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Structural Characterization and Unusual Reactivity of Oxosulfido-Mo(V) Compounds: Implications for the Structure and Electronic Description of the Very Rapid Form of Xanthine Oxidase

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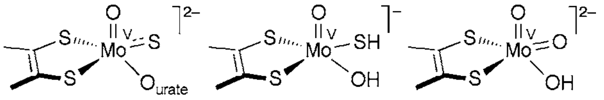
Ⓢ *Supporting Information*

ABSTRACT: The first structural characterization of a mononuclear, EPR-active, oxosulfido-Mo(V) compound related to the very rapid form of xanthine oxidase (VR-XnO) is reported. The compound, $[CoCp_2][Tp^{iPr}Mo^{V}OS(2\text{-}OC_6H_4CO_2Et)]$ [Cp = cyclopentadienyl; Tp^{iPr} = hydrotris(3-isopropylpyrazol-1-yl)borate], exhibits a distorted octahedral geometry with Mo═O and Mo=S distances of 1.761(5) and 2.215(2) Å, respectively, and an O═Mo=S angle of 107.33(14)°. Significantly, the Mo^{V}=S distance is much shorter than the value of 2.36 Å reported for oxosulfido-Mo(V) compounds (Singh, R.; et al. *Inorg. Chem.* **1989**, *28*, 8) but close to the range established for VR-XnO by protein crystallography. The methyl and phenyl esters were also prepared but the latter is highly reactive and undergoes an intramolecular, radical-based cyclization/elimination reaction to form $[CoCp_2][Tp^{iPr}Mo^{IV}O\{2\text{-}OC_6H_4C(O)S\text{-}\kappa O,\kappa S\}]$. This study provides the first definitive measurement of the Mo^{V}=S bond distance in an unambiguously characterized oxosulfido-Mo(V) compound and supports the presence of a short (ca. 2.22 Å) Mo=S bond in VR-XnO. It also demonstrates that the Mo^{V}=S moiety participates in radical-based reactions that are facilitated by the facile redox interplay of Mo and S and by substrates susceptible to radical eliminations.

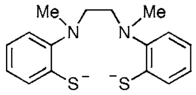
Electron paramagnetic resonance (EPR) signals typical of mononuclear Mo(V) centers are readily elicited from preparations of xanthine oxidase (XnO) and related Mo hydroxylases.[1−3] The so-called very rapid (VR), rapid, and slow signals are attributed to $[(MPT)Mo^{V}OS(urate)]^{2-}$, $[(MPT)Mo^{V}O(SH)(OH)]^{-}$, and desulfo (inactive) $[(MPT)Mo^{V}O_2(OH)]^{2-}$ (MPT = molybdopterin) enzyme centers, respectively (Figure 1).[2,3] The VR center, identified as the only true Mo(V) intermediate in the catalytic cycle of XnO,[4] has been examined by a range of structural and spectroscopic techniques, including EPR spectroscopy,[2,3] electron−nuclear double resonance spectroscopy,[4] and protein crystallography.[5] The results support the presence of a short (ca. 2.0 ± 0.2 Å) sulfido-Mo(V) unit and a monodentate O-donor oxidized substrate (urate) at a five-coordinate square-pyramidal (or pseudotetrahedral[6]) active site (Figure 1; n.b., for convenience, terminal oxo−Mo bonds are represented as double bonds).



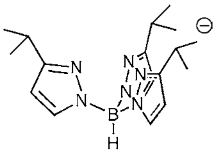
(a) Very Rapid (b) Rapid (c) Slow

Figure 1. Structures giving rise to the very rapid, rapid, and slow EPR signals observed for XnO (the dithiolene moiety represents the MPT ligand).

Our understanding of the VR center has been underpinned by in situ spectroscopic studies of complexes containing the ligands *N*,*N*′-dimethyl-*N*,*N*′-bis(2-benzenethiolato)-ethylenediamine ($L\text{-}N_2S_2$, **A**) and hydrotris(3-isopropylpyrazol-1-yl)borate (Tp^{iPr}, **B**);[7,8] biologically more relevant oxosulfido-Mo(V) dithiolene complexes appear to be unstable and have not been reported to date.[8,9] EPR studies have shown that the Mo=S π* singly occupied molecular orbital (SOMO) in oxosulfido-Mo(V) complexes is highly delocalized with significant sulfido ligand character;[7,8] however, as few such compounds have been isolated, the structural implications of this delocalization have been difficult to gauge.



(**A**) $L\text{-}N_2S_2$



(**B**) Tp^{iPr}

In the first contribution to this area, Singh et al.[10] reported the isolation and characterization of $PPh_4[Mo^{V}OS(L\text{-}N_2S_2)]$. However, the unexpected properties of this compound, such as its stability in air and water, the absence of S K-edge X-ray absorption near-edge structure (XANES) transitions, and the presence of a long Mo−S distance, cast some doubt on the claim that it is an oxosulfido-Mo(V) compound. Indeed, the Mo−S distance of 2.36 Å derived by extended X-ray absorption fine structure (EXAFS) spectroscopy is closer to that expected for a Mo−S single bond (ca. 2.41 Å[8,11]) than a Mo−sulfido multiple bond (2.1−2.2 Å for Mo═S[8,11]) and stands in contrast to the value obtained for the very rapid form of xanthine oxidase (VR-XnO) by protein crystallography.[5] The X-ray structure of the compound has not been determined, but

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computational studies supporting a thiyl radical formulation have been reported.[12]

More recently, we described the isolation and partial characterization of $[CoCp_2][Tp^{iPr}Mo^{V}OS(OPh)]$ (Cp = cyclopentadienyl), an air- and water-sensitive oxosulfido-Mo(V) species exhibiting strong S K-edge XANES transitions.[13,14] However, oxo/sulfido ligand disorder has thwarted the definitive structural characterization of this compound. Therefore, uncertainty about the geometrical and (by implication) electronic structures of oxosulfido-Mo(V) moieties in model compounds and enzymes persists.

Here we report the synthesis and characterization of the oxosulfido-Mo(V) compounds $[CoCp_2][Tp^{iPr}Mo^{V}OS(2\text{-}OC_6H_4CO_2R)]$ [R = Me (**1**), Et (**2**), Ph (**3**)], the first X-ray crystal structure of an oxosulfido-Mo(V) compound (**2**), and an unusual reaction of the terminal sulfido ligand of compound **3**. The isolation, structural characterization, and observed radical-based chemistry of these rare yet biologically relevant Mo(V) species are significant achievements.

The reactions of dark-brown $Tp^{iPr}Mo^{VI}OS(2\text{-}OC_6H_4CO_2R)$ (R = Me, Et)[15] with cobaltocene in toluene resulted in the precipitation of air- and water-sensitive, light-red-brown crystals of **1** and **2**, respectively.[16] The complexes were characterized by microanalysis, mass spectrometry, and a variety of spectroscopic techniques.[16] The IR bands assigned to the ν(Mo=O) and ν(Mo⩵S) vibrations were observed at 888 and 435 cm^{-1}, respectively, which are considerably lower in energy than those of the Mo(VI) precursors (ca. 917 and 484 cm^{-1}, respectively).[15] This is consistent with a significant weakening of both bonds upon reduction, as reflected in the lengthening of the Mo=O and Mo⩵S bonds of **2** relative to those of the Mo(VI) precursor (vide infra). Bands characteristic of the Tp^{iPr} and phenolate ligands and $[CoCp_2]^+$ cations were also observed in IR spectra.

Both compounds exhibited EPR spectra characteristic of previously reported in situ-generated oxosufido-Mo(V) species (Figure 2).[7,8] The rhombic spectra are highly anisotropic ($\Delta_{1,3}$ = 0.149) with g_1 values close to the g value of the free electron (g_e = 2.0023). The VR-XnO EPR signal is also rhombic and anisotropic ($\Delta_{1,3}$ = 0.076) with a large g_1 value (2.0252).[17] The large g_1 values are indicative of the presence of a strongly covalent Mo⩵S bond in both cases.[17,18] The differences in the anisotropies of the spectra of the models and VR-XnO can be attributed to differences in the coordination numbers, geometries, coligands, and environments (solution vs enzyme pocket) of the Mo centers present.

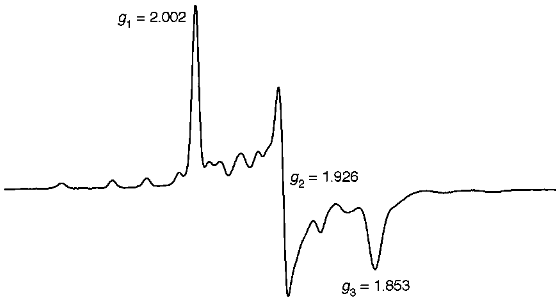

Figure 2. Frozen-glass EPR spectrum of **1** in 10:1 THF/CH_3CN.

The crystal structure of $\mathbf{2}\cdot 2CH_2Cl_2$ revealed the presence of discrete $[CoCp_2]^+$ cations, Mo-containing anions, and ordered and disordered solvent molecules (Figure 3). The ions are associated by a variety of interionic interactions, including nonclassical hydrogen bonds and $\pi-\pi$ interactions, to form the dimeric unit shown in Figure 4. There are two short, interionic $[CoCp_2]^+\cdots O{=}Mo$ interactions, the stronger being characterized by H···O and C···O distances and a C−H···O angle of 2.42(5) Å, 2.98(1) Å, and 118.7(6)°, respectively, and the weaker one by distances and angles of 2.84(4) Å, 3.18(1) Å, and 102.5(6)°, respectively (nb., H atoms are in calculated positions); the stronger interaction is associated with distances that are significantly shorter than the sum of the relevant van der Waals radii ($\sum_{OH}$ = 2.65 Å, $\sum_{OC}$ = 3.22 Å[19]). The thermal ellipsoid of the oxo ligand is also directed toward the C−H group (but not sufficiently to elicit a Hirschfeld alert), and the Cp ring involved adopts a static conformation. These metrical and thermal parameters are indicative of the presence of stabilizing C−H···O hydrogen bonds.[20−22] These bonds are typically nondirectional and are facilitated by strong donor−

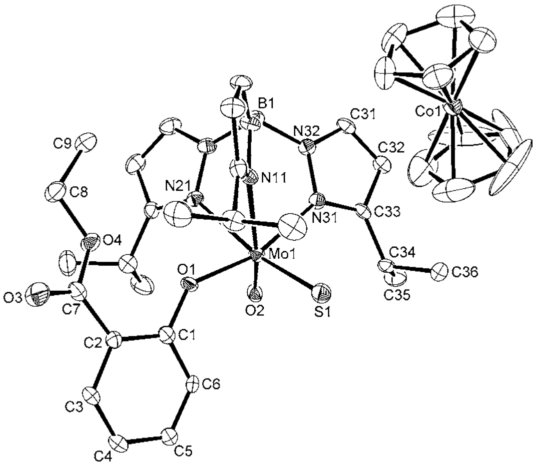

Figure 3. ORTEP projection of **2** drawn at 30% ellipsoid probability. Lattice solvent molecules and H atoms have been omitted for clarity. Additional distances (Å) and angles (deg): Mo1−N11, 2.381(6); Mo1−N21, 2.328(6); Mo1−N31, 2.214(5); O1−C1, 1.324(7); O3−C7, 1.205(8); Mo1−O1−C1, 137.8(4); O1−Mo1−O2, 100.9(2); O1−Mo1−S1, 96.22(14).

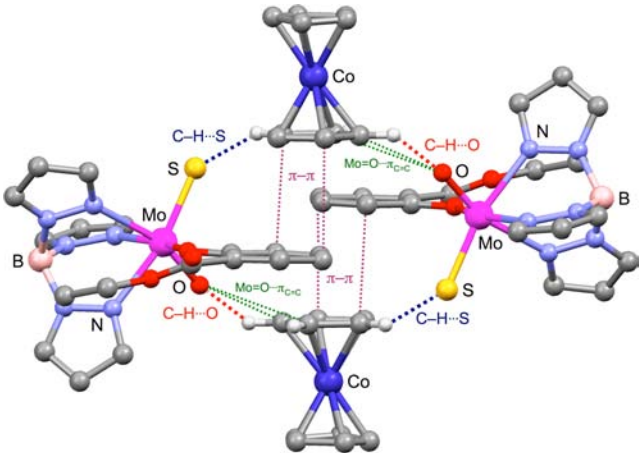

Figure 4. Dimer unit of **2** showing the different types of interionic interactions. Isopropyl groups, solvent molecules, and nonparticipating H atoms have been omitted for clarity. Atom colors: Mo (magenta); Co (dark blue); O (red); S (yellow); N (blue); B (pink); C (gray); H (white).

acceptor polarization (induced here by the low and high effective nuclear charges of Mo^V and Co^{III}, respectively, and the interionic interactions) and the sp^2 hybridization of C_{Cp}.[20−22] A red shift in the ν(C−H) modes of $[CoCp_2]^+$ is also indicative of the presence of C−H···O interactions.[23] Similar, albeit weaker, lattice interactions were observed in related dioxo-Mo(V) compounds.[24,25] A single, intermolecular C−H···S=Mo hydrogen-bonding interaction is also present within the dimer units, with H···S and C···S distances of 2.66(2) and 3.53(1) Å, respectively, and a C−H···S angle of 156.7(7)°. Once again, the H···S distance is less than the sum of the relevant van der Waals radii ($\sum_{SH}$ = 2.88 Å[19]). Significant $\pi-\pi$ interactions (d_{CC} < 3.3 Å) between the Cp and phenolate rings are also observed. The aforementioned interactions play a major role in the positional ordering of the oxo and sulfido ligands.

The Mo atom of **2** exhibits a distorted octahedral geometry and is coordinated by tridentate facial Tp^{iPr} and mutually cis oxo, sulfido, and phenolate ligands; it lies 0.256(2) Å out of the equatorial plane defined by O1, S1, N21, and N31 toward the terminal oxo ligand. The Mo═O distance of 1.761(5) Å is at the high end of the range typical of Mo═O bonds (1.65−1.85 Å, av 1.706 Å with std dev 0.079 Å[11,26]). Long Mo═O distances (ca. 1.74 Å) are typical of related dioxo-Mo(V) compounds,[24,25] other Mo S-donor-ligand complexes (e.g., monooxo-Mo dithiolene species[8,27]), and reduced molybdenum enzymes.[28] The lengthening of the Mo═O distance is consistent with the weakening of the bond observed by IR spectroscopy; indeed, a Mo═O distance of 1.75 Å was estimated using the isolated harmonic oscillator approximation[29] and Badger's rule.[30] However, we cannot exclude the possibility that the long Mo═O bond length is the result of a small amount (<5%) of oxo/sulfido ligand disorder.[31,32] The deviation of the observed Mo=S bond length from its true value would be negligible at this level of disorder (vide infra).

The Mo=S bond length of 2.215(2) Å in **2** is significantly longer than that observed for the Mo(VI) complex $Tp^{iPr}MoOS(OC_6H_4{}^sBu)$ [2.132(2) Å][33] and other sulfido-Mo complexes (av 2.154 Å with std dev 0.087 Å[26]). This bond lengthening is consistent with occupation of a Mo=S π^* orbital and the weakening of the Mo=S bond revealed by IR spectroscopy (a Mo=S distance of 2.25 Å was estimated using Badger's rule[29,30]). The O═Mo=S angle of 107.33(14)° is also greater than that in $Tp^{iPr}MoOS(OC_6H_4{}^sBu)$ [103.7(2)°],[33] in keeping with structural trends observed in dioxo-Mo(VI) and -Mo(V) complexes.[24,25] The increase in O−Mo−E (E = O, S) angles upon reduction is attributed to repulsion between the d^1 (π^*) SOMO and the Mo═O/E π orbitals. Significantly, the Mo=S bond in **2** is much shorter than that reported for $PPh_4[Mo^VOS(L\text{-}N_2S_2)]$ (2.36 Å)[10] but close to the range estimated by crystallographic studies of VR-XnO (2.0 ± 0.2 Å).[5] The trans influence of the monodentate ligands is in the expected order (viz., oxo > sulfido > phenolate).

The phenyl derivative, **3**, was generated in situ (as determined by EPR spectroscopy) but was unstable and could not be isolated in pure form. Recrystallization of the initial mixture from $MeCN/Et_2O$ yielded $[CoCp_2][Tp^{iPr}Mo^{IV}O\{2\text{-}OC_6H_4C(O)S\text{-}\kappa O,\kappa S\}]\cdot 2MeCN$ (**4**), which was characterized by X-ray crystallography. This compound appears to result from molybdothiyl radical-induced cyclization (chelate ligand formation) involving homolytic cleavage of the C−OPh bond, elimination of the highly reactive phenoxyl radical,[34] and reduction of Mo(V) to Mo(IV) (π_{MoS} → Mo d_{xy}); the fate of the phenoxyl radical has not been established.

The anion of **4** (Figure 5) displays a distorted octahedral geometry defined by tridentate facial Tp^{iPr} and mutually cis oxo and bidentate O,S-donor ligands. The Mo1 atom is 0.303(2) Å out of the equatorial N21−N31−O1−S1 plane toward the terminal oxo ligand. The Mo═O and Mo−O distances of 1.688(4) and 2.033(4) Å, respectively, are comparable to those observed for related oxo-Mo(IV) complexes.[35] The Mo−S distance of 2.3942(15) Å is consistent with the presence of a Mo−S single bond. The fold angle of the chelate ligand (viz., the dihedral angle along O1···S1) is 25.1(2)°. The Mo−N11 bond is longer than the other Mo−N bonds as a result of the strong trans influence of the oxo ligand. Finally, to our knowledge, **4** is the first 2-hydroxythiobenzoate-*κO*,*κS* compound to be structurally characterized.

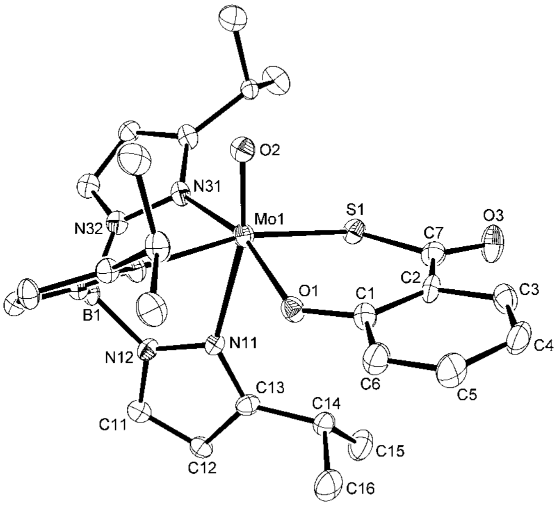

Figure 5. ORTEP projection of the anion of **4** drawn at the 30% probability level. H atoms have been omitted for clarity. Additional distances (Å) and angles (deg): Mo1−N11, 2.416(4); Mo1−N21, 2.217(5); Mo1−N31, 2.203(4); O1−C1, 1.330(6); S1−C7, 1.765(6); O3−C7, 1.230(6); Mo1−O1−C1, 132.8(4); Mo1−S1−C7, 112.5(2); O1−Mo1−S1, 88.52(11).

This study has provided the first definitive measurement of the Mo^V=S bond distance in an unambiguously characterized oxosulfido-Mo(V) compound, demonstrating that the Mo^V=S bond in such compounds is ca. 2.22 Å in length, consistent with the presence of a π^* SOMO and a Mo−S bond order of 1.5. This bond length is much shorter than the value of 2.36 Å reported for $PPh_4[Mo^VOS(L\text{-}N_2S_2)]$ by Singh et al.,[10] the only other Mo=S distance for an oxosulfido-Mo(V) compound in the literature. The markedly different Mo=S distances and S K-edge XANES of the title compounds and $PPh_4[Mo^VOS(L\text{-}N_2S_2)]$ are difficult to reconcile on the basis of available information.

Notably, the Mo=S distance in **2** is close to the range established for VR-XnO by protein crystallography.[5] This result supports the likely presence of a *short* (ca. 2.22 Å) Mo=S bond in VR-XnO. The structure of **2** also supports the existence of a relatively weak Mo═O bond ($d \approx$ 1.76 Å), a possible indication of the absence of a formal triple bond in the oxo-Mo moiety in the title compounds and VR-XnO.

The relative stability of compounds **1**−**3** is testimony to the stabilizing influence of second-generation tris(pyrazolyl)borate ligands.[36] However, the conversion of **3** to **4** is consistent with the participation of the π^* SOMO, with its significant S p-orbital character,[17,18] in radical-based reactions on susceptible substrates (e.g., those capable of radical eliminations). Here, bidirectional electron flow, namely, one-electron $\pi^*_{\mathrm{MoS}} \rightarrow$ substrate and two-electron $\pi_{\mathrm{MoS}} \rightarrow$ Mo d_{xy}, is facilitated by the high radial expansion of the Mo 4d and S 3p orbitals and the small energy difference between them. Facile redox interplay between Mo and S is a feature of Mo/S chemistry and biochemistry that is likely to underpin the unique reactivity of molybdenum hydroxylases.[7,9]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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■ REFERENCES

(1) Bray, R. C. *Q. Rev. Biophys.* **1988**, *21*, 299−329.

(2) Hille, R. *Biol. Magn. Res.* **2010**, *29*, 91−120.

(3) Pushie, M. J.; George, G. M. *Coord. Chem. Rev.* **2011**, *255*, 1055−1084.

(4) Manikandan, P.; Choi, E.-Y.; Hille, R.; Hoffman, B. M. *J. Am. Chem. Soc.* **2001**, *123*, 2658−2663.

(5) Pauff, J. M.; Zhang, J.; Bell, C. E.; Hille, R. *J. Biol. Chem.* **2008**, *283*, 4818−4824.

(6) Young, C. G. *J. Biol. Inorg. Chem.* **1997**, *2*, 810−816.

(7) Young, C. G. In *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Meunier, B., Ed.; Imperial College Press: London, 2000; pp 415−459.

(8) Young, C. G. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier-Pergamon: Amsterdam, 2004; Vol. *4*, Chapter 4.7, pp 415−527.

(9) Young, C. G. *J. Inorg. Biochem.* **2007**, *101*, 1562−1585.

(10) Singh, R.; Spence, J. T.; George, G. N.; Cramer, S. P. *Inorg. Chem.* **1989**, *28*, 8−10.

(11) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

(12) Peng, G.; Nichols, J.; McCullough, E. A., Jr.; Spence, J. T. *Inorg. Chem.* **1994**, *33*, 2857−2864.

(13) Smith, P. D.; Slizys, D. A.; George, G. N.; Young, C. G. *J. Am. Chem. Soc.* **2000**, *122*, 2946−2947.

(14) Doonan, C. J.; Rubie, N. D.; Peariso, K.; Harris, H. H.; Knottenbelt, S. Z.; George, G. N.; Young, C. G.; Kirk, M. L. *J. Am. Chem. Soc.* **2008**, *130*, 55−65.

(15) Ng, V. W. L.; Taylor, M. K.; Young, C. G. *Inorg. Chem.* **2012**, *51*, 3202−3211.

(16) *Synthesis and Charaterization*: Reactions and workups were performed under an atmosphere of N_2 using dried and deoxygenated solvents. A solution of cobaltocene (0.30 g, 1.59 mmol) in toluene (10 mL) was cannula-filtered into a stirred solution of $\mathrm{Tp}^{i\mathrm{Pr}}\mathrm{MoOS}(2\text{-}\mathrm{OC_6H_4CO_2R})$ (R = Me, Et) (1.0 mmol) in toluene (5 mL), and the mixture was stirred for 30 min. The brown microcrystalline solid formed (**1** or **2**, respectively) was isolated by filtration, washed with dry toluene (5 mL), and dried in vacuo. These derivatives were purified by recrystallization from dichloromethane/*n*-hexane or acetonitrile/diethyl ether. A similar procedure applied to the R = Ph derivative (**3**) yielded crystals of **4** (characterized by X-ray diffraction). R = Me (**1**): Yield: 0.56 g (68%). Anal. Calcd for $\mathrm{C_{36}H_{45}BMoN_6O_4SCo}$: C, 52.50; H, 5.51; N, 10.21; S, 3.89. Found: C, 52.21; H, 5.48; N, 9.77; S, 4.13. IR (KBr) $\mathrm{cm^{-1}}$: ν(BH) 2475 w and 2446 w, ν(C═O) 1676 s, ν(CN) 1510 s, $\nu([\mathrm{CoCp_2}]^+)$ 1414 m, ν(Mo═O) 888 vs, $\nu([\mathrm{CoCp_2}]^+)$ 461 s, ν(Mo═S) 434 vs. EPR (THF/MeCN): 298 K, $g_{\mathrm{iso}} = 1.924$, $A(^{95,97}\mathrm{Mo}) = 41.45 \times 10^{-4}\ \mathrm{cm^{-1}}$; 77 K, $g_1 = 2.002$, $g_2 = 1.926$, $g_3 = 1.853$. R = Et (**2**): Yield: 0.60 g (72%). Anal. Calcd for $\mathrm{C_{37}H_{47}BMoN_6O_4SCo}$: C, 53.06; H, 5.66; N, 10.04; S, 3.83. Found: C, 52.77; H, 5.76; N, 9.75; S, 3.76. IR (KBr) $\mathrm{cm^{-1}}$: ν(BH) 2475 w and 2446 w, ν(C═O) 1669 s, ν(CN) 1509 s, $\nu([\mathrm{CoCp_2}]^+)$ 1414 m, ν(Mo═O) 888 vs, $\nu([\mathrm{CoCp_2}]^+)$ 460 s, ν(Mo═S) 435 vs. EPR (THF/MeCN): 298 K, $g_{\mathrm{iso}} = 1.923$, $A(^{95,97}\mathrm{Mo}) = 45.09 \times 10^{-4}\ \mathrm{cm^{-1}}$; 77 K, $g_1 = 2.000$, $g_2 = 1.923$, $g_3 = 1.850$.

(17) George, G. N.; Bray, R. C. *Biochemistry* **1988**, *27*, 3603−3609.

(18) Wilson, G. L.; Greenwood, R. J.; Pilbrow, J. R.; Spence, J. T.; Wedd, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 6803−6812.

(19) Rowland, R. S.; Taylor, R. *J. Phys. Chem.* **1996**, *100*, 7384−7391.

(20) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290−296.

(21) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441−449.

(22) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375−1406.

(23) Diana, E.; Stanghellini, P. L. *J. Am. Chem. Soc.* **2004**, *126*, 7418−7419.

(24) Xiao, Z.; Gable, R. W.; Wedd, A. G.; Young, C. G. *J. Am. Chem. Soc.* **1996**, *118*, 2912−2921.

(25) Ng, V. W. L.; Taylor, M. K.; White, J. M.; Young, C. G. *Inorg. Chem.* **2010**, *49*, 9460−9469.

(26) Trnka, T. M.; Parkin, G. *Polyhedron* **1997**, *16*, 1031−1045.

(27) Samuel, P. P.; Horn, S.; Döring, A.; Havelius, K. G. V.; Reschke, S.; Leimkühler, S.; Haumann, M.; Schulzke, C. *Eur. J. Inorg. Chem.* **2011**, 4387−4399.

(28) Doonan, C. J.; Kappler, U.; George, G. N. *Inorg. Chem.* **2006**, *45*, 7488−7492.

(29) Czernuszewicz, R. S.; Spiro, T. G. In *Inorganic Electronic Structure and Spectroscopy*; Solomon, E. I., Lever, A. B. P., Eds.; Wiley: New York, 1999; Vol. *1*, pp 353−441.

(30) Badger, R. M. *J. Chem. Phys.* **1935**, *3*, 710−714.

(31) Parkin, G. *Chem. Rev.* **1993**, *93*, 887−911.

(32) Parkin, G. *Acc. Chem. Res.* **1992**, *25*, 455−560.

(33) Doonan, C. J.; Nielsen, D. J.; Smith, P. D.; White, J. W.; George, G. N.; Young, C. G. *J. Am. Chem. Soc.* **2006**, *128*, 305−316.

(34) Neta, P.; Grodkowski, J. *J. Phys. Chem. Ref. Data* **2005**, *34*, 109−199.

(35) Ng, V. W. L.; Taylor, M. K.; Hill, L. M. R.; White, J. M.; Young, C. G. *Eur. J. Inorg. Chem.* **2010**, 3261−3269.

(36) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.