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Degree and Influence of MoS··S Interactions in Oxo−Molybdenum(VI,V,IV) Complexes

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The facile redox interplay of molybdenum and sulfur[1−3] and transformations involving sulfur-donor ligands[1,4] may facilitate many of the reactions catalyzed by Mo−S centers. In purine oxidation by xanthine oxidase, the involvement of an oxo−thio−Mo(VI) center is supported by EXAFS evidence for a short 2.15−2.25 Å Mo═S interaction.[5] However, a short 2.227(2) Å Mo═S distance *and* an Mo═S··S interaction coexist in $\mathrm{LMo^{VI}OS(S_2PPr^{\mathit{i}}_2\text{-}\mathit{S})}$ [L = hydrotris(3,5-dimethylpyrazol-1-yl)borate];[6] thus, the short Mo−S interaction does not preclude the stabilization of the enzyme's "terminal" thio ligand. As well, known oxo−thio−Mo(V) complexes exhibit EPR spectra which are considerably more anisotropic and are of lower g_{iso} than the Very Rapid signal of xanthine oxidase, also postulated to arise from an oxo−thio−Mo(V) center,[5,7] and it is possible that an interaction involving the thio ligand could reduce the anisotropy of the enzyme EPR signal. We have sought, through the variation of the monoanion X in $\mathrm{[LMo^{VI,V}OSX]^{0/-}}$ complexes, to explore the structural, spectroscopic, and chemical ramifications of modulating the degree of S··S interaction at oxo−thio−Mo centers and to assess implications for related enzyme centers. Here, we draw a contrast between the molecular and electronic structures of the oxo−thio−Mo(VI) complex $\mathrm{LMo^{VI}OS(S_2PPr^{\mathit{i}}_2\text{-}\mathit{S})}$[6] and the dithio−oxo−Mo(IV) complex $\mathrm{LMo^{IV}O(pyS_2\text{-}\mathit{N,S})}$ ($\mathrm{pyS_2}$ = pyridyl-2-dithio), reported herein. Furthermore, we report the generation of Mo(V) species by the reduction *or* oxidation of these *formally* Mo(VI) and Mo(IV) complexes—a spectacular demonstration of the redox versatility of Mo−S centers.

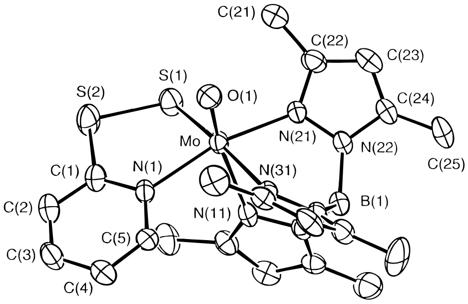

Figure 1. Structure of $\mathrm{LMo^{IV}O(pyS_2)}$. Additional bond lengths (Å) and angles (deg): Mo−N(1) 2.190(6), Mo−N(11) 2.371(6), Mo−N(21) 2.163(5), Mo−N(31) 2.267(6); O−Mo−S(1) 99.9(2), O−Mo−N(1) 101.5(2), S(1)−Mo−N(1) 83.6(2), Mo−S(1)−S(2) 103.0(1), S(1)−S(2)−C(1) 101.3(3), Mo−N(1)−C(1) 123.8(5).

Reaction of propylene sulfide with $\mathrm{LMo^{IV}O(pyS\text{-}\mathit{N,S})}$ (pyS = pyridyl-2-thio) resulted in the formation of $\mathrm{LMo^{IV}O(pyS_2\text{-}\mathit{N,S})}$. Microanalytical and mass spectrometric studies confirmed the transfer of a single sulfur atom to the oxo−Mo(IV) precursor. The infrared spectrum of $\mathrm{LMo^{IV}O(pyS_2)}$ revealed bands assignable to the Mo═O group (960 $\mathrm{cm^{-1}}$) and the L and $\mathrm{pyS_2}$ ligands; no ν(Mo═S) band was observed. The ^{1}H NMR spectrum confirmed molecular C_1 symmetry, while the electronic spectrum displayed d−d bands consistent with an oxo−Mo(IV) species.

The structure of $\mathrm{LMo^{IV}O(pyS_2)}$ (Figure 1) features a six-coordinate, distorted octahedral Mo center coordinated by tridentate L, terminal oxo, and bidentate *N,S*-donor $\mathrm{pyS_2}$ ligands.[8] The Mo−O distance of 1.681(6) Å is typical of oxo−Mo(IV) complexes,[9] but the Mo−S(1) distance of 2.323(2) Å is much longer than those of π-bonded Mo−S moieties, e.g., Mo═S ligands (2.09−2.13 Å),[9] some $\mathrm{Mo(S_4)}$ units,[10] and $\mathrm{LMo^{VI}OS(S_2PPr^{\mathit{i}}_2)}$.[6] In fact, the Mo−S(1) distance approaches

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[1] Wedd, A. G. In *Sulfur, its Significance for Chemistry, for the Geo-, Bio-, and Cosmospheres and Technology*; Müller, A., Krebs, B., Eds.; Elsevier: Amsterdam, 1984; p 181.

[2] In induced internal electron transfer reactions involving Mo and S, reduction of oxidant and Mo(VI) is coupled to oxidation of thio ligands to disulfido ligands: Coyle, C. L.; Harmer, M. A.; George, G. N.; Daage, M.; Stiefel, E. I. *Inorg. Chem.* **1990**, *29*, 14 and references therein.

[3] Attempts to prepare thio− or thiolato−Mo(VI) complexes frequently yield polysulfido−Mo(V,IV) complexes or disulfides and Mo(V,IV) species, respectively. (a) Harpp, D. N.; MacDonald, J. G. *Tetrahedron Lett.* **1984**, *25*, 703. (b) Dhar, P.; Chandrasekaran, S. *J. Org. Chem.* **1989**, *54*, 2998.

[4] The elegant work of Coucouvanis illuminates the facile transformation of sulfur ligands on molybdenum: Coucouvanis, D.; Toupadakis, A.; Lane, J. D.; Koo, S. M.; Kim. C. G.; Hadjikyriacou, A. *J. Am. Chem. Soc.* **1991**, *113*, 5271 and references therein.

[5] (a) Enemark, J. H.; Young, C. G. *Adv. Inorg. Chem.* **1993**, *40*, 1. (b) Young, C. G.; Wedd, A. G. In *Encyclopedia of Inorganic Chemistry*, King, R. B., Ed.; Wiley: New York, 1994; p 2330.

[6] Eagle, A. A.; Laughlin, L. J.; Young, C. G.; Tiekink, E. R. T. *J. Am. Chem. Soc.* **1992**, *114*, 9195.

[7] (a) Greenwood, R. J.; Wilson, G. L.; Pilbrow, J. R.; Wedd, A. G. *J. Am. Chem. Soc.* **1993**, *115*, 5385 and references therein. (b) Xiao, Z.; Bruck, M. A.; Doyle, C.; Enemark, J. H.; Grittini, C.; Gable, R. W.; Wedd, A. G.; Young, C. G. *Inorg. Chem.* **1995**, *34*, 5950. (c) Laughlin, L. J.; Young, C. G. *Inorg. Chem.* **1996**, *35*, 1050.

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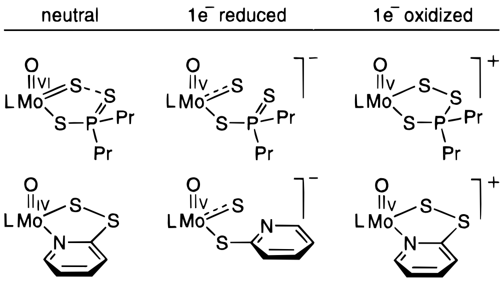
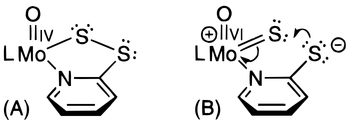
Chart 1



that typical of a Mo−S single bond, e.g., Mo−SR, with a mean Mo−S distance of 2.40 Å.[9] The S(1)−S(2) distance of 2.108(3) Å is slightly longer than those characteristic of single S−S bonds (ca. 2.05 Å).[11−13] The five-membered MoS_2NC ring exhibits a nonplanar, envelope structure. Extreme canonical forms **A** and **B**, formally dithio−oxo−Mo(IV) and oxo−thio−



Mo(VI) species, respectively, may be drawn for $LMo^{IV}O(pyS_2)$; they are related by the shift, indicated in structure **B**, of a pair of electrons between the metal and distal sulfur. Evidence favors an electronic structure dominated by canonical structure **A**, structure **B** being destabilized by an unfavorable charge separation. In contrast, the structural and spectroscopic properties of $LMo^{VI}OS(S_2PPr^i_2)$ favor its formulation as an oxo−thio−Mo(VI) complex.[6]

The redox behavior of $LMo^{VI}OS(S_2PPr^i_2)$ and $LMo^{IV}O(pyS_2)$ is especially interesting (see Chart 1). As expected, reduction of $LMo^{VI}OS(S_2PPr^i_2)$ produced the oxo−thio−Mo(V) anion $[LMo^{V}OS(S_2PPr^i_2\text{-}S)]^-$. This complex exhibited a highly anisotropic frozen-glass EPR spectrum characteristic of anions of this type.[14] EPR spectra showed no evidence of ^{31}P superhyperfine coupling, consistent with the severing of the S··S interaction and spatial separation of the phosphorus and Mo(V) centers. Interestingly, the reduction of $LMo^{IV}O(pyS_2)$ also produced an oxo−thio−Mo(V) anion, $[LMo^{V}OS(pyS)]^-$, which also exhibited a highly anisotropic frozen-glass EPR spectrum.[14,15] One-electron reduction of $LMo^{IV}O(pyS_2)$ results in a one-electron oxidation of Mo(IV) to Mo(V) and an overall two-electron reduction of the disulfide moiety. Disruption of the S−S interaction upon reduction is consistent with the irreversible cathodic wave in the cyclic voltammograms of both complexes.

Oxidation of $LMo^{IV}O(pyS_2)$ resulted in the formation of a cationic oxo−Mo(V) species, $[LMo^{V}O(pyS_2)]^+$, which retained the disulfide bond. Interestingly, in terms of g_{ii} values at least, its EPR spectrum closely resembles the enzyme Very Rapid signals; certainly, the presence of a disulfide interaction greatly reduces the $\boldsymbol{g}$ anisotropy compared to that of oxo−thio−Mo(V) complexes.[14] Notably, however, this cation does not exhibit the conspicuously high g_1 characteristic of the Very Rapid signal or oxo−thio−Mo(V) complexes. Oxidation of $LMo^{VI}OS(S_2PPr^i_2)$ also resulted in the generation of a cationic Mo(V) species, formulated as $[LMo^{V}O(S_3PPr^i_2\text{-}S,S')]^+$. The EPR spectra of this complex exhibited clear ^{31}P superhyperfine coupling, with $a(^{31}P) = 24.2 \times 10^{-4}$ cm^{-1},[16] consistent with the tethering of the phosphorus atom near the molybdenum via a sulfur−sulfur interaction. EPR spectra are less anisotropic than those of oxo−thio−Mo(V) species but exhibit some features common to oxo−thio anions, notably a low g_{iso}. Here, one-electron oxidation is associated with a formal one-electron reduction of Mo(VI) to Mo(V) and a two-electron oxidation of the S··S group to a disulfide. These observations are consistent with the electrochemical reversibility of the anodic process in the cyclic voltammograms of both complexes.

The contrasting structures and electronic descriptions of the Mo^{VI}═S··S and Mo^{IV}−S−S fragments of $LMo^{VI}OS(S_2PPr^i_2)$ and $LMo^{IV}O(pyS_2)$ and their fascinating redox behavior underscore the versatility of Mo−S centers. In a related system, the shorter than expected S··S distance (2.76 Å) in $MoO_2(MeNHCH_2CMe_2S)_2$ was interpreted in terms of a substantial disulfide-like interaction in this *formally* Mo(VI) complex.[17] Echoing the view of Stiefel,[17] we believe the redox interplay of molybdenum and sulfur and its fine-tuning by the coligands and the redox level at particular stages of catalysis may be crucially important in a full description of enzyme behavior. With regard the novel phenomena described in this work, an assessment of their roles in enzymes must await the identification of any moieties involved in interactions with the thiomolybdenum group.

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Council.

Supporting Information Available: Text giving the synthetic procedure and spectroscopic data for $LMo^{IV}O(pyS_2)$, figures showing selected EPR spectra, and listings of structure determination details, crystal data, atomic coordinates, thermal parameters, bond lengths, bond angles, and torsion angles for $LMo^{IV}O(pyS_2)$ (13 pages). Ordering information is given on any current masthead page.

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(8) Crystallographic data: $LMo^{IV}O(pyS_2)$, $C_{20}H_{26}BMoN_7OS_2$, fw 551.35, monoclinic space group $P2_1/c$ with $a = 16.325(2)$ Å, $b = 10.587(2)$ Å, $c = 15.365(3)$ Å, $\beta = 113.92(1)$ °, $V = 2427.4(7)$ Å^3, and $D_c = 1.509$ g·cm^{-3} for $Z = 4$. A total of 4268 unique data with 2853 reflections having $I > 2\sigma(I)$ were collected. The structure was solved by Patterson and direct methods and refined on F^2 by a full-matrix least-squares procedure using all data to conventional R_1 [$I > 2\sigma(I)$] $= 0.0644$ and wR_2 (all data) $= 0.1840$.

(9) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(10) $LMo(S_4)Cl$: Young, C. G.; McInerney, I. P.; Bruck, M.; Enemark, J. H. *Inorg. Chem.* **1990**, *29*, 412.

(11) $[Mo_2O_2(\mu\text{-}S)_2\{S_2C_2(CO_2Me)_2\}_2]^{2-}$: Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476.

(12) $(C_5H_5)_2Mo(S_3C_2RR')$: Pilato, R. S.; Eriksen, K. A.; Greaney, M. A.; Stiefel, E. I.; Goswami, S.; Kilpatrick, L.; Spiro, T. G.; Taylor, E. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 9372.

(13) For mononuclear M−S−S−R complexes, see: (a) Shaver, A.; Hartgerink, J.; Lai, R. D.; Bird, P.; Ansari, N. *Organometallics* **1983**, *2*, 938. (b) John, E.; Bharadwaj, P. K.; Krogh-Jespersen, K.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1986**, *108*, 5015. (c) Giolando, D. M.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1987**, *6*, 667.

(14) (a) EPR data are summarized as follows.[14b] Mo(V) complex, g_{iso}, g_1, g_2, g_3: $[LMoOS(S_2PPr^i_2)]^-$, 1.941, 2.013, 1.933, 1.880; $[LMoOS(pyS)]^-$, 1.952, 2.021, 1.944, 1.892; $[LMoOS(SCH_2Ph)]^-$,[7b] 1.954, 2.022, 1.948, 1.898; $[LMoO(S_3PPr^i_2)]^+$,[14c] 1.949, 1.993, 1.938, 1.916; $[LMoO(pyS_2)]^+$, 1.965, 1.992, 1.961, 1.943; Very Rapid signal,[5] 1.976, 2.025, 1.955, 1.949. (b) Anisotropic parameters obtained from frozen-glass samples at 77 K. Anions generated by reaction of neutral compounds with excess Bu^n_4NSH in THF/CH_3CN (9/1). Cations generated upon reaction of neutral compounds with $[Fe(C_5H_5)_2]PF_6$. (c) The g_2 value was estimated from $g_2 = 3g_{iso} - g_1 - g_3$; g_1 and g_3 were estimated by inspection.

(15) The complex's EPR parameters are very similar to those of other N_3OS_2-donor anions,[14a] and unresolved (possibly ^{14}N) coupling and EPR line broadening are evident in the spectra; the presence of the *S*-bound linkage isomer (see Chart 1) is implicated but must be confirmed. Rupture of the S−S bond would facilitate the switch from *N*- to *S*-bonding in the pyS ligand.

(16) ^{31}P coupling is evident in other d^1 dithiophosphinate complexes: (a) Miller, G. A.; McClung, R. E. D. *Inorg. Chem.* **1973**, *12*, 2552. (b) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1979**, *35*, 93. (c) See ref 7c.

(17) Berg, J. M.; Spira, D. J.; Hodgson, K. O.; Bruce, A. E.; Miller, K. F.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1984**, *23*, 3412.