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Synthesis and Characterization of Tetrasulfidomolybdenum(IV) Complexes of Hydrotris(3,5-dimethyl-1-pyrazolyl)borate and the X-ray Crystal Structure of $\{HB(3,5\text{-}Me_2C_3N_2H)_3\}MoCl(S_4)\cdot 0.5Et_2O$

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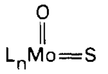
The reactions of *cis*-$\{HB(Me_2pz)_3\}MoO_2X$ [$HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate anion; X = F, Cl, Br, NCS] with sulfiding agents in refluxing 1,2-dichloroethane result in the formation of the intensely colored (blue, X = F, Cl, Br; green, X = NCS), monomeric, diamagnetic tetrasulfidomolybdenum(IV) complexes $\{HB(Me_2pz)_3\}MoX(S_4)$. $\{HB(Me_2pz)_3\}MoCl(S_4)\cdot 0.5Et_2O$ crystallizes in triclinic space group $P\bar{1}$ with a = 10.236 (1) Å, b = 15.359 (3) Å, c = 17.333 (3) Å, α = 102.30 (1)°, β = 97.85 (1)°, γ = 104.00 (1)°, V = 2531.9 Å^3, and Z = 4. The structure was solved by Patterson and Fourier methods, followed by least-squares refinement, for 6090 reflections, to a conventional R value of 0.046 (R_w = 0.055). The complex possesses a distorted octahedral coordination sphere composed of *facial* tridentate $HB(Me_2pz)_3^-$, bidentate tetrasulfido, and monodentate chloride ligands. The MoS_4 fragment exhibits an unusual planar geometry with very short Mo-S bonds (average 2.192 Å) and alternating S-S bond distances.

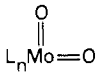
Introduction

A variety of sulfur donor ligands have been identified in the active sites of molybdoenzymes. In the unique iron-molybdenum active site of the nitrogenases, sulfur is present as sulfide and is thought to be integrated into the framework of a Fe-Mo cluster site.[2] Different types of sulfur ligands are present in the various oxo-type molybdoenzymes. Terminal thio and thiolate ligands are present in the enzymes xanthine oxidase and xanthine dehydrogenase.[3,4] Present models for the oxidized active enzymes, based on EXAFS[4] and ESR[5] studies, postulate a *cis*-oxothio-Mo(VI) center (I) coordinated by thiolate ligands. The other



$L_n\overset{\overset{O}{\|}}{Mo}{=}S$

I



$L_n\overset{\overset{O}{\|}}{Mo}{=}O$

II

known oxo-type molybdoenzymes, for example sulfite oxidase, aldehyde oxidase, and nitrate reductase, contain only thiolate-type sulfur ligands.[3,6] There is a notable absence of terminal thio ligation in these enzymes, which, in contrast to xanthine oxidase and xanthine dehydrogenase, contain *cis*-dioxo-Mo(VI) active sites (II) in their oxidized forms. Mo-co, the cofactor common to all the oxo-type molybdoenzymes, is also postulated to contain two sulfur donor atoms.[7] With respect to synthetic models for the oxo-type molybdoenzymes, we have recently reported the synthesis of monomeric thio-Mo(IV)[8] and thio-Mo(V)[9] complexes of $HB(Me_2pz)_3^-$ as well as the participation of oxo-Mo(IV,VI) complexes of $HB(Me_2pz)_3^-$ in oxygen atom transfer catalysis.[10] Our current exploration of the reactions of high-valent oxomolybdenum complexes of $HB(Me_2pz)_3^-$ with sulfiding reagents aims to model the oxothio-Mo(VI) site (I) and its oxygen atom transfer chemistry. In this regard, it is important to note that very few *cis*-$[MoOS]^{2+}$ complexes have been reported to date. These include the oxothiomolybdates $[MoO_{4-n}S_n]^{2-}$ (n = 1-3)[11] and the *cis*-$MoOS(R_2NO)_2$ complexes studied by Wieghardt[12] and others.[13] Two aspects of these compounds have a bearing on the current study. First, they are prepared from the analogous oxo complexes by reaction with sulfiding reagents such as H_2S, B_2S_3, and $(Me_3Si)_2S$, and second, the complexes and the oxo precursors possess tetrahedral or pseudotetrahedral geometries that may be important determinants of their reactivity and stability. In general, the conversion of pseudooctahedral $[MoO_2]^{2+}$ complexes into analogous $[MoOS]^{2+}$ complexes would appear to require more careful control of the redox capacity of the sulfiding reagent. This is indeed supported by the present study, which describes the preparation and characterization of the tetrasulfido-Mo(IV) complexes $\{HB(Me_2pz)_3\}MoX(S_4)$ (X = F, Cl, Br, NCS), which are formed upon the reductive sulfurization of *cis*-$\{HB(Me_2pz)_3\}MoO_2X$ species.

Experimental Section

Materials and Methods. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate was prepared by the method of Trofimenko.[14] The reactions of $K\{HB(Me_2pz)_3\}$ with $MoO_2X_2(OPPh_3)_2$ (X = F, Cl),[15] $MoO_2Br_2(Me_2SO)_2$,[16] and $(NEt_4)_2[MoO_2(NCS)_4]$,[17] were employed for the preparation of $\{HB(Me_2pz)_3\}MoO_2X$ (X = F, Cl, Br, NCS, respectively).[18] Boron sulfide was purchased from Alfa Chemicals. All other chemicals were laboratory grade reagents or better. The solvents employed were dried and deoxygenated, and all reactions were performed under an atmosphere of dinitrogen by using standard Schlenk line techniques. Workups were performed in air without precaution. Microanalyses were performed by Atlantic Microlabs. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer as KBr disks. NMR spectra were recorded on a JEOL JNM FX-200 spectrometer using $CHCl_3$ as internal reference (δ = 7.23). Electronic spectra were recorded on a Shimdazu UV-240 spectrophotometer using quartz cells.

Preparation of Complexes. $\{HB(Me_2pz)_3\}MoF(S_4)$ **(1).** A mixture of $\{HB(Me_2pz)_3\}MoO_2F$ (0.5 g, 1.13 mmol), boron sulfide (0.5 g), and sulfur (0.25 g) in 1,2-dichloroethane (40 mL) was refluxed for 2 h while

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a steady stream of H_2S was passed through the solution. The mixture was allowed to cool and then filtered to remove the brown byproducts. The filtrate was reduced to dryness in vacuo and the residue chromatographed on a column of silica gel (Merck Art. 7734, Kieselgel 60, 70–230 mesh) with dichloromethane/pentane (2:3) used as eluent. The blue band was collected and rechromatographed if necessary. The compound may be recrystallized from a minimum amount of cold diethyl ether. Only milligram quantities of this derivative were obtained.

Insufficient sample was obtained for an analysis. Infrared spectrum (KBr): 2960 w, 2923 w, ν(BH) 2550 m, 1540 s, 1446 s, 1414 s, 1380 m, 1355 s, 1209 s, 1148 w, 1115 w, 1065 s, 1040 s, 985 w, 905 w, 857 m, 814 m, 692 m, 645 m, 475 m, 415 m, 315 m cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ -0.05 and 2.11 (s, 2 × 3 H, 2 × CH_3 of $HB(Me_2pz)_3^-$), 2.58 and 3.07 (s, 2 × 6 H, 4 × CH_3 of $HB(Me_2pz)_3^-$), 5.03 (s, 1 H, 1 × CH of $HB(Me_2pz)_3^-$), 6.24 (s, 2 H, 2 × CH of $HB(Me_2pz)_3^-$). Electronic spectrum (CH_2Cl_2): 610 nm (ϵ 2160 M^{-1} cm^{-1}), 320 (ϵ 10 800), 230 (ϵ 22 700).

$\{HB(Me_2pz)_3\}MoX(S_4)$ (2, X = Cl; 3, X = Br). Compounds **2** and **3** may be prepared by methods analogous to that given above for **1**, and the yields given below apply to such reactions. The compounds may also be prepared by using the method described below for the thiocyanate derivative **4**; however, only small yields are obtained.

2. Yield: 0.28 g (45%). Anal. Calcd for $C_{17}H_{27}BClO_{0.5}MoN_6S_4$: C, 34.38; H, 4.58; N, 14.15; S, 21.59; Cl, 5.97. Found: C, 34.8; H, 4.7; N, 14.3; S, 21.8; Cl, 6.0. Infrared spectrum: 2966 w, 2923 w, ν(BH) 2552 m, 1541 s, 1446 s, 1414 s, 1380 m, 1360 s, 1209 s, 1148 w, 1115 w, 1069 s, 1043 s, 985 w, 963 w, 857 m, 814 m, 692 m, 475 m, 423 m, 322 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ -0.02 and 2.14 (s, 2 × 3 H, 2 × CH_3 of $HB(Me_2pz)_3^-$), 1.21 (t, J = 7.0 Hz, 3 H, CH_3 of Et_2O), 2.60 and 3.10 (s, 2 × 6 H, 4 × CH_3 of $HB(Me_2pz)_3^-$), 3.48 (q, J = 7.0 Hz, 2 H, CH_2 of Et_2O), 5.06 (s, 1 H, 1 × CH of $HB(Me_2pz)_3^-$), 6.26 (s, 2 H, 2 × CH of $HB(Me_2pz)_3^-$). Electronic spectrum (CH_2Cl_2): 610 nm (ϵ 4000 M^{-1} cm^{-1}), 322 (ϵ 18 900).

3. Yield: 0.34 g (50%). Anal. Calcd for $C_{15}H_{22}BBrMoN_6S_4$: C, 29.96; H, 3.69; N, 13.98; S, 21.33. Found: C, 30.0; H, 3.7; N, 13.9; S, 21.3. Infrared spectrum: 2960 w, 2920 w, ν(BH) 2555 m, 1540 s, 1445 s, 1410 s, 1380 m, 1355 s, 1205 s, 1148 w, 1115 w, 1070 s, 1040 s, 985 w, 910 s, 857 m, 814 m, 792 m, 730 m, 690 m, 645 m, 475 m, 420 m, 320 s cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ 0.00 and 2.16 (s, 2 × 3 H, 2 × CH_3 of $HB(Me_2pz)_3^-$), 1.24 (t, J = 7.0 Hz, 3 H, CH_3 of Et_2O), 2.63 and 3.12 (s, 2 × 6 H, 4 × CH_3 of $HB(Me_2pz)_3^-$), 3.49 (q, J = 7.0 Hz, 2 H, CH_2 of Et_2O), 5.07 (s, 1 H, 1 × CH of $HB(Me_2pz)_3^-$), 6.29 (s, 2 H, 2 × CH of $HB(Me_2pz)_3^-$).

$\{HB(Me_2pz)_3\}Mo(NCS)(S_4)$ (4). A mixture of $\{HB(Me_2pz)_3\}MoO_2(NCS)$ (0.75 g, 1.55 mmol), sulfur (0.75 g), and Na_2SO_4 (3.0 g) was refluxed in 1,2-dichloroethane (60 mL) for 4.5 h while a steady stream of H_2S gas was passed through the suspension. Upon cooling, the mixture was filtered in air and the filtrate was evaporated to dryness. The black residue was extracted with diethyl ether (ca. 3 × 80 mL). The combined ether extracts were evaporated to dryness and redissolved in a minimum of CH_2Cl_2/pentane (2:3). This solution was loaded onto a silica gel (Merck Art. 7734, Kieselgel 60, 70–230 mesh) column, which was eluted with CH_2Cl_2/pentane (2:3). The first green band was collected and rechromatographed if necessary. The compound was recrystallized from a minimum volume of CH_2Cl_2 by addition of diethyl ether (1:1 v/v) and standing. Yield: 0.5 g, 56%.

Anal. Calcd for $C_{16}H_{22}BMoN_7S_5$: C, 33.16; H, 3.83; N, 16.92; S, 27.66. Found: C, 33.1; H, 3.9; N, 16.9; S, 27.6. Infrared spectrum: 2960 w, 2930 w, 2550 m, ν(CN) 2020 vs, 1535 s, 1445 s, 1410 s, 1355 s, 1209 s, 1060 s, 1040 m, 855 m, 810 m, 780 m, 690 m, 645 m, 470 m, 410 w, 300 m cm^{-1}. ^1H NMR spectrum ($CDCl_3$): δ -0.11 and 2.44 (s, 2 × 3 H, 2 × CH_3 of $HB(Me_2pz)_3^-$), 2.59 and 2.98 (s, 2 × 6 H, 4 × CH_3 of $HB(Me_2pz)_3^-$), 5.07 (s, 1 H, 1 × CH of $HB(Me_2pz)_3^-$), 6.26 (s, 2 H, 2 × CH of $HB(Me_2pz)_3^-$). Electronic spectrum (CH_2Cl_2): 619 nm (ϵ (5500 M^{-1} cm^{-1}), 454 (ϵ 9200), 345 (ϵ 23 600).

Crystal Structure Determination. Deep blue crystals of **2**·$0.5Et_2O$ were grown from a cold solution of **2** in diethyl ether; a crystal of dimensions 0.33 × 0.45 × 0.04 mm was used in the diffraction experiment. Crystal data and experimental details are reported in Table I. Cell constants and an orientation matrix were obtained from least-squares refinement, by using setting angles of 25 reflections in the range $20 < 2\theta < 30°$. Three intense reflections were recollected every 46 reflections and showed no change in intensity throughout data collection. Lorentz and polarization corrections were applied to the raw data. Absorption corrections did not improve the final agreement factors and were not applied to the structure.

The positions of the 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.[19] Anomalous dispersion effects were included in F_c;[20] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[21] In the final cycles of full-matrix least-squares refinement the non-hydrogen atoms were refined anisotropically. All calculations were performed on a PDP-11 computer using SDP-PLUS.[22] The final atomic coordinates for all non-hydrogen atoms may be found in Table II.[23] 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.

Table I. Experimental Details of the Crystal Structure Determination for $\{HB(Me_2pz)_3\}MoCl(S_4)\cdot 0.5Et_2O$

A. Crystal Data

chem formula	$C_{17}H_{27}BClMoNO_{0.5}S_4$	a, Å	10.236 (1)
fw	593.91	b, Å	15.359 (3)
cryst dimens, mm	0.33 × 0.45 × 0.04	c, Å	17.333 (3)
peak width at half-height, deg	0.25	α, deg	102.30 (1)
		β, deg	97.85 (1)
cryst color	blue	γ, deg	104.00 (1)
Mo Kα radiation		V, $Å^3$	2531.9
λ, Å	0.71073	Z	4
temp, °C	23 ± 1	ρ, g cm^{-3}	1.56
space group	$P\bar{1}$	μ, cm^{-1}	9.5

B. Intensity Measurements

instrument	Syntex (Nicolet) $P2_1$ with modified software
monochromator	graphite crystal, incident beam
scan type	θ–2θ
scan rate, deg min^{-1}	2–8
scan width, deg	Kα_1 - 1.0 to Kα_2 + 1.0
max 2θ, deg	50
portion of sphere collcd	$h,\pm k,\pm l$
no. of reflcns measd	9536 tot., 8984 unique
corrcn	Lorentz–polarization, reflcn averaging (agreement on I = 2.1%)

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	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares wt	$4F_o^2/(\sigma(I)^2 + (pF_o^2)^2)$; $p = 0.04$
anomalous dispersion	all non-hydrogen atoms
no. of reflcns included	6090 with $F_o^2 > 3.0(\sigma(F_o))^2$
no. of params refined	525
unwtd agreement factor	$\sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum \lvert F_o\rvert = 0.046$
wtd agreement factor	$(\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum wF_o^2)^{1/2} = 0.055$
esd of observn of unit wt	1.44
convergence, largest shift	0.32
highest peak in final diff map, e $Å^{-3}$	0.66 (10)

Results and Discussion

Syntheses and Properties. Small variable amounts of $\{HB(Me_2pz)_3\}MoX(S_4)$ (X = F (**1**), X = Cl (**2**), X = Br (**3**), X = NCS (**4**)) may be detected (by thin-layer chromatography) in the reactions of appropriate $\{HB(Me_2pz)_3\}MoO_2X$ or $\{HB(Me_2pz)_3\}MoOX_2$[24] complexes with either B_2S_3 or H_2S. Thus, while the reaction of $\{HB(Me_2pz)_3\}MoOCl_2$ and B_2S_3 at room

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(23) 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.

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Mo1	0.27201 (5)	0.77423 (3)	0.26928 (3)	2.42 (1)	Mo2	0.05718 (5)	0.80480 (3)	0.75323 (3)	2.62 (1)
Cl1	0.0535 (2)	0.6994 (1)	0.18432 (9)	3.63 (3)	Cl2	0.1405 (2)	0.9472 (1)	0.8532 (1)	4.14 (4)
S11	0.2214 (2)	0.8960 (1)	0.3342 (1)	3.51 (3)	S21	−0.1637 (2)	0.7909 (1)	0.7369 (1)	3.73 (4)
S12	0.1396 (2)	0.8832 (1)	0.4403 (1)	5.04 (4)	S22	−0.2468 (2)	0.8473 (1)	0.6446 (1)	4.95 (4)
S13	0.1593 (2)	0.7629 (1)	0.4602 (1)	5.05 (5)	S23	−0.0929 (2)	0.8915 (1)	0.5906 (1)	5.01 (4)
S14	0.2411 (2)	0.6987 (1)	0.36313 (9)	3.45 (3)	S24	0.0844 (2)	0.8611 (1)	0.64881 (9)	3.53 (3)
N111	0.4944 (5)	0.8303 (3)	0.3118 (3)	2.7 (1)	N211	0.0299 (5)	0.6601 (3)	0.6916 (3)	3.0 (1)
N112	0.5811 (5)	0.8276 (3)	0.2584 (3)	3.0 (1)	N212	0.0988 (5)	0.6070 (3)	0.7264 (3)	2.9 (1)
N121	0.3190 (5)	0.8429 (3)	0.1704 (3)	2.9 (1)	N221	0.0455 (5)	0.7444 (3)	0.8604 (3)	3.2 (1)
N122	0.4252 (5)	0.8292 (3)	0.1335 (3)	2.9 (1)	N222	0.1184 (5)	0.6826 (3)	0.8719 (3)	3.4 (1)
N131	0.3391 (5)	0.6579 (3)	0.1953 (3)	2.9 (1)	N231	0.2777 (5)	0.8013 (3)	0.7734 (3)	3.0 (1)
N132	0.4508 (5)	0.6795 (3)	0.1604 (3)	2.9 (1)	N232	0.3114 (5)	0.7301 (3)	0.8006 (3)	3.0 (1)
C113	0.7134 (6)	0.8626 (4)	0.2976 (4)	3.4 (1)	C213	0.0699 (6)	0.5211 (4)	0.6751 (4)	3.5 (1)
C114	0.7112 (6)	0.8897 (4)	0.3787 (4)	3.9 (1)	C214	−0.0181 (7)	0.5193 (4)	0.6084 (4)	3.5 (1)
C115	0.5750 (6)	0.8690 (4)	0.3856 (4)	3.2 (1)	C215	−0.0425 (6)	0.6047 (4)	0.6186 (4)	3.3 (1)
C116	0.8336 (7)	0.8685 (5)	0.2579 (5)	4.8 (2)	C216	0.1321 (7)	0.4490 (4)	0.6952 (4)	4.5 (2)
C117	0.5214 (7)	0.8819 (5)	0.4615 (4)	4.6 (2)	C217	−0.1325 (7)	0.6353 (5)	0.5616 (4)	4.4 (2)
C123	0.4267 (7)	0.8698 (4)	0.0714 (4)	3.6 (1)	C223	0.1011 (7)	0.6593 (4)	0.9415 (4)	3.9 (2)
C124	0.3203 (7)	0.9088 (4)	0.0683 (4)	4.0 (2)	C224	0.0184 (8)	0.7056 (5)	0.9754 (4)	4.6 (2)
C125	0.2537 (6)	0.8923 (4)	0.1305 (4)	3.3 (1)	C225	−0.0182 (7)	0.7584 (5)	0.9238 (4)	3.8 (2)
C126	0.5299 (9)	0.8695 (6)	0.0194 (4)	5.7 (2)	C226	0.170 (1)	0.5948 (6)	0.9723 (4)	6.2 (2)
C127	0.1360 (7)	0.9230 (5)	0.1515 (4)	4.8 (2)	C227	−0.1011 (8)	0.8250 (6)	0.9380 (4)	5.5 (2)
C133	0.4795 (7)	0.6010 (4)	0.1251 (4)	3.7 (1)	C233	0.4478 (6)	0.7422 (4)	0.8108 (4)	3.4 (1)
C134	0.3845 (7)	0.5280 (4)	0.1353 (4)	3.6 (1)	C234	0.5039 (6)	0.8240 (4)	0.7918 (4)	3.5 (1)
C135	0.2979 (6)	0.5645 (4)	0.1796 (3)	2.9 (1)	C235	0.3974 (6)	0.8587 (4)	0.7692 (4)	3.1 (1)
C136	0.6006 (8)	0.6029 (5)	0.0845 (5)	5.6 (2)	C236	0.5146 (7)	0.6741 (5)	0.8365 (5)	5.1 (2)
C137	0.1778 (7)	0.5124 (4)	0.2061 (4)	4.4 (2)	C237	0.4062 (7)	0.9445 (4)	0.7401 (5)	4.5 (2)
B1	0.5255 (7)	0.7810 (5)	0.1678 (4)	3.1 (1)	B2	0.1979 (7)	0.6487 (5)	0.8085 (4)	3.2 (2)
O71	0.4067 (6)	0.5147 (4)	0.6040 (3)	5.9 (1)*					
C72	0.4674 (9)	0.6062 (6)	0.6033 (5)	5.8 (2)*					
C73	0.3612 (9)	0.6513 (6)	0.5814 (6)	6.6 (2)*					
C74	0.4992 (9)	0.4645 (6)	0.6265 (6)	6.4 (2)*					
C75	0.427 (1)	0.3714 (8)	0.6218 (7)	8.7 (3)*					

[a] Starred values denote atoms refined isotropically. Values for 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 $\{HB(Me_2pz)_3\}MoCl(S_4)$[23]

dist	molecule 1	molecule 2	dist	molecule 1	molecule 2
Mo–Cl	2.372 (1)	2.365 (1)	Mo–N31	2.273 (4)	2.251 (4)
Mo–S1	2.182 (1)	2.192 (1)	S1–S2	2.149 (2)	2.147 (2)
Mo–S4	2.204 (1)	2.188 (1)	S2–S3	2.001 (3)	1.994 (3)
Mo–N11	2.189 (4)	2.183 (4)	S3–S4	2.140 (2)	2.154 (2)
Mo–N21	2.242 (4)	2.250 (4)			
angle	molecule 1	molecule 2	angle	molecule 1	molecule 2
Cl–Mo–S1	97.51 (6)	99.61 (6)	S4–Mo–N21	174.1 (1)	175.4 (1)
Cl–Mo–S4	96.63 (5)	97.39 (6)	S4–Mo–N31	90.9 (1)	90.7 (1)
Cl–Mo–N11	161.9 (1)	159.5 (1)	N11–Mo–N21	81.9 (2)	81.7 (2)
Cl–Mo–N21	85.4 (1)	83.2 (1)	N11–Mo–N31	81.2 (2)	80.4 (2)
Cl–Mo–N31	84.7 (1)	84.5 (1)	N21–Mo–N31	83.7 (2)	84.8 (2)
S1–Mo–S4	94.59 (6)	94.71 (6)	Mo–S1–S2	116.06 (8)	116.13 (8)
S1–Mo–N11	95.5 (1)	94.1 (1)	S1–S2–S3	106.10 (9)	106.22 (9)
S1–Mo–N21	90.6 (1)	89.7 (1)	S2–S3–S4	106.95 (9)	106.95 (9)
S1–Mo–N31	173.8 (1)	172.7 (1)	Mo–S4–S3	115.52 (8)	115.50 (8)
S4–Mo–N11	94.8 (1)	96.6 (1)			

temperature results in high yields of the novel thio–Mo(V) complex $\{HB(Me_2pz)_3\}MoSCl_2$,[9] milligram amounts of **2** may be isolated from the filtrate by chromatography. By subjecting $\{HB(Me_2pz)_3\}MoO_2X$ complexes to rather forcing sulfiding conditions, viz., the use of a combination of sulfiding agents in refluxing dichloroethane, we have developed reliable syntheses for **1**–**4** (see Experimental Section). During these reactions Mo(VI) is reduced to Mo(IV) and a net replacement of the *cis*-dioxo ligands with the chelating S_4^{2-} ligand takes place. Equation 1 may account

$$\{HB(Me_2pz)_3\}MoO_2X + 2H_2S + \tfrac{1}{4}S_8 \rightarrow \{HB(Me_2pz)_3\}MoX(S_4) + 2H_2O \quad (1)$$

for the conversion of $\{HB(Me_2pz)_3\}MoO_2X$ to **1**–**4** and is consistent with the increased yields in the presence of sulfur and failed syntheses when H_2S is employed in the absence of the drying agent (B_2S_3 or Na_2SO_4). The mechanism of formation of the S_4^{2-} ligand in these complex reactions is unknown.

The infrared spectra of the complexes are dominated by bands due to $HB(Me_2pz)_3^-$, which include a ν(BH) stretch at ca. 2550 cm^{-1}. Bands due to the monodentate X^- and bidentate S_4^{2-} ligands cannot be unambiguously assigned except in the case of the ν(CN) band of **4** at 2020 cm^{-1}. Solid-state IR spectra of **4** revealed a splitting of the ν(CN) band; however, in solution only a single sharp band was observed. The energy of the ν(CN) band indicates that the thiocyanate ligand in **4** is N bound.[25] NMR experiments indicate the complexes are diamagnetic. The ^{1}H NMR spectra of **1**–**4** are consistent with molecular C_s symmetry in solution. The mirror plane, which contains Mo and X and bisects the S_4^{2-} ligand, dictates the presence of six sets of equivalent protons integrating to 1:2:3:3:6:6. Assignments for these resonances are given in the Experimental Section. A most unusual feature of the ^{1}H NMR

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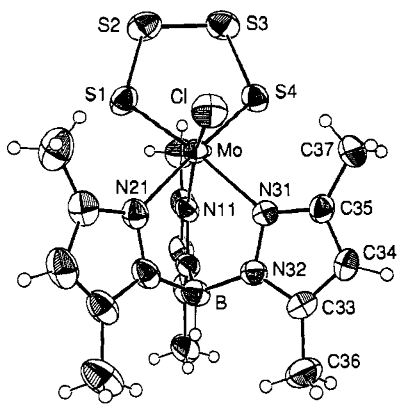

Figure 1. Molecular structure of molecule 2 of $\{HB(Me_2pz)_3\}MoCl(S_4)$ showing the atom-labeling scheme.[23] The numbering of atoms in the pyrazole rings containing N11 and N21 parallels that shown for the ring containing N31. Thermal ellipsoids are plotted at the 50% probability level, and hydrogen atoms (not numbered) are shown as spheres of arbitrary size.

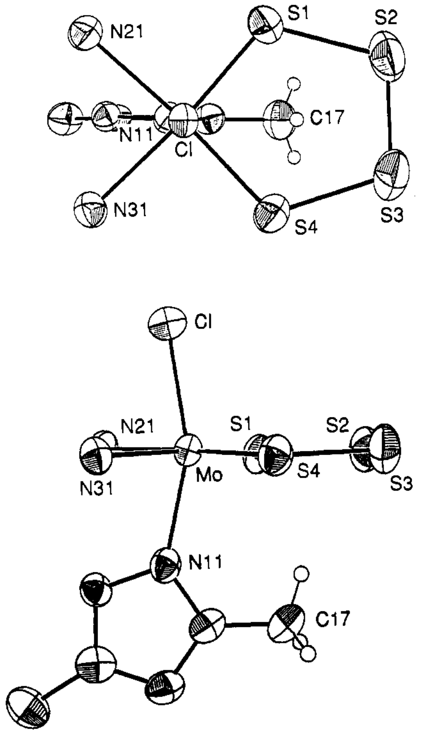

Figure 2. Views of the spatial relationship of the methyl group containing C17 and the MoS_4 ring of molecule 2 of $\{HB(Me_2pz)_3\}MoCl(S_4)$.

spectra is a ca. δ 0 resonance produced by an extremely shielded methyl group. The chemical shift of this methyl group is ca. 2 ppm more shielded than corresponding methyl groups in $\{HB(Me_2pz)_3\}MoO_2X$ or other known $\{HB(Me_2pz)_3\}MoX_2Y$ complexes. Inspection of the structure of $\{HB(Me_2pz)_3\}MoCl(S_4)$ (Figures 1 and 2) reveals that one particular methyl group (containing C17) is located directly beneath the MoS_4 ring. The distance of C17 from the plane of the MoS_4 fragment is 3.168 and 3.178 Å for molecules 1 and 2, respectively, and the closest approach of the hydrogen atoms on C17 to the MoS_4 plane is ca. 2.27 Å in both molecules. Moreover, the bond lengths within the five-membered MoS_4 ring of **2** (see below) are indicative of a degree of dithiolene character, i.e. significant π-bonding between the Mo and coordinated S atoms and the S2–S3 atoms of the ligand, which may be expected to create a unique electronic environment in the vicinity of the MoS_4 ring. For these reasons the ca. δ 0 resonances of **1–4** may be assigned to the methyl groups that reside directly beneath the MoS_4 ring. The complexes are intensely colored. The halide derivatives **1–3** are deep blue as a result of absorptions at 610 and 322 nm. For **4** an additional absorption at 454 nm results in a green coloration. The extinction coefficients for all absorptions are indicative of charge-transfer transitions.

Description of the Structure. The unit cell of $\mathbf{2}\cdot0.5Et_2O$ contains four formula units. There are two independent molecules of **2**, which have nearly identical structures. An ORTEP view of molecule 2 is shown in Figure 1. The mononuclear complexes possess distorted octahedral coordination spheres composed of chloride, bidentate tetrasulfido, and *facially* tridentate $HB(Me_2pz)_3^-$ ligands. The MoS_4 rings are characterized by very short Mo–S bonds and an alternation of the S–S bond distances. The Mo–S bond distances average 2.193 (10) and 2.190 (2) Å for molecules 1 and 2, respectively. The S–S bond distances fall into two groups. The first group includes the S1–S2 and S3–S4 bonds, which average 2.145 (5) and 2.151 (4) Å for molecules 1 and 2, respectively. The S2–S3 bond distances of 2.001 (2) Å (molecule 1) and 1.994 (2) Å (molecule 2) comprise the second group of S–S distances. The MoS_4 fragment in **2** is remarkably planar with a maximum atom displacement from the least-squares plane of 0.076 Å (for S1). The S_4^{2-} ligand displays an even greater planarity with a maximum displacement from the least-squares plane of 0.027 Å (for S2 and S3). Examination of Figure 2 reveals the small dihedral angle of 6.2° (7.3° for molecule 1) between the Mo–S1–S4 and S_4^{2-} ligand planes. In molecules 1 and 2, respectively, the Mo atom is 0.189 and 0.161 Å from the plane of the S_4^{2-} ligand. A number of other mononuclear tetrasulfido–Mo(IV) and dinuclear tetrasulfido–Mo(V) complexes have been structurally characterized over the past 15 years,[26] and the geometries of the MoS_4 fragments in these complexes have been discussed.[27] Known tetrasulfido complexes of molybdenum exhibit Mo–S distances that range from 2.331 to 2.450 Å with an average of 2.367 Å. The S–S distances have the following ranges and average values: S1–S2 and S3–S4, 2.083–2.116 Å range, 2.139 Å average; S2–S3, 1.97–2.019 Å range, 2.009 average. The S–Mo–S angle in these complexes ranges from 85.1 to 90.4° with an average of 89.2°. In comparison, the Mo–S distances in **2** are unusually short, being 0.175 Å shorter than average and 0.139 Å shorter than the previously reported minimum. We believe the absence of other strong π-donor ligands, such as the oxo and thio ligands present in previously characterized complexes, results in extreme S→Mo π-back-bonding, which in turn leads to unprecedented Mo–S bond distances. The high oxidation state of Mo(IV) also enhances S→Mo π-back-bonding and the shortening of the Mo–S bonds in the absence of other π-donors. The short Mo–S distances result in the opening of the S1–Mo–S4 angles to 94.65° (average), the largest yet reported for a tetrasulfido–Mo complex. As a consequence of the Mo–S bonding, the S1–S2 and S3–S4 bonds are slightly longer than the average of other determinations while the S2–S4 distance is slightly shorter than average. Another unusual feature of **2** is the planarity of the tetrasulfido ligand and associated MoS_4 fragment. In all previous cases, the ligands and MoS_4 fragments display a deviation, usually considerable, from planarity. There appears to be a slight trans influence associated with the Mo–S bonds as the Mo–N21 and Mo–N31 bonds are lengthened (average 2.255 Å) compared to the Mo–N11 bonds (average 2.186 Å) cis to the Mo–S bonds. This trans effect is a likely manifestation of the dπ–pπ bonding between Mo and S. Unless noted above, the bond lengths and angles within the $HB(Me_2pz)_3^-$ ligands are comparable to those found elsewhere.[28] The average Mo–Cl

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bond distance is 2.369 (3) Å. There are no short intermolecular contacts between the molecules in the unit cell.

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and calculated hydrogen atom positions (11 pages); a table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Poly(pyrazolyl)borate Complexes of Terbium, Samarium, and Erbium. X-ray Crystal Structure of $\{[\eta^3\text{-HB(pz)}_3]_2\text{Sm}(\mu\text{-O}_2\text{CPh})\}_2$ (pz = Pyrazolyl Ring)

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The reaction of MCl_3 (M = Tb, Sm, Er) with 3 equiv of $\text{K[H}_2\text{B(pz)}_2]$ yields $[\text{H}(\mu\text{-H})\text{B(pz)}_2]_3\text{M}$. These complexes have properties similar to those of the yttrium analogue, which has been shown to have a trigonal-prismatic structure possessing weak agostic B–H···Y three-center interactions. The reaction of the metal halides with 2 equiv of $\text{K[HB(pz)}_3]$ yields $[\text{HB(pz)}_3]_2\text{MCl}$, shown to be monomeric in solution for M = Sm. A similar reaction, which in addition contains 1 equiv of $\text{Na(O}_2\text{CCH}_3)$, yields $\{[\text{HB(pz)}_3]_2\text{M(O}_2\text{CCH}_3)\}_2$. NMR spectra for all three types of these paramagnetic complexes are resolved for M = Sm and are temperature dependent, showing these molecules are fluxional in solution. The complex $\{[\text{HB(pz)}_3]_2\text{Sm(O}_2\text{CPh)}\}_2$ was also prepared and the solid-state structure determined by X-ray diffraction: monoclinic, space group $P2_1/c$, $a = 13.264$ (3) Å, $b = 35.821$ (8) Å, $c = 15.544$ (4) Å, $\beta = 115.06$ (2)°, $V = 6690$ Å^3, and $Z = 4$. The structure is an acetate-bridged dimer in which the geometry about the samarium atoms fails to fit any regular polyhedron. Molecular weight studies show that this complex and $\{[\text{HB(pz)}_3]_2\text{Sm(O}_2\text{CCH}_3)\}_2$ are dimers in benzene solution.

Introduction

We have recently been developing the chemistry of the early-transition metals using poly(pyrazolyl)borate ligands. With tantalum and zirconium, a variety of stable complexes containing one tris(pyrazolyl)borate ligand, such as $[\text{RB(pz)}_3]\text{TaMe}_3\text{Cl}$ (R = H, pz; pz = pyrazolyl ring),[1a] $[\text{HB(3,5-Me}_2\text{pz)}_3]\text{TaMe}_3\text{Cl}$,[1a] $[\text{RB(pz)}_3]\text{ZrCl}_3$ (R = *n*-Bu, *i*-Pr),[1b] $[\text{HB(3,5-Me}_2\text{pz)}_3]\text{Zr(O-}t\text{-Bu)}_n\text{R}_{3-n}$ (n = 1, 2; R = Cl, Me, CH_2Ph, C≡CMe),[1c] and $[\text{HB(pz)}_3]\text{CpZrCl}_2$,[1d] have been prepared. It was not possible, however, to prepare complexes containing two tris(pyrazolyl)borate ligands on tantalum or zirconium. Using the larger metals yttrium and lanthanum, we have reported the following series of complexes containing two tris(pyrazolyl)borate ligands: $[\text{HB(pz)}_3]_2\text{YCl(H}_2\text{O)}$, $[\text{HB(pz)}_3]_2\text{LaCl(H}_2\text{O)}$,[2a] $[\text{HB(pz)}_3]_2\text{YCl}$, $[\text{HB(pz)}_3]_2\text{YCl}$ (HPz), $\{[\text{HB(pz)}_3]_2\text{Y}(\mu\text{-O}_2\text{CCH}_3)\}_n$, and $\{[\text{HB(pz)}_3]\text{Y}(\mu\text{-O}_2\text{CCH}_3)_2\}_2$.[2b] $[\text{HB(pz)}_3]_2\text{YCl(H}_2\text{O)}$[2a] and $[\text{HB(pz)}_3]_2\text{YCl(Hpz)}$[2b] have been structurally characterized by X-ray crystallography and shown to have distorted-square-antiprismatic geometry. $\{[\text{HB(pz)}_3]\text{Y}(\mu\text{-O}_2\text{CCH}_3)_2\}_2$ was also structurally characterized in the solid state and is an unusual example of seven-coordinate yttrium.[2b] We have also described the synthesis and characterization of $[\text{H}(\mu\text{-H})\text{B(pz)}_2]_3\text{Y}$,[3] a molecule that possesses three, three-center, bridging B–H···Y interactions. In the solid state, the six nitrogen donor atoms form a trigonal prism in which each rectangular face is capped by a B–H···Y agostic bond.

In addition to our work, Takats has reported the synthesis of $[\eta^3\text{-HB(pz)}_3]_2[\eta^2\text{-HB(pz)}_3]\text{M}$ complexes (M = Y, La, Ce, Pr, Sm, Gd, Er, Yb).[4a] The ytterbium derivative was characterized as eight-coordinate as indicated by the above formula in solution[4b] and in the solid state.[4c] The solid-state structure was described as a bicapped trigonal prism. The synthesis of $[\text{HB(pz)}_3]_2\text{ErCl(THF)}$ was also briefly mentioned, but no experimental details were given.[4a] Takats has also recently published the synthesis of $[\text{HB(pz)}_3]_2\text{M}(\beta\text{-diketonate})$ (M = Yb, Lu; β-diketonate = 2,2,6,6-tetramethyl-3,5-heptanedionate (dpm), 3-(trifluoroacetyl)-*d*-camphorate).[5] The Yb–heptanedione complex was characterized by X-ray crystallography and shown to have a square-antiprismatic solid-state geometry. The synthesis of $[\text{HB(pz)}_3]_2\text{M(acac)}$ complexes (M = Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Yb, Lu; acac = acetylacetonate) has been reported by Jones and co-workers.[6] X-ray crystallographic analysis determined that the cerium complex possesses a bicapped-trigonal-prismatic geometry, while that of the ytterbium complex is derived from a square antiprism. With the exception of the $[\eta^3\text{-HB(pz)}_3]_2[\eta^2\text{-HB(pz)}_3]\text{M}$ complexes, all of these tris(pyrazolyl)borate complexes in both reports undergo dynamic rearrangements in solution.

We report here the synthesis of complexes of the type $[\text{H}(\mu\text{-H})\text{B(pz)}_2]_3\text{M}$, $[\text{HB(pz)}_3]_2\text{MCl}$, and $\{[\text{HB(pz)}_3]_2\text{M(O}_2\text{CCH}_3)\}_2$ for the lanthanide metals samarium, terbium, and erbium. The synthesis and solid-state structure of $\{[\text{HB(pz)}_3]_2\text{Sm}(\mu\text{-O}_2\text{CPh})\}_2$ is also reported.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere either by standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. The ^{1}H, ^{11}B, and ^{13}C solution NMR spectra were recorded on a Bruker AM300 spectrometer using a 5-mm broad-band probe. An IBM NR-80 spectrometer was also used to collect ^{13}C NMR data. Proton chemical shifts are reported in ppm vs Me_4Si. All carbon resonances are singlets with chemical shifts reported vs TMS by using the solvents CD_2Cl_2 and CDCl_3 as internal standards (CD_2Cl_2 resonance at 53.85 ppm; CDCl_3 resonance at 77.00 ppm). Boron-11 chemical shifts are reported in ppm vs $\text{BF}_3\cdot\text{OEt}_2$. Proton and ^{13}C variable-temperature NMR analyses were also performed on the Bruker AM300 NMR spectrometer at resonant frequencies of 300.13 and 75.47 MHz, respectively. The samples for variable-temperature studies were dissolved in CD_2Cl_2 and then sealed in screw-capped 5-mm NMR tubes. Activation parameters were calculated at the coalescence temperature.[7]

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