4)*
C31	0.8192 (9)	−0.144 (2)	0.926 (1)	3.0 (4)*
C32	0.7492 (8)	−0.107 (1)	0.864 (1)	2.1 (4)*
C33	0.6803 (8)	−0.168 (2)	0.848 (1)	2.6 (4)*
C34	0.6309 (8)	−0.102 (2)	0.784 (1)	2.2 (4)*
C35	0.5506 (9)	−0.129 (2)	0.742 (1)	3.7 (4)*
B	0.6409 (9)	0.094 (2)	0.687 (1)	1.6 (4)*
Cl1	0.1847 (5)	0.2888 (9)	0.3262 (7)	14.8 (3)
Cl2	0.4172 (5)	0.360 (1)	0.4239 (6)	13.4 (3)
Cl3	0.0121 (5)	0.3807 (6)	0.1137 (5)	9.6 (2)
C1	0.280	0.265	0.383	6 (1)*
C1′	0.269	0.364	0.346	15 (2)*
C2	0.323	0.385	0.368	7 (1)*
C2′	0.334	0.286	0.404	10 (2)*
C3	−0.030	0.482	0.024	10 (1)*

[a] Starred values are for atoms refined isotropically. Anisotropically refined atoms are given with the isotropic equivalent thermal parameter defined as $8\pi^2(U_{11} + U_{22} + U_{33})/3$.

H, 4.36; N, 11.78. IR (KBr, cm^{-1}): ν(BH), 2540 m; ν(Mo=O), 965 s; ν(Mo=S), 508 m. EPR: no signal in solid or solution.

$[\{HB(Me_2pz)_3\}MoO]_2(\mu\text{-}O)(\mu\text{-}S_2)$ (2). This purple-brown compound was obtained in low yield when a slurry of 1 g (2 mmol) of $\{HB(Me_2pz)_3\}MoOCl_2$ and 0.42 g (2 mmol) of $NH_4[S_2P(OEt)_2]$ in 30 mL of dimethylacetamide was heated at 110 °C for 1.5 h. The solvent was removed in vacuo and the residue was extracted with dichloromethane, filtered, and evaporated to dryness.

$\{HB(Me_2pz)_3\}MoS(\mu\text{-}S)_2MoS(S_2CNEt_2)$ (3). This complex was isolated as a byproduct after preparation of $\{HB(Me_2pz)_3\}MoS(S_2CNEt_2)$[3] when the combined filtrate and washings were allowed to evaporate in air. The residue was chromatographed on silica with CH_2Cl_2 as the eluant. The first brown band was collected and recrystallized from CH_2Cl_2/methanol. Burgandy clusters of crystals were obtained in very low yield. IR (KBr, cm^{-1}): ν(BH), 2550; ν(CN), 1520 s; ν(Mo=S), 540, 505. ^{1}H NMR ($CDCl_3$, δ): 0.74, 2.18 (s, 2 × 3 H, Me of $HB(Me_2pz)_3^-$); 1.48 (t, J = 7.5 Hz, 6 H, 2 × CH_3); 2.57, 2.85 (s, 2 × 6 H, CH_3 of $HB(Me_2pz)_3^-$); 4.10 (m, second order, J_{AB} not determined, 4 H, 2 × CH_2); 5.16 (s, 1 H, CH of $HB(Me_2pz)_3^-$); 7.26 (s, 2 H, 2 × CH of $HB(Me_2pz)_3^-$).

Structure Determinations. Crystal data and details of the structure determinations are given in Table I. In each case, intensity data were collected on a Syntex $P2_1$ diffractometer, scattering factors were taken from Cromer and Waber,[11] anomalous dispersion effects were included for all non-hydrogen atoms with the values of Δf′, and Δf″ taken from Cromer,[12] and all calculations were performed on a PDP-11/34a computer using SDP-Plus.[13]

For $1\cdot 3C_2H_4Cl_2$, the lattice parameters are nearly consistent with a monoclinic C-centered cell, but the Laue symmetry is only $\bar{1}$. The data set was collected and the structure solved in the space group $C\bar{1}$, a nonstandard setting of $P\bar{1}$ (No. 2).[14] Data collection was initiated to 2θ = 45°, but after decay was observed, data collection was limited to 2θ = 35°. The positions of the two molybdenum atoms and three sulfur atoms were determined by direct methods. All other non-hydrogen atoms were found in succeeding difference electron density maps. Hydrogen atoms were added to the structure at calculated positions but not refined. An absorption correction by the method of Walker and Stuart[15] was performed. Because of the scarcity of data, only the molybdenum, sulfur, solvent chlorine, and oxygen atoms were refined anisotropically. Final R values for refinement with 188 variables and 1550 reflections with $F_o^2 > 2.5\sigma(F_o^2)$ were R = 0.060 and R_w = 0.079. Positional parameters for non-hydrogen atoms are given in Table II.

For $2\cdot{}^1/_2C_6H_6$, the positions of the molybdenum atoms were found from a Patterson map. All other non-hydrogen atoms were found in succeeding difference electron density maps. A benzene of solvation was found around the inversion center at $^1/_2$, $^1/_2$, $^1/_2$. Hydrogen atoms were added to the structure at calculated positions but not refined. Final R values for refinement with 487 variables and 3717 reflections with F_o^2

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(11) Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(12) Cromer, D. T. In *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(13) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R. van Konigsveldt, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 64–71.

(14) The reduced primitive cell corresponding to this centered cell has cell parameters a = 10.571 Å, b = 15.575 Å, c = 10.547 Å, α = 90.07°, β = 119.39°, and γ = 77.14°. The matrix for transformation from the C-centered to the primitive cell is

$$\begin{bmatrix} -0.5 & -0.5 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

(15) Walker, N.; Stuart, D. *Acta Crystallogr., Sect A: Found. Crystallogr.* **1983**, *A39*, 158–166.

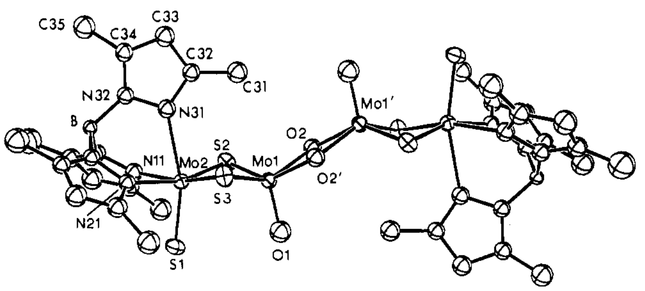

Figure 1. View of $[\{HB(Me_2pz)_3\}MoS(\mu\text{-}S)_2MoO(\mu\text{-}OH)]_2$ (**1**) showing the molecular structure and labeling scheme. Hydrogen atoms have been omitted. Pyrazole rings are labeled such that the first digit following the atomic symbol refers to the ring containing that atom and the second digit is a sequence number assigned in the same manner for all rings.

Table III. Positional Parameters for $[\{HB(Me_2pz)_3\}MoO]_2(\mu\text{-}O)(\mu\text{-}S_2)\cdot{}^1/_2C_6H_6$[a]

atom	x	y	z	B_{eq}, Å^2
Mo1	0.29191 (3)	0.01495 (3)	0.64803 (3)	3.18 (1)
Mo2	0.51131 (3)	0.09612 (3)	0.75818 (2)	3.08 (1)
S1	0.3677 (1)	−0.1101 (1)	0.71264 (9)	4.38 (4)
S2	0.5065 (1)	−0.0669 (1)	0.76311 (8)	4.04 (4)
O1	0.3034 (3)	−0.0120 (3)	0.5694 (2)	4.4 (1)
O2	0.4822 (3)	0.1260 (3)	0.8301 (2)	4.4 (1)
O3	0.3992 (2)	0.0801 (2)	0.6911 (2)	3.3 (1)
N11	0.2244 (3)	0.0545 (3)	0.7391 (2)	3.3 (1)
N12	0.1401 (3)	0.0985 (3)	0.7209 (2)	3.4 (1)
N21	0.1541 (3)	−0.0487 (3)	0.6184 (2)	3.3 (1)
N22	0.0764 (3)	0.0041 (3)	0.6145 (2)	3.4 (1)
N31	0.2200 (3)	0.1435 (3)	0.6034 (2)	3.5 (1)
N32	0.1340 (3)	0.1679 (3)	0.6068 (2)	3.1 (1)
N41	0.5939 (3)	0.0938 (3)	0.6754 (2)	3.6 (1)
N42	0.6635 (3)	0.1583 (4)	0.6806 (2)	3.8 (1)
N51	0.6569 (3)	0.1019 (3)	0.8217 (2)	3.9 (1)
N52	0.7144 (3)	0.1689 (3)	0.8092 (2)	3.8 (1)
N61	0.5234 (3)	0.2470 (3)	0.7375 (2)	3.4 (1)
N62	0.6062 (3)	0.2885 (3)	0.7395 (2)	3.8 (1)
C11	0.2485 (4)	0.0484 (4)	0.8084 (3)	3.8 (1)
C12	0.1811 (4)	0.0901 (5)	0.8337 (3)	4.4 (1)
C13	0.1144 (4)	0.1201 (4)	0.7777 (3)	3.9 (1)
C14	0.3307 (4)	−0.0010 (5)	0.8516 (3)	4.9 (2)
C15	0.0267 (5)	0.1667 (5)	0.7759 (3)	5.3 (2)
C21	0.1252 (4)	−0.1337 (4)	0.5938 (3)	4.2 (1)
C22	0.0301 (4)	−0.1360 (4)	0.5758 (3)	4.5 (2)
C23	0.0016 (4)	−0.0498 (5)	0.5887 (3)	4.0 (1)
C24	0.1893 (5)	−0.2092 (5)	0.5887 (4)	5.3 (2)
C25	−0.0945 (4)	−0.0145 (5)	0.5758 (4)	5.3 (2)
C31	0.2482 (4)	0.2100 (4)	0.5670 (3)	3.7 (1)
C32	0.1794 (4)	0.2763 (4)	0.5468 (3)	4.1 (1)
C33	0.1090 (4)	0.2481 (4)	0.5726 (3)	3.7 (1)
C34	0.3399 (4)	0.2064 (5)	0.5522 (3)	5.4 (2)
C35	0.0198 (4)	0.2951 (5)	0.5694 (4)	4.9 (2)
C41	0.5895 (4)	0.0447 (4)	0.6185 (3)	3.9 (1)
C42	0.6553 (4)	0.0765 (5)	0.5873 (3)	5.2 (2)
C43	0.7003 (4)	0.1477 (5)	0.6274 (3)	4.8 (2)
C44	0.5219 (4)	−0.0312 (5)	0.5938 (3)	4.9 (2)
C45	0.7764 (5)	0.2084 (6)	0.6179 (4)	6.8 (2)
C51	0.6974 (4)	0.0652 (4)	0.8842 (3)	4.2 (2)
C52	0.7804 (4)	0.1094 (5)	0.9097 (3)	4.8 (2)
C53	0.7891 (4)	0.1744 (5)	0.8631 (3)	4.5 (2)
C54	0.6557 (6)	−0.0077 (5)	0.9170 (4)	6.3 (2)
C55	0.8626 (5)	0.2451 (6)	0.8675 (4)	6.5 (2)
C61	0.4630 (4)	0.3155 (4)	0.7366 (3)	3.8 (1)
C62	0.5077 (4)	0.4002 (4)	0.7377 (3)	4.7 (2)
C63	0.5963 (5)	0.3818 (4)	0.7389 (3)	4.5 (2)
C64	0.3657 (4)	0.2986 (5)	0.7355 (4)	4.9 (2)
C65	0.6737 (5)	0.4474 (5)	0.7403 (4)	6.4 (2)
B1	0.0848 (4)	0.1033 (5)	0.6447 (4)	3.5 (2)
B2	0.6892 (5)	0.2250 (5)	0.7419 (4)	4.0 (2)
C71	0.5269 (7)	0.501 (1)	0.4415 (5)	12.0 (4)
C72	0.4759 (7)	0.5729 (9)	0.4564 (5)	10.6 (3)
C73	0.5483 (7)	0.427 (1)	0.4868 (5)	11.2 (4)

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

$> 3\sigma(F_o^2)$ were $R = 0.035$ and $R_w = 0.042$. Positional parameters for non-hydrogen atoms are given in Table III.

For $\mathbf{3}\cdot{}^2/_3CH_2Cl_2$, the suggested reduced primitive cell contains three crystallographically independent dimers and two solvent molecules. Attempts to find a cell of higher symmetry with the program TRACER[13] or the methods described in ref 16 were unsuccessful. The positions of the 6 molybdenum atoms and 24 sulfur atoms were found in the E map produced by the most probable solution from MULTAN. All other non-hydrogen atoms were found in succeeding difference electron density syntheses. After all three dimers in the asymmetric unit were completed, it became apparent that there were two dichloromethane molecules of solvation in the asymmetric unit. These were added to the structure, and refinement was pursued until convergence. Hydrogen atoms were not included in the calculations. Final R values for refinement with 577 variables and 6379 reflections with $F_o^2 > 3\sigma F_o^2$ were $R_1 = 0.069$ and $R_2 = 0.080$. Positional parameters are given in Table IV.

Results and Discussion

Structure of 1. The molecular structure of **1** is an unusual linear tetranuclear complex, shown with the atomic labeling scheme in Figure 1. The molecule has crystallographic $\bar{1}$ symmetry and contains two distinct molybdenum atoms. Mo1 is five-coordinate with square-pyramidal coordination, having one terminal oxo ligand in the apical position, two equatorial sulfido bridges to Mo2, and two equatorial oxygen bridges to a crystallographically identical Mo1. The sixth coordination site of Mo1 is blocked by a methyl group (Mo1–C31 = 3.58 Å, Mo1–H(calculated position) = 2.70 Å). Because of the imposed $\bar{1}$ symmetry, the central Mo_2O_4 portion of the molecule has anti stereochemistry. The structure can be described as an alternating linear chain of ligand-bridged molybdenum atoms with short–long–short metal–metal distances or as two Mo1–Mo2 dimers linked together by bridging oxygen atoms. The Mo2 atoms are assigned to be in the Mo(V) oxidation state, but Mo1 can be described as either Mo(VI) with the central fragment having an $[Mo_2O_4]^{4+}$ core or Mo(V) with an $[Mo_2O_2(OH)_2]^{4+}$ core.

The five-coordinate Mo1 atom is bonded to O1 in the apical position at a distance of 1.676 (6) Å. The sulfur atoms bridging to Mo2 are at distances of 2.296 (2) and 2.291 (2) Å from Mo1 while the oxygens bridging Mo1 and Mo1′ have bond distances of 2.098 (5) and 2.091 (4) Å to Mo1. These would be very long Mo–O distances if O2 were a bridging oxo ligand. Typical Mo–O distances for bridging oxygen atoms are 1.85–1.95 Å.[17] We know of no symmetrical, bridging Mo–O distances over 2.0 Å. Although nearly all Mo^{VI}–O bridges are linear, one complex is known for which an $[Mo_2O_4]^{4+}$ core has been structurally characterized, $(Et_4N)_2[Mo_2O_4(Et_2NO)_2(C_2O_4)]$.[18] In this complex, the Mo–O(bridging) bond distances are 1.98 and 1.91 Å. Thus, the observed Mo1–O2 distance of 2.09 Å appears to be too long for an Mo^{VI}–O oxo bridge. Methoxy-bridged dimers have been characterized and have Mo–O bond distances of 2.0–2.2 Å.[19] Thus, the formulation of Mo1 as Mo(V) and the core as a hydroxo-bridged fragment, $[Mo_2O_2(OH)_2]^{4+}$, is most consistent with the structural data. The lack of an EPR signal, even at 77 K, is also consistent with the formulation as a Mo(V) tetramer. Mo1 and Mo2, if both Mo(V), should be strongly coupled through the bis(μ-sulfido) bridge, resulting in a diamagnetic complex. If Mo1 were in the Mo(VI) oxidation state, little or no coupling of the two Mo(V) centers would be expected since the Mo2 atoms are separated by 7.47 Å.

The Mo2 atom has distorted-octahedral coordination geometry, with the $HB(Me_2pz)_3^-$ ligand occupying one trigonal face. A terminal sulfido ligand (Mo–S1 = 2.124 (2) Å) and two bridging sulfido ligands (Mo2–S2 = 2.332 (2) Å; Mo2–S3 = 2.325 (2)

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Table IV. Positional Parameters for $\{HB(Me_2pz)_3\}MoS(\mu\text{-}S)_2MoS(S_2CNEt_2)\cdot{}^2/_3CH_2Cl_2$[a]

atom	x	y	z	B_{eq}, Å^2	atom	x	y	z	B_{eq}, Å^2
Mo11	0.5384 (1)	0.4561 (1)	0.68807 (6)	2.47 (4)	C133	0.792 (2)	0.245 (1)	0.6890 (7)	3.3 (4)*
Mo12	0.3609 (1)	0.5460 (1)	0.63919 (7)	2.79 (4)	C134	0.488 (2)	0.232 (1)	0.6835 (8)	4.5 (5)*
Mo21	0.1881 (1)	0.0502 (1)	0.60395 (6)	2.83 (4)	C135	0.913 (2)	0.218 (1)	0.6940 (9)	4.9 (5)*
Mo22	0.1630 (1)	0.1114 (1)	0.49885 (7)	2.98 (4)	C141	0.303 (2)	0.657 (1)	0.5438 (7)	3.2 (4)*
Mo31	0.2364 (2)	0.2556 (1)	0.05377 (7)	3.32 (4)	C142	0.284 (2)	0.799 (1)	0.4944 (8)	4.8 (5)*
Mo32	0.3495 (2)	0.1169 (1)	0.11078 (7)	3.76 (4)	C143	0.398 (3)	0.829 (2)	0.471 (1)	9.2 (9)*
S11	0.4883 (4)	0.5997 (3)	0.6788 (2)	3.3 (1)	C144	0.260 (2)	0.671 (1)	0.4538 (8)	4.3 (5)*
S12	0.4544 (4)	0.4235 (3)	0.6214 (2)	3.1 (1)	C145	0.138 (2)	0.671 (1)	0.4525 (9)	5.1 (5)*
S13	0.4365 (5)	0.4009 (3)	0.7559 (2)	3.8 (1)	C211	0.195 (1)	0.261 (1)	0.6163 (7)	2.4 (4)*
S14	0.2214 (4)	0.5170 (4)	0.6948 (2)	4.3 (1)	C212	0.192 (1)	0.308 (1)	0.6555 (7)	2.5 (4)*
S15	0.3042 (5)	0.5478 (3)	0.5536 (2)	3.9 (1)	C213	0.195 (2)	0.252 (1)	0.7015 (7)	2.8 (4)*
S16	0.3297 (5)	0.6934 (3)	0.5975 (2)	3.9 (1)	C214	0.192 (2)	0.295 (1)	0.5593 (8)	3.9 (4)*
S21	0.0318 (4)	0.1155 (3)	0.5693 (2)	3.2 (1)	C215	0.192 (2)	0.269 (1)	0.7548 (7)	3.6 (4)*
S22	0.3237 (4)	0.1021 (3)	0.5367 (2)	3.4 (1)	C221	−0.022 (2)	−0.016 (1)	0.6952 (8)	3.8 (4)*
S23	0.1823 (5)	−0.0787 (3)	0.5973 (2)	4.5 (1)	C222	−0.050 (2)	−0.026 (1)	0.7481 (8)	3.7 (4)*
S24	0.1538 (5)	−0.0036 (4)	0.4739 (2)	4.6 (1)	C223	0.034 (2)	0.008 (1)	0.7659 (8)	4.3 (5)*
S25	0.2677 (5)	0.2044 (4)	0.4273 (2)	4.3 (1)	C224	−0.088 (2)	−0.040 (1)	0.6558 (8)	4.6 (5)*
S26	0.0317 (5)	0.2085 (4)	0.4503 (2)	4.1 (1)	C225	0.044 (2)	0.014 (2)	0.823 (1)	7.0 (7)*
S31	0.4027 (5)	0.1846 (3)	0.0284 (2)	3.8 (1)	C231	0.432 (2)	−0.025 (1)	0.6432 (8)	4.4 (5)*
S32	0.1620 (5)	0.1519 (4)	0.1195 (2)	4.4 (1)	C232	0.484 (2)	−0.031 (1)	0.6890 (9)	4.9 (5)*
S33	0.2872 (6)	0.3472 (4)	0.0932 (2)	5.2 (2)	C233	0.410 (2)	0.009 (1)	0.7238 (8)	3.8 (4)*
S34	0.4207 (6)	0.1772 (4)	0.1612 (3)	6.2 (2)	C234	0.470 (2)	−0.064 (1)	0.5954 (9)	5.0 (5)*
S35	0.2976 (5)	−0.0231 (4)	0.1606 (2)	4.9 (2)	C235	0.431 (2)	0.019 (2)	0.7763 (9)	6.0 (6)*
S36	0.4836 (5)	0.0067 (4)	0.0822 (2)	5.0 (2)	C241	0.141 (2)	0.242 (1)	0.4056 (7)	3.2 (4)*
N111	0.696 (1)	0.4966 (9)	0.6260 (5)	2.6 (3)*	C242	0.237 (2)	0.314 (1)	0.3243 (8)	4.6 (5)*
N112	0.801 (1)	0.4693 (9)	0.6367 (5)	2.8 (3)*	C243	0.283 (2)	0.250 (2)	0.291 (1)	7.4 (7)*
N121	0.663 (1)	0.4842 (9)	0.7379 (5)	2.7 (3)*	C244	0.022 (2)	0.320 (1)	0.3444 (9)	5.6 (6)*
N122	0.770 (1)	0.4501 (9)	0.7338 (8)	3.1 (3)*	C245	−0.012 (3)	0.279 (2)	0.305 (1)	9.0 (8)*
N131	0.638 (1)	0.3315 (9)	0.6849 (6)	3.4 (3)*	C311	0.152 (2)	0.102 (1)	−0.0079 (8)	4.3 (5)*
N132	0.753 (1)	0.3272 (9)	0.6885 (5)	2.7 (3)*	C312	0.080 (2)	0.095 (1)	−0.0448 (9)	4.9 (5)*
N141	0.284 (1)	0.7032 (9)	0.5004 (6)	3.3 (3)*	C313	0.042 (2)	0.179 (1)	−0.0628 (8)	4.4 (5)*
N211	0.200 (1)	0.1768 (9)	0.6370 (6)	2.9 (3)*	C314	0.217 (2)	0.027 (1)	0.0203 (9)	5.5 (6)*
N212	0.202 (1)	0.1736 (9)	0.6881 (5)	2.6 (3)*	C315	−0.042 (2)	0.209 (1)	−0.0997 (9)	5.5 (6)*
N221	0.074 (1)	0.0253 (9)	0.6802 (6)	3.2 (3)*	C321	0.363 (2)	0.382 (1)	−0.0444 (8)	4.3 (5)*
N222	0.111 (1)	0.0393 (9)	0.7239 (5)	2.9 (3)*	C322	0.345 (2)	0.425 (1)	−0.0940 (8)	4.7 (5)*
N231	0.326 (1)	0.018 (1)	0.6529 (6)	3.8 (4)*	C323	0.238 (2)	0.407 (1)	−0.1006 (8)	3.8 (4)*
N232	0.318 (1)	0.0395 (9)	0.7015 (6)	3.3 (3)*	C324	0.468 (2)	0.385 (1)	−0.0201 (9)	5.6 (6)*
N241	0.134 (1)	0.287 (1)	0.3599 (6)	3.6 (3)*	C325	0.177 (2)	0.433 (1)	−0.1461 (8)	4.6 (5)*
N311	0.157 (1)	0.1824 (9)	−0.0022 (6)	3.5 (3)*	C331	−0.008 (2)	0.345 (1)	0.0929 (8)	4.8 (5)*
N312	0.091 (1)	0.2301 (9)	−0.0371 (6)	3.4 (3)*	C332	−0.095 (2)	0.394 (1)	0.0702 (9)	5.3 (5)*
N321	0.270 (1)	0.3424 (9)	−0.0222 (6)	3.5 (3)*	C333	−0.072 (2)	0.396 (1)	0.0190 (8)	4.4 (5)*
N322	0.193 (1)	0.3587 (9)	−0.0565 (6)	3.4 (3)*	C334	0.012 (2)	0.324 (2)	0.151 (1)	6.3 (6)*
N331	0.066 (1)	0.318 (1)	0.0549 (6)	3.8 (4)*	C335	−0.140 (2)	0.442 (2)	−0.023 (1)	6.4 (6)*
N332	0.022 (1)	0.350 (1)	0.0088 (6)	3.7 (4)*	C341	0.417 (2)	−0.067 (1)	0.1276 (8)	4.0 (5)*
N341	0.452 (1)	−0.147 (1)	0.1365 (6)	3.8 (4)*	C342	0.546 (2)	−0.183 (1)	0.1055 (8)	4.5 (5)*
C111	0.707 (2)	0.550 (1)	0.5798 (7)	3.4 (4)*	C343	0.649 (2)	−0.187 (2)	0.130 (1)	7.1 (7)*
C112	0.823 (2)	0.556 (1)	0.5628 (7)	3.4 (4)*	C344	0.387 (2)	−0.209 (1)	0.1788 (9)	5.4 (6)*
C113	0.879 (2)	0.507 (1)	0.5999 (7)	3.1 (4)*	C345	0.310 (3)	−0.258 (2)	0.156 (1)	10.1 (9)*
C114	0.613 (2)	0.593 (1)	0.5505 (8)	3.9 (4)*	B1	0.819 (2)	0.409 (1)	0.6861 (8)	2.9 (5)*
C115	1.004 (2)	0.486 (1)	0.5998 (8)	3.9 (5)*	B2	0.214 (2)	0.088 (1)	0.7245 (9)	3.0 (5)*
C121	0.650 (2)	0.522 (1)	0.7805 (7)	3.3 (4)*	B3	0.076 (2)	0.324 (1)	−0.0443 (9)	3.7 (5)*
C122	0.750 (2)	0.511 (1)	0.8030 (8)	4.8 (5)*	Cl1	0.853 (2)	0.152 (1)	0.0665 (7)	10.1 (5)*
C123	0.823 (2)	0.467 (1)	0.7723 (7)	3.2 (4)*	Cl2	0.783 (2)	0.168 (1)	0.2534 (8)	10.7 (5)*
C124	0.543 (2)	0.566 (1)	0.8009 (8)	4.3 (5)*	Cl3	0.286 (2)	0.782 (1)	0.0012 (8)	11.2 (5)*
C125	0.944 (2)	0.434 (2)	0.777 (1)	6.4 (6)*	Cl4	0.700 (2)	0.306 (2)	0.198 (1)	16.0 (8)*
C131	0.609 (1)	0.254 (1)	0.6837 (7)	2.5 (4)*	C1s	0.693 (4)	0.243 (3)	0.273 (2)	5 (1)*
C132	0.701 (2)	0.197 (1)	0.6864 (8)	3.7 (4)*	C2s	0.712 (5)	0.212 (4)	0.052 (2)	10 (2)*

[a] Starred values are for atoms refined isotropically. Anisotropically refined atoms are given with the isotropic equivalent thermal parameter defined as $8\pi^2(U_{11} + U_{22} + U_{33})/3$.

Å) occupy the opposite face. The Mo2–N distances show the usual trans influence with Mo2–N31 trans to S1 being longer than the other Mo2–N bond distances. Other bond distances and angles in the $HB(Me_2pz)_3^-$ ligand and the coordination spheres are normal.[20] The dihedral angle between the Mo1–S2–S3 plane and the Mo2–S2–S3 plane is 148°, similar to that for other $[Mo_2S_3O]^{2+}$ units with syn stereochemistry.[21]

Most tetranuclear molybdenum-containing complexes heretofore structurally characterized do not have an extended geometry but rather bend back upon themselves to form cubane-like or ring structures.[22] The steric constraints of the $HB(Me_2pz)_3^-$ ligand prevent the formation of such structures, whereas linear arrays such as observed in this complex and in the complex $Mo_4\{HB(pz)_3\}_2O_4(\mu\text{-}O)_4(\mu\text{-}OMe)_2(MeOH)_2$[23] sterically isolate the polypyrazolylborate ligands.

Structure of 2. The molecular structure of **2** is shown in Figure 2. This dinuclear complex contains identical $\{HB(Me_2pz)_3\}MoO$ fragments bridged by an oxo and a disulfido group. The molybdenum is six-coordinate with the oxo group, the oxo bridge,

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Table V. Selected Bond Distances (Å) and Angles (deg) in the Coordination Spheres and Bridging Atoms of **1–3**

[{HB(Me_2pz)$_3$}MoS(μ-S)$_2$MoO(μ-OH)]$_2$ (**1**)							
Mo1–Mo2	2.825 (1)	Mo1–O1	1.676 (6)	Mo2–S1	2.124 (2)	Mo2–N11	2.227 (7)
Mo1–Mo1′	3.457 (1)	Mo1–O2	2.098 (5)	Mo2–S2	2.332 (2)	Mo2–N21	2.253 (7)
Mo1–S2	2.296 (2)	Mo1–O2′	2.091 (4)	Mo2–S3	2.325 (2)	Mo2–N31	2.378 (7)
Mo1–S3	2.291 (2)						
Mo1–S2–Mo2	75.22 (7)	S3–Mo1–O2	141.5 (2)	S1–Mo2–S2	103.8 (1)	S2–Mo2–N21	163.4 (2)
Mo1–S3–Mo2	75.46 (7)	O1–Mo1–O2	106.9 (3)	S1–Mo2–S3	104.1 (1)	S2–Mo2–N31	85.8 (2)
Mo1–O2–Mo1′	111.2 (2)	N11–Mo2–N21	86.2 (2)	S1–Mo2–N11	88.5 (2)	S3–Mo2–N11	164.1 (2)
S2–Mo1–S3	102.12 (8)	N11–Mo2–N31	78.9 (2)	S1–Mo2–N21	90.7 (2)	S3–Mo2–N21	83.9 (2)
S2–Mo1–O1	102.5 (2)	N21–Mo2–N31	78.3 (2)	S1–Mo2–N31	163.7 (2)	S3–Mo2–N31	86.8 (2)
S2–Mo1–O2	84.3 (2)	S2–Mo1–O2′	142.6 (3)	S2–Mo2–S3	100.02 (8)	S3–Mo1–O2′	85.4 (2)
S3–Mo1–O1	106.8 (2)	O1–Mo1–O2′	104.1 (3)	S2–Mo2–N11	86.1 (2)	O2–Mo1–O2′	68.8 (2)
[{HB(Me_2pz)$_3$}MoO]$_2$(μ-O)(μ-S_2) (**2**)							
Mo1–S1	2.328 (2)	Mo2–S2	2.346 (2)	Mo1–N21	2.205 (4)	Mo2–N51	2.226 (4)
Mo1–O1	1.685 (4)	Mo2–O2	1.681 (4)	Mo1–N31	2.207 (4)	Mo2–N61	2.224 (5)
Mo1–O3	1.869 (3)	Mo2–O3	1.872 (3)	S1–S2	2.159 (2)	Mo1–Mo2	3.65
Mo1–N11	2.399 (5)	Mo2–N41	2.341 (5)				
Mo1–S1–S2	107.99 (8)	Mo2–S2–S1	107.72 (7)	O1–Mo1–N21	89.0 (2)	O2–Mo2–N51	86.9 (2)
Mo1–O3–Mo2	153.8 (2)			O1–Mo1–N31	88.6 (2)	O2–Mo2–N61	88.1 (2)
S1–Mo1–O1	100.8 (2)	S2–Mo2–O2	101.5 (2)	O3–Mo1–N11	91.3 (2)	O3–Mo2–N41	92.2 (2)
S1–Mo1–O3	83.9 (1)	S2–Mo2–O3	82.9 (1)	O–Mo1–N21	166.0 (2)	O3–Mo2–N51	168.2 (2)
S1–Mo1–N11	90.1 (1)	S2–Mo2–N41	92.6 (1)	O–Mo1–N31	92.2 (2)	O3–Mo2–N61	95.1 (2)
S1–Mo1–N21	96.7 (1)	S2–Mo2–N51	92.9 (1)	N11–Mo1–N21	74.8 (2)	N41–Mo2–N51	76.9 (2)
S1–Mo1–N31	170.5 (1)	S2–Mo2–N61	170.4 (1)	N11–Mo1–N31	81.3 (2)	N41–Mo2–N61	78.1 (2)
O1–Mo1–O3	104.6 (2)	O2–Mo2–O3	104.7 (2)	N21–Mo1–N31	85.0 (2)	N51–Mo2–N61	87.3 (2)
O1–Mo1–N11	161.5 (2)	O2–Mo2–N41	159.1 (2)				
{HB(Me_2pz)$_3$}MoS(μ-S)$_2$MoS(S_2CNEt_2) (**3**)[a,b]							
Mo1–Mo2	2.829 (2)	Mo1–S3	2.122 (5)	Mo2–S4	2.094 (5)	Mo1–N11	2.38 (2)
Mo1–S1	2.315 (5)	Mo2–S1	2.281 (6)	Mo2–S5	2.461 (6)	Mo1–N21	2.25 (2)
Mo1–S2	2.319 (6)	Mo2–S2	2.288 (5)	Mo2–S6	2.462 (5)	Mo1–N31	2.24 (2)
Mo1–S1–Mo2	76.0 (2)	S2–Mo2–S5	82.7 (2)	S1–Mo1–N11	85.4 (4)	S3–Mo1–N11	164.0 (4)
Mo1–S2–Mo2	75.8 (2)	S2–Mo2–S6	142.1 (2)	S1–Mo1–N21	86.2 (4)	S3–Mo1–N21	89.5 (4)
S1–Mo2–S2	100.8 (2)	S4–Mo2–S5	107.0 (2)	S1–Mo1–N31	162.3 (4)	S3–Mo1–N31	90.7 (4)
S1–Mo2–S4	107.6 (2)	S4–Mo2–S6	106.6 (2)	S2–Mo1–S3	103.7 (2)	N11–Mo1–N21	78.2 (5)
S1–Mo2–S5	141.2 (2)	S5–Mo2–S6	70.6 (2)	S2–Mo1–N11	87.8 (4)	N11–Mo1–N31	77.7 (5)
S1–Mo2–S6	85.2 (2)	S1–Mo1–S2	98.8 (2)	S2–Mo1–N21	163.8 (4)	N21–Mo1–N31	85.0 (5)
S2–Mo2–S4	107.9 (2)	S1–Mo1–S3	104.6 (2)	S2–Mo1–N31	85.9 (4)		

[a] Distances and angles are the average for three crystallographically independent molecules. [b] Numbers in parentheses are the esd's of individual measurements. In all cases, the variation among the individual measurements is less than 2 times the esd.

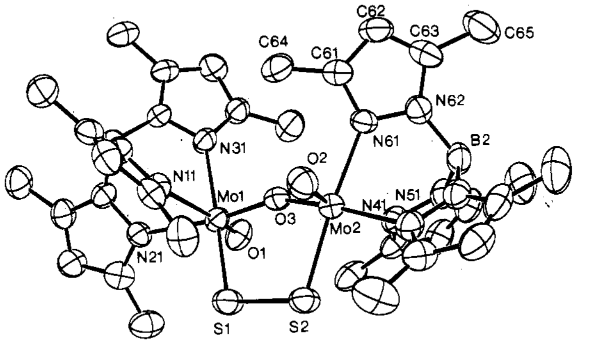

Figure 2. View of [{HB(Me_2pz)$_3$}MoO]$_2$(μ-O)(μ-S_2) (**2**) showing the molecular structure and labeling scheme. Hydrogen atoms have been omitted. Pyrazole rings are labeled as in Figure 1.

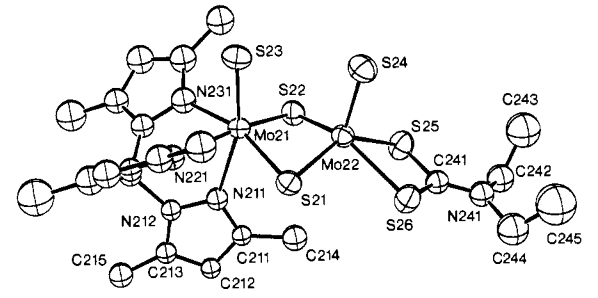

Figure 3. View of molecule 2 in {HB(Me_2pz)$_3$}MoS(μ-S)$_2$MoS(S_2CNEt_2) (**3**) showing the molecular structure and labeling scheme. Hydrogen atoms have been omitted. The first digit in each atom name refers to the crystallographically independent molecule. Pyrazole rings are labeled such that the second digit following the atomic symbol refers to the ring containing that atom and the third digit is a sequence number assigned in the same manner for all rings.

and a sulfur atom of the disulfide bridge occupying one face of the distorted octahedron and the pyrazolylborate ligand the other. The Mo1–Mo2 distance is 3.65 Å, and the Mo1–O3–Mo2 angle is 153.8°. Selected bond distances and angles within the coordination spheres are given in Table V. These bond distances and angles and those of the HB(Me_2pz)$_3^-$ ligand are not unusual.[20]

The disulfido group forms an unusual symmetric cis end-on bridge in which each sulfur is bonded to only one molybdenum atom. Generally, in molybdenum chemistry at least one of the molybdenum atoms is bonded to both sulfurs of the bridging disulfide group.[24] In each case where a cis end-on disulfide bridge has been observed, another bridging ligand has also been present.[25,26] In **2**, the unusual bridge is dictated by the presence of the oxo bridging group. The S–S bond length of 2.15 Å is longer than the S–S bond lengths previously reported for bridging disulfides (2.01–2.11 Å).[24]

Structure of 3. A drawing of one of the three crystallographically independent molecules of **3** is shown in Figure 3. The

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binuclear structure contains a distorted-octahedral Mo1 atom coordinated by the facial $HB(Me_2pz)_3^-$ ligand, a terminal sulfido ligand, and two bridging sulfido ligands. The Mo2 atom is five-coordinate and square-pyramidal with two bridging sulfido ligands, the $S_2CNEt_2^-$ ligand, and the apical sulfido ligand. The central $[Mo_2S_4]^{2+}$ unit exhibits syn stereochemistry; the terminal sulfido ligands are eclipsed, with an S=Mo—Mo=S torsion angle of 1.0° (average of three independent molecules). There are five significantly different Mo–S bonds in this molecule; Mo1=S (2.123 Å), Mo2=S (2.094 Å), Mo1—S(bridging) (2.31 Å), Mo2-S(bridging) (2.28 Å), and Mo2-S(dithiocarbamate) (2.46 Å). The Mo2=S bond is shorter than the Mo1=S bond because of the pyrazolylborate ligand nitrogen atom in the position trans to Mo1=S. In general, Mo=E (E = O, S) bonds are shorter in square-pyramidal than in octahedral complexes.[3] Mo2 is shifted 0.7 Å out of the plane of the equatorial ligands toward the sulfido group, not unusual for square-pyramidal molybdenum.[3] The Mo1–N distances show the expected trans influence. Bond distances and angles in the organic ligands and the coordination sphere are not unusual.[3,20]

There are no significant differences in bond distances or angles in the molybdenum coordination sphere between the crystallographically independent molecules. The three complexes differ only in the orientation of the ethyl groups of the dithiocarbamate ligands. Molecules 1 and 3 are identical, with an anti conformation of the ethyl groups (the average torsional angle C43–C42–C44–C45 is −147°), whereas for molecule 2 the ethyl groups are syn (C43–C42–C44–C45 torsion angle is −18°). Whenever more than one identical molecule exists in the unit cell, the possibility of missed symmetry must be considered. Molecule 2 has near-mirror symmetry. If crystallographic *m* symmetry is present, the pyrazole ring containing N211 is required to lie on the mirror. However, this ring is canted by 7° from the mirror plane and the methyl group carbon atoms of this ring, C214 and C215, lie 0.2 Å from the possible mirror plane. Also, the other complexes and solvent molecules in the unit cell are not related to each other by this proposed mirror plane. Consequently, crystallographic *m* symmetry does not exist and the description of the structure in this unit cell seems justified.

Formation of Complexes. Compound **1**, which contains the novel linear $[Mo_4S_6O_2(OH)_2]^{2+}$ core, is a minor byproduct from the oxidative decarbonylation of $[\{HB(Me_2pz)_3\}Mo(CO)_3]^-$ by excess sulfur. The major product of the reaction[10] is $[\{HB(Me_2pz)_3\}Mo(CO)_2]_2S$. The oxo groups of **1** probably result from the reaction of an unstable sulfur-rich species with adventitious water or with silica gel used in chromatography of the reaction mixture. The formation of **1** from the $[\{HB(Me_2pz)_3\}Mo(CO)_3]^-$ ion also involves the loss of the $HB(Me_2pz)_3$ ligand from half the molybdenum atoms in the complex.

Compound **2**, which contains the hitherto unknown $[MoO(\mu\text{-}O)(\mu\text{-}S_2)MoO]^{2+}$ core, is formed in low yield from the reaction of $\{HB(Me_2pz)_3\}MoOCl_2$ and $NH_4[S_2P(OEt)_2]$ in dimethylacetamide. Clearly the bridging S_2^{2-} ligand is derived from the dithiophosphate; the bridging oxo ligand probably arises from trace amounts of water in the dimethylacetamide. The related complex $\{HB(pz)_3\}MoOCl_2$ is known to react with water to form $[\{HB(pz)_3\}MoOCl]_2O$.[23] The isolation of **2** is yet another example of the ability of the polypyrazolylborate ligands to stabilize unusual structural features.

Compound **3** contains the well-known $[Mo_2S_2(\mu\text{-}S)_2]^{2+}$ core. However, to our knowledge **3** is the first such complex that contains a different capping ligand on each molybdenum atom. Compound **3** is formed as a minor byproduct during the preparation and purification of $\{HB(Me_2pz)_3\}MoS(S_2CNEt_2)$ from B_2S_3 and $\{HB(Me_2pz)_3\}MoO(S_2CNEt_2)$. Boron sulfide can produce polysulfide species in reactions with molybdenum complexes. For example, $\{HB(Me_2pz)_3\}MoCl(S_4)$ is formed from the reaction of B_2S_3 with $\{HB(Me_2pz)_3\}MoOCl_2$.[27] Internal redox reactions and dimerization reactions of molybdenum polysulfide complexes could lead to the $[Mo_2S_2(\mu\text{-}S)_2]^{2+}$ core of **3**.[28,29] Coordination of a $HB(Me_2pz)_3^-$ ligand to each Mo atom is prevented by the severe steric interactions that would occur between the methyl groups of the ligands due to the short Mo–Mo distance (2.83 Å) of the $[Mo_2S_2(\mu\text{-}S)_2]^{2+}$ unit.

Conclusions

The steric constraints of the $HB(Me_2pz)_3^-$ ligand inhibit the formation of the polynuclear complexes that are a dominant feature of oxomolybdenum(IV–VI) chemistry. However, minor amounts of polynuclear species can be isolated from reaction mixtures. The specific steric demands of the $HB(Me_2pz)_3^-$ ligand can lead to unusual polynuclear structures, as shown above, which in turn suggest intriguing chemical and structural transformations. Unfortunately, the extremely low yields for formation of these polynuclear complexes have precluded a systematic investigation of their chemistry to date. Finally, it seems reasonable to suspect that similar unusual bridging groups and molecular geometries may occur in other systems, possibly as reaction intermediates.

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Supplementary Material Available: Tables of anisotropic thermal parameters, calculated atomic positions, and bond distances and angles for **1** and **2** and of anisotropic thermal parameters and bond distances and angles for **3** (13 pages); tables of observed and calculated structure factors for **1**–**3** (67 pages). Ordering information is given on any current masthead page.

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