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Polypyrazolylborate Complexes Containing the [MoSMo]$^{2+}$ and [MoSeMo]$^{2+}$ Units

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The hydrotripyrazolylborate complexes (HB(pz)$_3$)Mo(CO)$_3$H and [NEt$_4$][(HB(Me$_2$pz)$_3$)Mo(CO)$_3$] react with elemental sulfur to produce the dark green compounds [(HB(pz)$_3$)Mo(CO)$_2$]$_2$S (**1**) and [(HB(Me$_2$pz)$_3$)Mo(CO)$_2$]$_2$S (**2**), which have been characterized by X-ray structure determination. Crystal data for **1**: monoclinic, $P2_1/c$, a = 7.843 (2) Å, b = 13.063 (3) Å, c = 16.941 (5) Å, β = 93.86 (2)°, Z = 2. Crystal data for **2**: monoclinic, $A2/a$, a = 13.976 (5) Å, b = 14.957 (7) Å, c = 20.701 (8) Å, β = 102.70 (3)°, Z = 4. Both compounds contain a linear [Mo–S–Mo]$^{2+}$ unit. The Mo–S distances are unusually short, 2.180 (1) Å in **1** and 2.200 (2) Å in **2**. The remaining ligands adopt approximate octahedral stereochemistry about the metal with the hydrotripyrazolylborate ligand occupying three *fac* positions. In **2** the Mo–N distance trans to the bridging S atom (2.188 (3) Å) is shorter than the other two Mo–N distances (2.254 (10) Å). For **1** the three Mo–N distances are indistinguishable (average 2.214 (3) Å). The selenium analogue of **1** ([(HB(pz)$_3$)Mo(CO)$_2$]$_2$Se (**3**)) has a similar structure with a linear [Mo–Se–Mo] bridge with Mo–Se distances of 2.323 (1) Å. Crystal data for **3**: triclinic, $P\bar{1}$, a = 11.021 (1) Å, b = 12.448 (1) Å, c = 7.935 (1) Å, α = 97.93 (1)°, β = 107.80 (1)°, γ = 106.45 (1)°, Z = 1. The similarity of the bonding in the [Mo–S–Mo]$^{2+}$ and [Mo–S–Mo]$^{6+}$ triatomic units is discussed.

Introduction

Binuclear and polynuclear molybdenum compounds containing sulfido groups bridging two or more metal atoms are a common feature of molybdenum–sulfur chemistry.[2] In general μ-sulfido bridges show acute Mo–S–Mo angles (~75°).[3] However, in the case of [(NC)$_6$MoSMo(CN)$_6$]$^{6-}$, a linear [Mo–S–Mo]$^{6+}$ unit with an unusually short Mo–S distance is observed.[4]

In the course of investigating the reactions of polypyrazolylborate complexes of molybdenum(0) with elemental sulfur, we have isolated complexes of the type L(CO)$_2$Mo–S–Mo(CO)$_2$L (L is hydrotripyrazolylborate or hydrotris(3,5-dimethylpyrazolyl)borate), which contain the linear [Mo–S–Mo]$^{2+}$ unit. The prepartion and structural features of these complexes and a selenium analogue are described here. These molybdenum compounds are similar to [(η^5-C$_5$H$_5$)Cr(CO)$_2$]$_2$S, which results from oxidation of (η^5-C$_5$H$_5$)Cr(CO)$_3^-$ with (NSCl)$_3$[5a] or from the reaction of [(η^5-C$_5$H$_5$)Cr(CO)$_3$]$_2$ with sulfur.[5b]

Experimental Section

Synthesis of [(HB(pz)$_3$)Mo(CO)$_2$]$_2$S (1). A slurry of 1.0 g (2.54 mmol) of (HB(pz)$_3$)Mo(CO)$_3$H[6] and 0.49 g (15.2 mmol) of sulfur in toluene was heated under dinitrogen at 70 °C for 3 h. The blue-green crystals, which formed on standing, were filtered and recrystallized from THF (60% yield). Mass spectra of both the initial blue-green crystals and the recrystallized product gave a molecular weight of 762 (calcd 762). IR data (Nujol mull): 2460 cm^{-1}, ν(BH); 1945, 1863 cm^{-1}, ν(CO). IR data (HCCl$_3$): 1880 (m), 1895 (m), 1940 (s), 1985 (m) cm^{-1}. ^{1}H NMR (Me$_2$SO-d_6): δ 6.23 (1 H, t), 6.45 (2 H, t), 7.65 (1 H, d), 7.92 (1 H, d), 7.98 (2 H, d), 8.02 (2 H, d). Electronic spectrum (THF): 600 nm (ϵ = 682 M^{-1} cm^{-1}), 395 (7.86 × 10^4).

Synthesis of [(HB(Me$_2$pz)$_3$)Mo(CO)$_2$]$_2$S (2). [Et$_4$N][(HB(Me$_2$pz)$_3$)Mo(CO)$_3$][7] (0.40 g, 0.69 mmol) and sulfur (0.16 g, 0.62 mmol) were refluxed in C$_2$H$_4$Cl$_2$ for 1 day. The resulting dark green solution was chromatographed on Florisil with CH$_2$Cl$_2$ as the eluent. Green crystals were isolated upon slow evaporation of the solvent; yield 0.16 g, 50%. Compound **2** is also formed when [(HB(Me$_2$pz)$_3$)Mo(CO)$_3$]$^-$ reacts with (NSCl)$_3$. The IR spectra from both preparations are the same.[8] IR data (KBr): 1976 (s), 1920 (s), 1890 (s), 1875, 1867 cm^{-1}, ν(CO). IR data (CH$_2$Cl$_2$): 1982 (m), 1929 (s), 1892 (m), 1898 (m) cm^{-1}.

Synthesis of [(HB(pz)$_3$)Mo(CO)$_2$]$_2$Se (3). (HB(pz)$_3$)Mo(CO)$_3$H (0.48 g, 1.2 mmol) was reacted with excess black selenium (0.58 g, 7.3 mmol) in dry toluene under N$_2$ for 12 h at 70 °C. A mixture of green and red precipitates was filtered from the cooled reaction mixture and washed twice with toluene. The green compound was separated from the insoluble red compound by recrystallization from hot THF. The yield of green crystals was 62%. IR data (Nujol mull): 2469 cm^{-1}, ν(BH); 1855 (s), 1925 (s), 1974 (vw) cm^{-1}, ν(CO). IR data (CH$_2$Cl$_2$): 1883 (m), 1893 (m), 1928 (s), 1980 (m) cm^{-1}. ^{1}H NMR (DCCl$_3$): δ 6.07 (1 H, t), 6.29 (2 H, t), 7.48 (1 H, d), 7.54 (1 H, d), 7.71 (2 H, d), 7.96 (2 H, d). Electronic spectrum (THF): 676 nm (ϵ = 522 M^{-1} cm^{-1}), 419 (40 000).

Spectroscopic Measurements. The ^{95}Mo NMR spectrum was recorded at 16.2 MHz in CH$_2$Cl$_2$ solution with a Bruker WM 250 spectrometer as previously described.[9] Infrared spectra were recorded on a Perkin-Elmer 567 spectrometer. Electronic spectra were recorded on a Cary 17 spectrophotometer.

X-ray Structure Determinations

[(HB(pz)$_3$)Mo(CO)$_2$]$_2$S·C$_6$H$_5$CH$_3$. A dark blue-green crystal was mounted on a glass fiber and examined on an Enraf-Nonius CAD4A automated diffractometer under the control of a PDP 11/45 computer. The lattice parameters were derived from a least-squares fit of the setting angles of 25 of the strongest reflections in the range 24° < 2θ < 26°. Other pertinent crystal data are given in Table I. The data were reduced and the structure was solved and refined by using the programs of the Enraf-Nonius[10] structure determination package. The molybdenum atom was located from a Patterson map, and the other non-hydrogen atoms of the molecule were found by using standard methods. A difference electron density map revealed the six ring carbons of a toluene solvent molecule with a center of inversion located at the ring center. The ring carbon atoms of the toluene molecule were refined isotropically, but the methyl carbon position could not be located in a subsequent difference map that did, however, clearly reveal all of the hydrogen atoms of the pyrazolylborate ligand. For the final refinement, the ligand hydrogen atoms were assigned fixed isotropic temperature factors. A final difference electron density map showed peaks of 0.6 e/Å^3, about 12% of the height of a typical light-atom peak, which were associated with the toluene of crystallization. Final positional and thermal parameters with their standard deviations are given in Table II; a listing of $|F_o|$ and $|F_c|$ is available as supplementary material.

[(HB(Me$_2$pz)$_3$)Mo(CO)$_2$]$_2$S. A single crystal was mounted on a Syntex P2$_1$ autodiffractometer. The results from automatic centering, indexing, and least-squares routines and axial photographs were consistent with a centered monoclinic unit cell (Table I). The nonstandard space group $A2/a$ having conditions hkl, $k + l = 2n$, and $h0l$, $h = 2n$,

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Table I. Crystallographic Data

compd	$[(HB(pz)_3)Mo(CO)_2]_2S{\cdot}C_6H_5CH_3$	$[(HB(Me_2pz)_3)Mo(CO)_2]_2S$	$[(HB(pz)_3)Mo(CO)_2]_2Se{\cdot}2THF$
formula	$Mo_2SO_4N_{12}C_{29}B_2H_{28}$	$Mo_2SO_4N_{12}C_{34}B_2H_{44}$	$Mo_2SeO_6N_{12}C_{30}B_2H_{36}$
fw	854.2	930.38	953.16
color/form	blue-green	green plate	green
a, Å	7.843 (2)	13.976 (5)	11.021 (1)
b, Å	13.063 (3)	14.597 (7)	12.448 (1)
c, Å	16.941 (5)	20.701 (8)	7.935 (1)
α, deg	90.0	90	97.93 (1)
β, deg	93.86 (2)	102.70 (3)	107.80 (1)
γ, deg	90	90	106.45 (1)
V, $Å^3$	1731.7 (1.3)	4119.8 (30)	963.5 (5)
density calcd (obsd), g/cm^{-3}	1.597	1.500 (1.47 (3))	1.64
space group	$P2_1/c$	$A2/a$	$P\bar{1}$
Z	2	4	1
cryst dimens, mm	0.13 × 0.35 × 0.45	0.16 × 0.09 × 0.10	0.3 × 0.3 × 0.2
temp	ambient (23 °C)	ambient	ambient
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
monochromator	graphite	graphite	graphite
linear abs coeff, cm^{-1}	8.250	6.92	17.16
scan mode	θ–2θ	θ–2θ	θ–2θ
2θ range	$0° < 2\theta < 54°$	$3° < 2\theta < 45°$	$0° < 2\theta < 50°$
no. of unique data collcd	2753	2789	6965
no. of data used in refinements	1931, $\lvert F_o\rvert^2 > 3\sigma\lvert F_o\rvert^2$	1395, $\lvert F_o\rvert^2 > 2\sigma\lvert F_o\rvert^2$	4274, $\lvert F_o\rvert^2 > 3\sigma\lvert F_o\rvert^2$
quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.032	0.076	0.041
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o{}^2]^{1/2}$	0.045	0.062	0.060
std error in observn of unit wt	1.114	1.40	1.318

Table II. Final Atomic Parameters for **1**

atom	*x*	*y*	*z*	*B*,[a] $Å^2$
Mo1	0.42531 (4)	0.09187 (3)	0.09949 (2)	
S	0.5000 (0)	0.0000 (0)	0.0000 (0)	
O1	0.0753 (5)	0.1323 (4)	0.0036 (2)	
O2	0.5539 (6)	0.2888 (3)	0.0176 (2)	
N1	0.3393 (4)	−0.0384 (2)	0.1706 (2)	
N2	0.6627 (4)	0.0710 (2)	0.1760 (2)	
N3	0.3493 (4)	0.1798 (2)	0.2031 (2)	
N11	0.3786 (4)	−0.0432 (2)	0.2500 (2)	
N21	0.6582 (4)	0.0510 (3)	0.2546 (2)	
N31	0.3898 (4)	0.1452 (2)	0.2776 (2)	
C1	0.2004 (6)	0.1162 (4)	0.0398 (3)	
C2	0.5076 (7)	0.2166 (4)	0.0472 (3)	
C11	0.3138 (6)	−0.1285 (4)	0.2797 (3)	
C12	0.2286 (6)	−0.1813 (3)	0.2186 (3)	
C13	0.2474 (6)	−0.1216 (3)	0.1518 (3)	
C21	0.8172 (6)	0.0410 (3)	0.2869 (3)	
C22	0.9309 (6)	0.0559 (4)	0.2302 (3)	
C23	0.8299 (5)	0.0744 (3)	0.1612 (3)	
C31	0.3321 (6)	0.2115 (3)	0.3295 (2)	
C32	0.2520 (6)	0.2913 (4)	0.2904 (3)	
C33	0.2661 (5)	0.2689 (3)	0.2103 (3)	
B	0.4845 (6)	0.0432 (4)	0.2912 (3)	
C4	0.952 (2)	0.4126 (7)	0.0198 (7)	12.1 (3)
C41	0.877 (2)	0.5818 (7)	−0.0227 (6)	12.3 (3)
C42	0.857 (1)	0.5014 (7)	0.0251 (5)	10.6 (2)

[a] Where no entry is given, the atom was refined anisotropically.

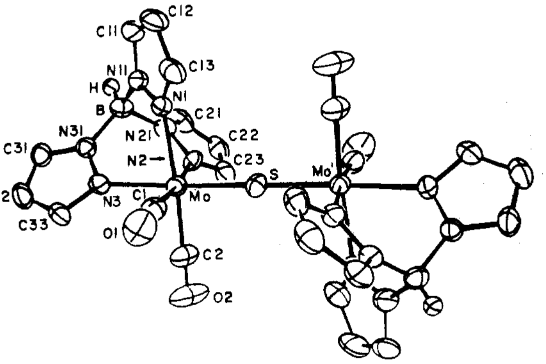

Figure 1. ORTEP diagram of **1**. The halves of the molecule are related to one another by a center of symmetry.

Table III. Final Atomic Parameters for **2**

atom	*x*	*y*	*z*	*B*,[a] $Å^2$
Mo	0.12905 (13)	0.27001 (11)	−0.44806 (8)	
S	0.250000 (0)	0.2813 (5)	−0.500000 (0)	
O1	0.1198 (14)	0.4829 (10)	−0.4370 (8)	
O2	−0.0263 (10)	0.3017 (10)	−0.5795 (7)	
N11	0.1240 (10)	0.1154 (9)	−0.4554 (8)	
N12	0.1285 (10)	0.0650 (12)	−0.3979 (7)	
N21	0.0167 (9)	0.2430 (10)	−0.3917 (6)	
N22	0.0300 (10)	0.1725 (10)	−0.3446 (7)	
N31	0.2292 (10)	0.2491 (7)	−0.3482 (6)	
N32	0.2156 (10)	0.1728 (9)	−0.3112 (6)	
C1	0.1228 (15)	0.4028 (14)	−0.4397 (10)	
C2	0.0304 (14)	0.2881 (13)	−0.5326 (9)	
C11	0.1195 (13)	0.0842 (11)	−0.5744 (8)	4.2 (4)
C12	0.1251 (11)	0.0529 (11)	−0.5056 (8)	3.0 (4)
C13	0.1339 (13)	−0.0314 (12)	−0.4771 (10)	3.9 (4)
C14	0.1337 (13)	−0.0260 (15)	−0.4142 (10)	4.3 (5)
C15	0.1470 (14)	−0.0965 (13)	−0.3599 (9)	5.5 (5)
C21	−0.1103 (15)	0.3579 (14)	−0.4341 (10)	6.8 (5)
C22	−0.0741 (13)	0.2788 (13)	−0.3895 (8)	4.2 (4)
C23	−0.1107 (14)	0.2302 (14)	−0.3430 (9)	4.9 (4)
C24	−0.0485 (14)	0.1694 (12)	−0.3152 (9)	4.0 (4)
C25	−0.0535 (14)	0.1012 (13)	−0.2641 (9)	5.4 (5)
C31	0.3519 (13)	0.3753 (12)	−0.3385 (9)	4.8 (4)
C32	0.3147 (13)	0.2887 (12)	−0.3140 (8)	3.8 (4)
C33	0.3519 (11)	0.2373 (12)	−0.2584 (7)	3.4 (3)
C34	0.2914 (12)	0.1674 (11)	−0.2565 (8)	3.0 (4)
C35	0.2968 (12)	0.0943 (11)	−0.2065 (8)	4.3 (4)
B	0.1229 (15)	0.1125 (14)	−0.3340 (10)	3.3 (4)

[a] Where no entry is given, the atom was refined anisotropically.

was chosen. The structure was solved by standard Patterson and difference electron density map techniques. The relatively small crystal limited the number of data with significant intensity. In the final cycle of refinement the Mo, S, and N atoms and the atoms of the carbonyl groups were refined anisotropically. Hydrogen atoms were included as fixed contributors with a temperature factor 1 $Å^2$ larger than the carbon to which they were bonded. The effects of anomalous dispersion were included for Mo and S. Additional details appear in Table I; final atomic parameters are given in Table III, and a listing of $|F_o|$ and $|F_c|$ is available as supplementary material.

$[(HB(pz)_3)Mo(CO)_2]_2Se{\cdot}2THF$. A green crystal was sealed in a glass capillary and examined on an Enraf-Nonius CAD4A diffractometer. Lattice parameters and other crystal data are given in Table I. The structure was solved by using normal Patterson and Fourier techniques. The hydrogen atom positions for the pyrazolylborate ligand were calculated and used in the structure factor calculation but were not refined. A difference electron density map revealed a THF molecule of crystallization. Isotropic refinement of the five ring atoms did not result in definitive location of the oxygen atom. Final positional and thermal

Table IV. Final Atomic Parameters for **3**

atom	x	y	z
Mo1	0.46956 (3)	0.31856 (2)	0.05792 (4)
Se	0.5000 (0)	0.5000 (0)	0.0000 (0)
O1	0.7538 (3)	0.3362 (3)	0.0435 (6)
O2	0.6105 (4)	0.4392 (3)	0.4752 (4)
N1	0.2603 (3)	0.2738 (2)	0.0589 (4)
N2	0.3604 (3)	0.2163 (2)	−0.2308 (4)
N3	0.4443 (3)	0.1470 (2)	0.1137 (4)
N11	0.1666 (3)	0.1661 (2)	−0.0334 (4)
N21	0.2564 (3)	0.1155 (2)	−0.2737 (4)
N31	0.3273 (3)	0.0571 (2)	0.0217 (4)
C1	0.6502 (4)	0.3317 (3)	0.0476 (6)
C2	0.5580 (4)	0.3948 (3)	0.3215 (5)
C10	0.0471 (3)	0.1593 (4)	−0.0154 (5)
C11	0.0615 (4)	0.2638 (4)	0.0872 (6)
C12	0.1975 (3)	0.3328 (3)	0.1323 (5)
C20	0.2114 (4)	0.0688 (4)	−0.4544 (5)
C21	0.2866 (5)	0.1427 (4)	−0.5276 (5)
C22	0.3763 (4)	0.2322 (3)	−0.3869 (5)
C30	0.3342 (4)	−0.0376 (3)	0.0797 (5)
C31	0.4609 (4)	−0.0087 (3)	0.2167 (6)
C32	0.5252 (4)	0.1065 (3)	0.2335 (5)
C40	0.8672 (8)	0.2311 (6)	0.5276 (12)
C41	0.0116 (9)	−0.2678 (9)	−0.5186 (12)
C42	−0.0726 (9)	−0.3784 (8)	−0.6531 (14)
C43	−0.0366 (10)	0.4095 (7)	−0.2827 (12)
C44	0.8431 (8)	0.2992 (8)	0.6486 (16)
B1	0.2079 (4)	0.0726 (3)	−0.1257 (5)

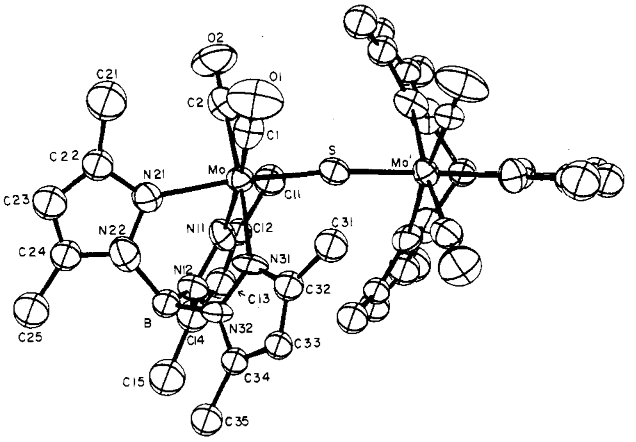

Figure 2. Perspective view of the structure of **2**. Hydrogen atoms have been omitted for clarity. The halves of the molecule are related to one another by C_2 symmetry.

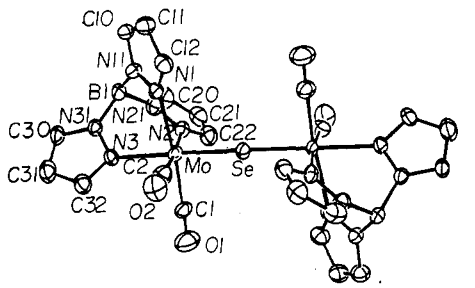

Figure 3. ORTEP diagram of **3**. The halves of the molecule are related to one another by a center of symmetry.

parameters are given in Table IV; a listing of $|F_o|$ and $|F_c|$ is available as supplementary material.

Results

Description of the Structures. The structures of **1**, **2**, and **3** are shown in Figures 1–3, respectively. A striking feature is the linear Mo–X–Mo (X = S, Se) unit. In **1** and **3** this unit is required to be strictly linear by a center of symmetry at the chalcogen atom. Compound **2** is required to have C_2 symmetry and the Mo–S–Mo angle is 171.5 (4)°. The Mo–S distances are unusually short for sulfido groups bridging Mo atoms (2.180 (1) Å for **1** and 2.200 (2) Å for **2**). In **3** the Mo–Se distance is 2.323 (1) Å; the increase in the Mo–chalcogen distance is comparable with the difference in the covalent radii of selenium and sulfur.[11] The coordination geometry at the Mo atoms in all three structures is approximately octahedral with the nitrogen atoms of the hydrotripyrazolylborate

Table V. Bond Distances (Å) and Bond Angles (deg) for **1**

	Bond Distances		
Mo–S	2.181 (1)	Mo–C1	1.998 (5)
Mo–N1	2.216 (3)	Mo–C2	1.984 (5)
Mo–N2	2.213 (3)	C1–O1	1.141 (6)
Mo–N3	2.212 (3)	C2–O2	1.139 (5)
	Bond Angles		
Mo-S-Mo	180.0	C2-Mo-N3	92.3 (2)
C1-Mo-C2	86.9 (2)	S-Mo-N1	96.0 (1)
C1-Mo-S	88.3 (1)	S-Mo-N2	97.2 (1)
C2-Mo-S	89.7 (1)	S-Mo-N3	177.9 (1)
C1-Mo-N1	96.1 (2)	N1-Mo-N2	82.1 (1)
C1-Mo-N2	174.3 (1)	N1-Mo-N3	81.9 (1)
C1-Mo-N3	92.4 (2)	N2-Mo-N3	82.0 (1)
C2-Mo-N1	173.6 (1)	Mo–C1–O1	177.3 (4)
C2-Mo-N2	94.4 (2)	Mo–C2–O2	179.3 (5)

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) for **2**

	Bond Distances		
Mo-S	2.200 (2)	Mo–C1	1.955 (21)
Mo-N11	2.260 (14)	Mo–C2	1.993 (21)
Mo-N21	2.188 (13)	C1–O1	1.168 (18)
Mo-N31	2.247 (13)	C2–O2	1.129 (19)
	Bond Angles		
Mo-S-Mo	171.5 (4)	N11-Mo-N31	86.0 (5)
S-Mo-N11	93.2 (5)	N11-Mo–C1	175.4 (7)
S-Mo-N21	172.9 (5)	N11-Mo–C2	94.0 (7)
S-Mo-N31	94.0 (4)	N21-Mo-N31	81.8 (5)
S-Mo-C1	91.2 (7)	N21-Mo-C1	94.8 (8)
S-Mo-C2	91.0 (5)	N21-Mo-C2	93.2 (6)
N11-Mo-N21	80.8 (6)	N31-Mo–C1	94.7 (7)

Table VII. Bond Distances (Å) and Bond Angles (deg) for **3**

	Bond Distances		
Mo-Se	2.323 (1)	Mo-C1	1.981 (11)
Mo-N1	2.213 (6)	Mo–C2	1.975 (9)
Mo-N2	2.218 (6)	C1–O1	1.149 (10)
Mo-N3	2.196 (6)	C2–O2	1.150 (9)
	Bond Angles		
Mo-Se-Mo	180.0	C2-Mo-N3	91.4 (3)
C1-Mo–C2	89.2 (3)	Se-Mo-N1	99.67 (15)
C1-Mo-Se	88.9 (2)	Se-Mo-N2	97.11 (15)
C2-Mo-Se	88.3 (2)	Se-Mo-N3	179.3 (2)
C1-Mo-N1	170.8 (3)	N1-Mo-N2	81.8 (2)
C1-Mo-N2	94.0 (3)	N1-Mo-N3	80.9 (2)
C1-Mo-N3	90.5 (3)	N2-Mo-N3	83.3 (2)
C2-Mo-N1	94.3 (3)	Mo–C1–O1	178.4 (7)
C2-Mo-N2	173.8 (3)	Mo–C2–O2	177.5 (8)

Table VIII. Comparison of Average Bond Distances (Å) and Bond Angles (deg) in 1, **2**, and 3

	1	2	3
Mo–S(Se)	2.180 (1)	2.200 (2)	2.323 (1)
Mo–N_t[a]	2.212 (3)	2.188 (13)	2.196 (6)
Mo–N_c[b]	2.215 (2)	2.254 (10)	2.216 (6)
Mo–C[c]	1.991 (4)	1.974 (15)	1.978 (11)
Mo–S(Se)–Mo	180 (0)[d]	171.5 (4)	180 (0)[d]

[a] N_t refers to the N atom that is trans to the S (Se) atom.
[b] Average distance to the N atoms that are cis to the S (Se) atom.
[c] Average Mo–C distance. [d] Required to be 180° by symmetry.

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ligands occupying *fac* positions.

Selected distances and angles for **1**, **2**, and **3** appear in Tables V–VII. The values for **1** are somewhat more precies because of the larger data crystal. The average bond distances for the inner coordination spheres of **1**, **2**, and **3** are compared in Table VIII. The major difference between compounds **1** and **2** is that **2** exhibits two different types of Mo–N distances whereas the three Mo–N distances in **1** are not significantly different. In **2** the Mo–N distance trans to the bridging S atom (2.188 (13) Å) is 0.066 Å (5σ) shorter than the average Mo–N (2.2544 (10) Å) distances that are cis to the bridging S atoms and trans to a carbonyl ligand. For the related monomeric compound $(HB(Me_2pz)_3)Mo(CO)_2SC_6H_4Cl$ the Mo–N distance trans to S (2.169 (3) Å) is also shorter than the average Mo–N distance trans to CO (2.225 (3) Å).[12e] The Mo–N distances in **1** and **3** are within experimental error; the substitution of S by Se has little effect on the remaining ligands. The Mo–N distances in other pyrazolylborate complexes range from 2.14 to 2.27 Å.[12]

Discussion

Compounds **1** and **2** are the first examples of linear $[Mo–S–Mo]^{2+}$ complexes while **3** is only the third example of a linear M–Se–M unit for any metal.[22,23] Previously, a complex containing the linear $[Mo–S–Mo]^{6+}$ unit, $\{[Mo(CN)_6]_2S\}^{6-}$, has been reported.[4] The chromium compound $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$, which contains a linear $[Cr–S–Cr]^{2+}$ unit, has been described by Legzdins and co-workers.[5a] Linear M–S–M units have also been described for Ni, Co, and V.[13,22] All of these compounds involve unusually short metal–sulfur distances. The Mo–S distances (2.17–2.20 Å) are somewhat longer than the range of Mo–S distances for terminal sulfido groups bound to Mo(IV), Mo(V), or Mo(VI)[2] but about 0.13 Å shorter than typical Mo–S distances in μ-sulfido-bridged binuclear Mo(V) compounds.[3] Clearly some multiple bonding between M and S occurs in all these linearly bridged complexes of group 6 metals. The Mo–Se distance in **3** is comparable to those of the terminal selenido groups in $[MoSe_4]^{2-}$.[2]

Two kinds of valence-bond structures have been used to describe the bonding in the above complexes. The structure Mo=S=Mo used[4] to describe $\{[Mo(CN)_6]_2S\}^{6-}$ emphasizes multiple bonding between the metal d orbitals and the sulfur p orbitals. The metal–sulfur bonding in the chromium complexes has been represented as Cr≡S≡Cr, which corresponds to participation of the sulfur d orbitals in the bonding with the metal.[5a] Recently molecular orbital descriptions of the bonding in linear M–S–M systems have appeared.[14,15] The calculations on $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2S$ and the hypothetical compound $[(CO)_5CrSCr(CO)_5]^{2+}$ serve as a bonding model for **1** and **2**. The multiple bond in linear M–S–M units involves (1) σ-bonds between the two sp hybrid orbitals on the S and metal d_{z^2} orbitals and (2) $d\pi$–$p\pi$ bonds between metal d_{xz}, d_{yz} orbitals and p_x, p_y orbitals on the S atom, which are perpendicular to the M–S–M axis.[14,15] The $d\pi$–$p\pi$ interactions produce a pair of bonding molecular orbitals, a pair of nonbonding molecular orbitals, and a pair of strongly antibonding molecular orbitals. This same bonding pattern is well-known for linear triatomics of first-row elements.[16] For the $[Cr–S–Cr]^{2+}$ triatomic species both the bonding and nonbonding π levels of the M–S–M unit are fully occupied.[14,15] In addition, each metal atom has one pair of electrons in a nonbonding orbital that is normal to the M–S–M axis but which can be involved in π-bonding to the CO ligands of the complex. Thus, the $[M–S–M]^{2+}$ triatomic unit (M = Cr, Mo, W) has a total of 16 valence electrons in bonding and nonbonding molecular orbitals and is formally isoelectronic with CO_2. The linearity of the $[M–S–M]^{2+}$ unit and the short M–S distances can both be explained without invoking sulfur d orbitals. However, some additional stabilization does result from including sulfur 3d orbitals in the molecular orbital calculations.[15]

The molecular orbital bonding model for **1** and **2**[14] also accounts for the linearity of the $[Mo–S–Mo]^{6+}$ unit of the $[(NC)_6Mo–S–Mo(CN)_6]^{6-}$ anion and explains why Mo–S distances of this anion are nearly identical with the Mo–S distances in **1** and **2**. The 12 valence electrons of the $[Mo–S–Mo]^{6+}$ unit will completely fill the two σ-bonding orbitals and the four bonding and nonbonding π-type orbitals of the M–S–M triatomic unit that were described above. The $[(NC)_6Mo–S–Mo(CN)_6]^{6-}$ anion differs from **1** and **2** in that in the anion each Mo atom has five CN^- ligands in the plane normal to the Mo–S–Mo axis, whereas in **1** and **2** each Mo atom has four ligands and a pair of nonbonding electrons in the plane normal to the Mo–S–Mo axis.

The dark green color of **1** and **2** is due to a broad absorption band near 600 nm. In **1** this band occurs at 606 nm with an extinction coefficient of 682. A second more intense band (395 nm, $\epsilon = 7.8 \times 10^4$) is also observed. In **3** the two bands are shifted to lower energy. From the molecular orbital diagram in Figure 2 of Mealli and Sacconi[15] the transition near 600 nm can be assigned to the $e_g \rightarrow e_{2u}$ transition of the Mo–S–Mo unit. The e_g orbitals are nonbonding orbitals localized on the metals (d_{xz}, d_{yz}), but e_{2u} is the π-antibonding orbital of the M–S–M unit and ha substantial sulfur p character. The dark green color of $[(NC)_6Mo–S–Mo(CN)_6]^{6-}$ (629 nm, $\epsilon = 116$)[4c] is probably due to the same transition since the bonding in its Mo–S–Mo fragment is similar to the bonding in **1** and **2**.

The ^{95}Mo NMR spectrum of **2** shows a peak at 314 ppm. This is more deshielded than typical ^{95}Mo NMR resonances from monomeric Mo(II) compounds containing the $[Mo(CO)_2]^{2+}$ fragment, which usually occur at negative chemical shifts.[17,18] Compound **1** is not sufficiently soluble to characterize by ^{95}Mo NMR. Compounds **1** and **3** have crystallographic C_i symmetry and approximate C_{2h} symmetry. Considering the C_{2h} symmetry, **1** and **3** should have two allowed CO stretches in the infrared region. This is in fact the case for **1** and **3** in a Nujol mull. However, in solution four bands are observed, which indicates the existence of a mixture of rotamers. These observations are consistent with the experimental results for $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]^2$ and the theoretical calculations, which indicate a low barrier to rotation about the M–X–M bonds. The ^1H NMR spectra of **1** and **3** indicate two different pyrazole rings in relative ratio 2 to 1. These

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spectra are consistent with the local structure about each Mo atom, with two pyrazole rings trans to the CO's and one pyrazole ring trans to S (Se), but they provide no evidence concerning the existence of rotamers. However, the proton NMR spectra of **2** and its tungsten analogue, investigated by Hubbard and Lichtenberger,[8] do clearly show hindered rotation of each (HB($Me_2pz)_3)(CO)_2M$ fragment about the M–S bonds.

Several complexes with linear M–X–M (X = S, Se) units are now known for group 6 metals in different oxidation states. The chemistry of these compounds has not yet been extensively explored. For molybdenum both $[Mo\text{–}S\text{–}Mo]^{2+}$ and $[Mo\text{–}S\text{–}Mo]^{6+}$ complexes are known. The existence of two stable classes of complexes differeing by four electrons suggests that a wealth of redox chemistry should exist for these systems.

Mo–S coordination is important in heterogeneous catalysts[19] and in biological systems.[20] Linear M–S–M units with short M–S bonds have now been demonstrated in both Co and Mo compounds. The possibility of a linear Co–S–Mo unit in CoMoS hydrodesulfurization catalysts should be considered. Finally, we note the unusually short Mo–S distances in **1** and **2** raise the interesting question as to whether such linear Mo–S–Mo structural features can be present in the enzyme xanthine oxidase, for which EXAFS spectroscopy has indicated[21] an Mo–S distance of ~2.15 Å. Current chemical and physical evidence strongly favors a mononuclear molybdenum site. However, the Mo···Mo distance of 4.4 Å for the Mo–S–Mo centers in **1** and **2** would probably not be detected by EXAFS spectroscopy.

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Registry No. **1**·$C_6H_5CH_3$, 95156-31-3; **2**, 90641-19-3; **3**·2THF, 95156-33-5; $(HB(pz)_3)Mo(CO)_3H$, 95156-34-6; S, 7704-34-9; $[Et_4N][(HB(Me_2pz)_3)Mo(CO)_3]$, 22357-70-6; Se, 7782-49-2.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen positions, and structure factors for **1**, **2**, and **3** (39 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Hong Kong, Hong Kong, and Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Cis Ruthenium Complexes of 1,4,8,11-Tetraazacyclotetradecane (cyclam): Crystal and Molecular Structure of *cis*-$[Ru(cyclam)Cl_2]Cl$

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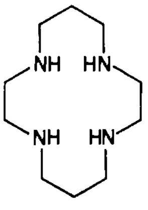
The crystal and molecular structure of *cis*-$[Ru(cyclam)Cl_2]Cl$ (cyclam = $C_{10}H_{24}N_4$) prepared by the $Ru(ox)_3^{3-}$ (ox = $C_2O_4^{2-}$) method has been determined: monoclinic, space group $P2_1/c$, a = 7.579 (1) Å, b = 14.414 (4) Å, c = 14.718 (3) Å, β = 102.33 (1)°, V = 1570.8 (5) Å^3, Z = 4. The average Ru–Cl distance, 2.371 (1) Å in the present complex, is substantially longer than that found in the corresponding trans isomer [2.342 (1) Å], reflecting the greater σ-trans effect of the secondary amine N atom over the chloride ligand. Reaction of *cis*-$[Ru(cyclam)Cl_2]Cl$ with N heterocyclic amines and Zn(Hg) yielded *cis*-$[Ru(cyclam)L_2]^{2+}$ (L_2 = $(py)_2$, bpy, phen), the metal-to-ligand charge-transfer transitions of which have been found to be blue shifted from those of the corresponding *cis*-$[Ru(NH_3)_4L_2]^{2+}$ species.

Introduction

In 1980, Isied reported the isolation of *cis*-$[Ru(cyclam)Cl_2]Cl$[2] (cyclam = 1,4,8,11-tetraazacyclotetradecane) as a by product



cyclam

during the synthesis of the *trans* isomer by the method of Chan et al. by reacting $K_2[RuCl_5H_2O]$ with cyclam in methanol.[3] Following this work, we reported a reaction scheme for the preparation of cis ruthenium(III) macrocyclic tetraamine species, utilizing $K_3[Ru(ox)_3]$ (ox = $C_2O_4^{2-}$) as the starting material.[4] The IR spectrum of our *cis*-$[Ru(cyclam)Cl_2]Cl$ in the most discriminating 800–900-cm^{-1} region is very similar to those of all other well-characterized *cis*-$[M(cyclam)Cl_2]^+$ species[4] [M = Co(III), Cr(III), Fe(III)]; however, Isied's species showed a different IR spectrum. As for the electronic spectrum, the observed ϵ values (200–500 dm^3 mol^{-1} cm^{-1}) for the bands above 300 nm of Isied's species are too low to be consistent with what would have been expected for ligand-to-metal charge-transfer transitions. Apparently, our cis-$[Ru(cyclam)Cl_2]Cl$ and Isied's species could not be the same compound. In order to resolve this structural ambiguity we have recently carried out an X-ray crystal structural determination of our *cis*-$[Ru(cyclam)Cl_2]Cl$ prepared by the $Ru(ox)_3^{3-}$ method. The results clearly indicate a cis configuration. This paper describes the X-ray structural analysis of our *cis*-$[Ru(cyclam)Cl_2]Cl$ and the synthetic chemistry of this species with some N heterocyclic amine ligands.

Experimental Section

$K_2[RuCl_5H_2O]$ (Johnson and Matthey) was used as supplied. cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) was twice recrystallized before use. All other reagents used were of analytical grade, and doubly distilled water was used throughout the experiments. $K_3[Ru(ox)_3]$ and *cis*-$[Ru(cyclam)Cl_2]Cl$ were prepared by literature methods,[4] with some minor modifications.

$K_3[Ru(ox)_3]$. $K_2[RuCl_5H_2O]$ (2 g, 5.3 mmol) and oxalic acid dihydrate (2.3 g, 18 mmol) in H_2O were refluxed for 2$^1/_2$ h during which the solution turned brown. Solid potassium carbonate was added continually in small amounts until the the solution reached ca pH 7 and the evolution of CO_2 subsided. After heating at just boiling for another 20 min, the resulting olive green solution was ready for use in the preparation of *cis*-$[Ru(cyclam)Cl_2]Cl$, without the need of isolating the pure $K_3[Ru(ox)_3]$.

***cis*-$[Ru(cyclam)Cl_2]Cl$.** A partially neutralized aqueous solution of cyclam was first prepared by adding HCl (2 M) to an aqueous solution of cyclam (1 g in 25 cm^3 H_2O) until the pH of the solution was ca. 6.5. This solution was slowly added to a freshly prepared solution of $[Ru(ox)_3]^{3-}$, and the pH was adjusted to ca. 7 with either potassium carbo-

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