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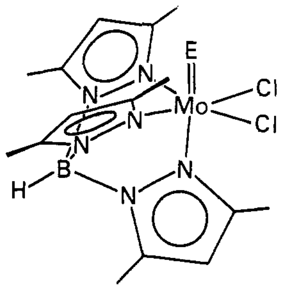
The First Mononuclear Molybdenum(V) Complex with a Terminal Sulfido Ligand: $[HB(Me_2C_3N_2H)_3]MoSCl_2$

Sir:

There is considerable evidence that active xanthine oxidase in its oxidized resting state contains both a terminal sulfido ligand and a terminal oxo ligand bound to Mo(VI).[1,2] The transient molybdenum(V) states that are produced during turnover of the functional enzyme exhibit EPR spectra with relatively low $A(^{95,97}Mo)$ values and relatively high g values.[3] These EPR parameters are generally ascribed to the presence of thiolate ligands coordinated on an oxo–Mo(V) center, but a terminal sulfido ligand has also been proposed[4] to be present in these transient states, particularly that producing the very rapid EPR signal. The ability of RS^- ligands to increase g values and lower $A(^{95,97}Mo)$ values in oxo–Mo(V) complexes is now well documented[5-7] for model compounds. Thiolate groups cis to the terminal oxo group are especially effective in producing trends in the g and $A(^{95,97}Mo)$ values that are similar to those observed in molybdenum enzymes.[7] To date, however, it has not been possible to assess the effect of a terminal sulfido ligand on the EPR spectrum of a Mo(V) complex because no model compounds containing an $[Mo{=}S]^{3+}$ center were known.[6] Previous attempts to prepare such centers invariably yielded diamagnetic binuclear or polynuclear molybdenum compounds.[6] Recently we have used the sterically encumbering hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand ($[HB(Me_2pz)_3]^-$) to stabilize a wide range of mononuclear oxo–Mo(V) complexes (**1**).[7] This same ligand has now been used to stabilize the first isolable mononuclear sulfido–Mo(V) complex (**2**). Herein we present EPR and other spectroscopic data for this novel complex and compare the data to those for the oxo analogue.

The reaction of $[HB(Me_2pz)_3]MoOCl_2$ (**1**) with excess B_2S_3 in dry deoxygenated dichloromethane produces orange-brown $[HB(Me_2pz)_3]MoSCl_2$ (**2**) in 55% yield.[8] Compound **2**, which is mildly air and moisture sensitive, has been characterized by elemental analyses, infrared and mass spectroscopy, X-ray powder diffraction,[9] and electronic and EPR spectroscopy.



1, E = O
2, E = S

The electronic absorption spectra for **1** and **2** are summarized in Figure 1. The extinction coefficients of the lowest energy bands[8] are consistent with their assignments to d → d transitions from the essentially $d_{x^2-y^2}$ ground-state orbital to the metal d_{yz} and/or d_{xz} orbitals.[10] The lower energy for the first transition of **2** (9090 cm^{-1}) compared to that of **1** (14 180 cm^{-1}) is consistent with the weaker π-donor ability of a sulfido vs. an oxo ligand, which decreases the energy separation to the metal $d\pi^*$ orbitals (d_{xz}, d_{yz}) in **2** compared to that in **1**. These energy differences are supported by molecular orbital calculations.[11] A similar weak

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(8) Preparation of $[HB(Me_2pz)_3]MoSCl_2$ (**2**): A suspension of $[HB(Me_2pz)_3]MoOCl_2$ (**1**)[7] (1.5 g, 3.1 mmol) and B_2S_3 (0.9 g, 7.6 mmol) in dry, deoxygenated CH_2Cl_2 (80 mL) was stirred under nitrogen for 1 day. The reaction mixture was filtered anaerobically and the filtrate evaporated to dryness in vacuo. The resulting residue was dissolved in CH_2Cl_2 (50 mL), the mixture was filtered, and methanol (200 mL) was added to precipitate the complex. after the mixture was allowed to stand for 30 min, the brown solid was filtered off and washed with methanol. Yield = 0.85 g (1.7 mmol, 55%). Recrystallization from CH_2Cl_2/MeOH yielded orange-brown crystals. Anal. Calcd for $C_{15}H_{22}BCl_2MoN_6S$: C, 36.31; H, 4.47; N, 16.94; Cl, 14.29; S, 6.46. Found: C, 35.79; H, 4.55; N, 16.76; Cl, 15.51; S, 6.36. IR: 2556 (B—H); 523 (Mo═S); 338, 322 (Mo—Cl) cm^{-1}. Electronic absorption spectra [energy (10^3 cm^{-1}) (ϵ (L mol^{-1} cm^{-1}))]: **1**, 14.18 (50), 22.99 sh (~1000), 29.67 (5200); **2**, 9.90 (50), 22.22 (880), 32.26 (6980). Mass spectra for **1** and **2** obtained by using an AEI MS30 mass spectrometer with ionization effected by electron impact showed the respective parent ions for $[HB(Me_2pz)_3]MoOCl_2$ (m/z 481)[7] and $[HB(Me_2pz)_3]MoSCl_2$ (m/z 497) with the same relative intensity patterns (mass numbers on ^{12}C, ^1H, ^{14}N, ^{11}B, ^{16}O, ^{98}Mo, ^{32}S, and ^{37}Cl).

(9) The X-ray powder pattern for **2** is very similar to that of **1**, consistent with isomorphous substitution of S for O. The major difference is the peak at d = 9.0 Å, which is strong in **1** and very weak in **2**.

(10) The molecules have C_s symmetry. We have chosen the molecular z axis to be parallel to the Mo═E bond and the xz plane to be the mirror plane. The lobes of the $d_{x^2-y^2}$ orbital lie between the atoms in the N_2Cl_2 plane normal to the Mo═E bond.

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Table I. EPR Parameters

	g_{yy}	g_{zz}	g_{xx}	g_{xz}	$\langle g \rangle$	$\mathrm{cm}^{-1} \times 10^4$				α, deg
						A_{yy}	A_{zz}	A_{xx}	$\langle A \rangle$	
$[HB(Me_2pz)_3]MoOCl_2$	1.941	1.971	1.934	−0.017	1.947	18.1	71.4	38.1	46.0	33
$[HB(Me_2pz)_3]MoSCl_2$	1.921	1.941	1.919	−0.021	1.928	≤18.0	70.7	41.2	46.8	31

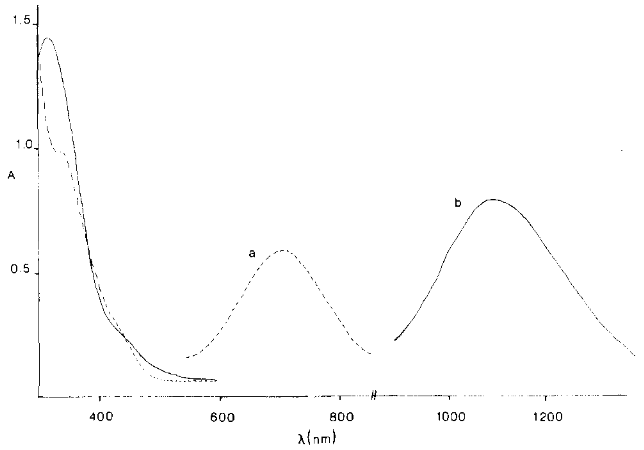

Figure 1. Electronic absorption spectra in CH_2Cl_2 of $[HB(Me_2C_3N_2H)_3]MoOCl_2$ (**1**) (---) and $[HB(Me_2C_3N_2H)_3]MoSCl_2$ (**2**) (—): (a) $A \times 50$ for **1**; (b) $A \times 80$ for **2**. Extinction coefficients appear in footnote 8.

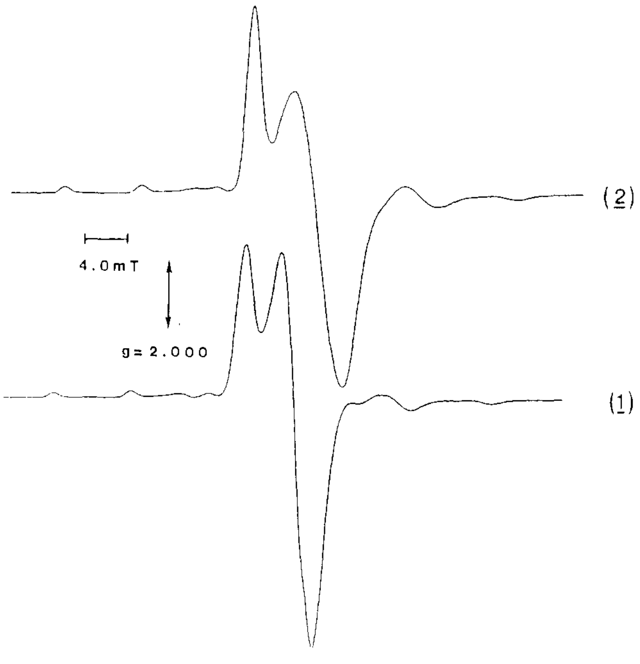

Figure 2. X-Band EPR spectra of **1** and **2** (top) in frozen toluene solutions at 77 K. The detailed EPR parameters appear in Table I.

π-donor effect for a terminal sulfido ligand was predicted for $[V{=}E]^{2+}$ (E = O, S) complexes[13] and has been experimentally verified for two different groups of square-pyramidal $[V{=}E]^{2+}$ complexes.[14,15]

The intense absorptions in the spectra of **1** and **2** above 23 000 cm^{-1} are assigned to charge-transfer transitions. Their intensities preclude the location of the other d → d transitions, but their positions set a lower limit on the energies of the other d → d bands. We would anticipate little change in the energy of the transition involving electronic promotion from the essentially $d_{x^2-y^2}$ ground state to the essentially d_{xy} excited state because the ligands perpendicular to the terminal oxo (sulfido) ligand remain the same. Furthermore, the similarity between the higher energy parts of the spectra of **1** and **2** indicates that the charge-transfer transitions are controlled by the ligands cis to the terminal ligand.

A comparison of the EPR spectra of **1** and **2** in both fluid and frozen solutions (Table I, Figure 2) shows that the **g** tensor elements in **2** are all significantly smaller than those in **1**. Thus, the smaller $\langle g \rangle$ for the sulfido complex is a consequence of the lowering of all the **g** tensor elements and is not due to any changes in the sense of the anisotropy. The **A** tensor and $\langle A \rangle$, on the other hand, show little difference for **1** and **2**. These EPR spectral changes upon converting **1** to **2** (lowering of the **g** tensor elements with a virtually constant **A** tensor) are in marked contrast to the EPR changes observed upon systematically substituting RS^- ligands for RO^- ligands cis to a terminal oxo group[7] [cf. the following: $[HB(Me_2pz)_3]MoO(OMe)_2$, $g_1 = 1.960$, $g_2 = 1.942$, $g_3 = 1.904$, $\langle A \rangle = 45.2 \times 10^{-4}\ \mathrm{cm}^{-1}$; $[HB(Me_2pz)_3]MoO(SEt)_2$, $g_1 = 2.011$, $g_2 = 1.952$, $g_3 = 1.931$, $\langle A \rangle = 36.7 \times 10^{-4}\ \mathrm{cm}^{-1}$].

Simulation of the EPR spectra of **1** and **2** assuming C_s symmetry requires only that g_2 (g_{yy}) and A_2 (A_{yy}) be coincident and perpendicular to the mirror plane.[16] The remaining tensor axes cannot be directly related to molecular geometry, but we use the previous criterion that the **A** tensor will be close to metal–ligand directions or pseudo symmetry axes[17,18] and that largest value of A is close to that for Mo=E,[19,20] as occurs in high-symmetry (C_{4v}) $[MoOX_4]^-$ complexes. This leads to the assignment of the **g** and **A** tensor elements in Table I with reference to the axis system in the Appendix. The gross changes in the principal g values may be qualitatively understood by approximating the d-orbital splittings to those of a C_{4v} molecule, i.e. $\Delta_2 \approx \Delta_4[(d_{x^2-y^2})^1 \rightarrow (d_{xz})^1$ or $(d_{yz})^1]$. The reductions in g_{xx}, g_{yy}, and g_{zz} on substituting terminal oxo by sulfido correlate with the corresponding decrease in the lowest energy bands in the respective electronic spectra (Figure 1) that are assigned to Δ_2 and Δ_4. Equations A6–A8 show that smaller values of Δ_2 and Δ_4 lead to a lowering of all the g values for the same extent of d-orbital mixing and for constant $\Delta_3[(d_{x^2-y^2})^1 \rightarrow (d_{xy})^1]$.

A similar amount of d-orbital mixing in **1** and **2** is indicated by their similar Euler angles, α, the angle by which the **g** tensor is rotated relative to the **A** tensor in the mirror plane (x,z) of the molecule. If the smaller values for Δ_2 and Δ_4 for **2** are attributed to the poor π-donor ability of the terminal sulfido group, then we would also expect the molecular orbital coefficients δ and β to increase on changing from oxo to sulfido, thus reinforcing the trends in the g values caused by the changes in the transition energies. Similar but less marked changes have been observed[15] in g_{xx} and g_{yy} in $[VE(SCH_2CH_2S)_2]^{2-}$ (E = O, S), for which the spin–orbit coupling constant is smaller.

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(11) Fenske–Hall[12] molecular orbital calculations on the model pseudooctahedral Mo(V) complexes *fac*-$[(NH_3)_3MoOCl_2]^+$ and *fac*-$[(NH_3)_3MoSCl_2]^+$ show the same pattern of orbital orderings for both complexes. The highest occupied molecular orbital (HOMO) is $d_{x^2-y^2}$; the two lowest unoccupied molecular orbitals (LUMO's) are nearly degenerate and primarily d_{xz} and d_{yz}. The calculated HOMO–LUMO gap for the sulfido complex is 1.3 eV smaller than that for the oxo analogue.

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The ligands cis to the terminal oxo or sulfido ligand remain constant in **1** and **2**, and thus to a good approximation the character of the ground state remains unchanged.[11] Since the composition of the ground state mainly determines the magnitudes of the principal **A** tensor elements (see eq A10–A13 in Appendix), relatively little change in the principal **A** tensor values on substituting sulfido for oxo is anticipated.

Our present observations show that merely changing an oxygen donor ligand for a sulfur donor ligand does not necessarily increase the g values and decrease the A values of a Mo(V) complex. Such changes are dependent at least on the ligand type, and probably on the position of substitution relative to the other ligands. Three mechanisms that would lead to *increases* in the g values upon replacing an oxygen donor atom by a sulfur donor atom are as follows:

(i) Admixture of charge-transfer states involving significant contributions from appropriate metal d orbitals. Such excited charge-transfer states mix into the ground state under metal spin–orbit coupling to give contributions with the sign opposite from those involving simple d–d excitations.[21,22] This mechanism can give g values ≥ 2.0023.

(ii) Increased covalency of the metal–ligand bond leading to delocalization of the unpaired electron and reduction of the metal molecular orbital coefficients in the d–d contribution to the g values. This mechanism will only permit g values ≤ 2.0023.

(iii) The increased value of the single electron spin–orbit coupling constant of sulfur vs. oxygen. This mechanism can decrease the amount by which some g_{ii} are reduced from 2.0023.

It is difficult to completely separate these mechanisms from one another, but the $[HB(Me_2pz)_3]MoOXY$ complexes (X, Y = monoanions) and **1** and **2** have enabled us to investigate the effects of a variety of single-ligand substitutions on the EPR spectra of a six-coordinate Mo(V) center of known stereochemistry. Our previous study[7] showed that g values ≥ 2.0023 correlate with the observation of low-energy charge-transfer transitions and points to the importance of (i) since this mechanism is the only one cited that can raise g above 2.0023. That study also confirmed that two RS^- ligands cis to a terminal oxo ligand produce g values approaching or exceeding 2.

The present results for **1** and **2** demonstrate for the first time that a terminal sulfido ligand bound to Mo(V) produces *lower* g values than a terminal oxo ligand. The lower g values for **2** correlate with the lower energy of the first d–d transition of **2**, as expected from ligand field theory (Appendix). Mechanisms i–iii may also contribute to the final EPR parameters for **1** and **2**, but these mechanisms cannot be the dominant factors in the observed differences in g values between **1** and **2**.

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Appendix. For **g** and **A** tensors in C_s symmetry with z parallel to Mo═E and y perpendicular to the mirror plane, d-orbital mixings in the antibonding molecular orbitals are

$$\phi_1 = \alpha[a_1 d_{x^2-y^2} + b_1 d_{xz} + c_1 d_{z^2}] \qquad a_1 > b_1, c_1 \tag{A1}$$

$$\phi_2 = \beta[a_2 d_{x^2-y^2} + b_2 d_{xz} + c_2 d_{z^2}] \qquad b_2 > a_2, c_2 \tag{A2}$$

$$\phi_5 = \epsilon[a_5 d_{x^2-y^2} + b_5 d_{xz} + c_5 d_{z^2}] \qquad c_5 > a_5, b_5 \tag{A3}$$

$$\phi_3 = \gamma[e_3 d_{xy} + f_3 d_{yz}] \qquad e_3 > f_3 \tag{A4}$$

$$\phi_4 = \delta[e_4 d_{xy} + f_4 d_{yz}] \qquad f_4 > e_4 \tag{A5}$$

Using ϕ_1 (mainly $d_{x^2-y^2}$) as the ground state and Δ_i (i = 2–5) as the energy separations between ϕ_1 and ϕ_i, we have

$$g_{zz} = 2.0023 - \frac{2\xi(\alpha\gamma)^2(2a_1e_3 + b_1f_3)^2}{\Delta_3} - \frac{2\xi(\alpha\delta)^2(2a_1e_4 + b_1f_4)^2}{\Delta_4} \tag{A6}$$

$$g_{xx} = 2.0023 - \frac{2\xi(\alpha\gamma)^2[b_1e_3 + (a_1f_3 + 3^{1/2}c_1f_3)]^2}{\Delta_3} - \frac{2\xi(\alpha\delta)^2[b_1e_4 + (a_1f_4 + 3^{1/2}c_1f_4)]^2}{\Delta_4} \tag{A7}$$

$$g_{yy} = 2.0023 - \frac{2\xi(\alpha\beta)^2[(a_1b_2 - b_1a_2) + 3^{1/2}(b_1c_2 - c_1b_2)]^2}{\Delta_2} - \frac{2\xi(\alpha\epsilon)^2[(a_1b_5 - b_1a_5) + 3^{1/2}(b_1c_5 - c_1b_5)]^2}{\Delta_5} \tag{A8}$$

$$g_{xz} = g_{zx} = \frac{2\xi(\alpha\gamma)^2[b_1e_3 + a_1f_3 + 3^{1/2}c_1f_3][2a_1e_3 + b_1f_3]}{\Delta_3} + \frac{2\xi(\alpha\delta)^2[b_1e_4 + a_1f_4 + 3^{1/2}c_1f_4][2a_1e_4 + b_1f_4]}{\Delta_4} \tag{A9}$$

where ξ is the metal single-electron spin–orbit coupling constant. Ignoring terms in $1/\Delta$, we have

$$A_{zz} \approx P\left[-\alpha^2K - \frac{2\alpha^2}{7}(4a_1^2 + b_1^2 - 2) - (2.0023 - g_{zz})\right] \tag{A10}$$

$$A_{xx} \approx P\left[-\alpha^2K - \frac{2\alpha^2}{7}(a_1^2 + b_1^2 + 3c_1^2 + 2(3^{1/2})a_1c_1 - 2) - (2.0023 - g_{xx})\right] \tag{A11}$$

$$A_{yy} \approx P\left[-\alpha^2K - \frac{2\alpha^2}{7}(a_1^2 + 4b_1^2 + 3c_1^2 - 2(3^{1/2})a_1c_1 - 2) - (2.0023 - g_{yy})\right] \tag{A12}$$

$$A_{xz} = A_{zx} \approx P\left[\frac{2\alpha^2}{7}(3a_1b_1 + 3^{1/2}b_1c_1) + g_{xz}\right] \tag{A13}$$

Registry No. **1**, 31371-06-9; **2**, 109390-37-6; *fac*-$[(NH_3)_3MoOCl_2]^+$, 109390-38-7; *fac*-$[(NH_3)_3MoSCl_2]^+$, 109390-39-8.

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Structural, ESR, and Electrochemical Properties of Two $[Rh_2(ap)_4]^+$ Geometric Isomers (ap = 2-Anilinopyridinate). A True Mixed-Valent Rhodium(II)-Rhodium(III) Complex

Sir:

Numerous theoretical and experimental ESR studies have been reported for Rh_2^{5+} complexes containing carboxylate,[1,2] amidate,[3]

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