

Poly(methylthiomethyl)Borates: A New Class of Sulfur-Rich Ligands for Metal Ions

Pinghua Ge,[†] Brian S. Haggerty,[‡] Arnold L. Rheingold,[‡] and Charles G. Riordan^{*†}

Departments of Chemistry
Kansas State University
Manhattan, Kansas 66506
University of Delaware
Newark, Delaware 19716

Received June 10, 1994

Sulfur-rich metal environments are prevalent in metalloenzymes¹ including hydrogenases and CO dehydrogenase and in hydrosulfurization catalysis.² Consequently, the coordination chemistry of macrocyclic polythioethers has been well defined.³ The most extensively studied of these, 1,4,7-trithiacyclononane, is a powerful chelating ligand capable of facially capping metal ions.⁴ This neutral ligand when complexed to metal ions yields cationic species. Alternatively, we have prepared monoanionic, acyclic borates of the form $B(CH_2SR)_4^-$, which are potentially C_{3v} -symmetric face-capping ligands. These represent sulfur analogs of the versatile poly(pyrazolyl)borates first prepared by Trofimenko.⁵ The thioether ligand will provide a softer coordination sphere for metal ions and, consequently, a different metal-atom environment. Herein we describe the preparation, characterization, and molecular structure of two transition metal derivatives of the parent ligand RTt^- ,⁶ $fac-(RTt)Mo(CO)_3^-$ and $(RTt)_2Fe$, and place this new ligand in context with macrocyclic polythioethers and poly(pyrazolyl)borates.

$B(CH_2SCH_3)_4^-$, RTt^- , is readily prepared in good yield from the *in situ* reaction of an excess of $LiCH_2SCH_3$ with $BF_3 \cdot Et_2O$ in THF at $-78^\circ C$. The anion is precipitated from aqueous solutions as its Bu_4N^+ salt. $[Bu_4N][RTt]$ is soluble in THF, CH_2Cl_2 , and $CHCl_3$ and has been characterized by 1H , ^{13}C , and ^{11}B NMR spectroscopies.⁷ The ^{11}B spectrum displays a single resonance at -16.3 ppm relative to $BF_3 \cdot Et_2O$. This chemical shift is in the expected region for tetrahedral B bound to aliphatic substituents, for example, BMe_4^- , $\delta -21.0$.⁸

Addition of 1 equiv of $[Bu_4N][RTt]$ to a THF solution of $(C_7H_8)Mo(CO)_3$ under Ar results in a color change from orange

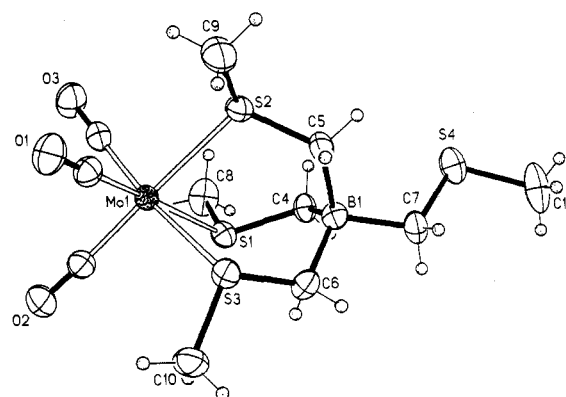


Figure 1. Molecular structure of $(RTt)Mo(CO)_3^-$. Thermal ellipsoids are drawn at the 35% probability level. Selected bond lengths (Å) and angles (deg): Mo(1)–S(1), 2.571(3); Mo(1)–S(2), 2.564(3); Mo(1)–S(3), 2.577(3); Mo(1)–C(1), 1.926(10); Mo(1)–C(2), 1.944(10); Mo(1)–C(3), 1.925(10); S(1)–Mo(1)–S(2), 83.8(1); S(1)–Mo(1)–S(3), 84.0(1); S(2)–Mo(1)–S(3), 82.6(1); S(1)–Mo(1)–C(1), 174.2(3); S(2)–Mo(1)–C(2), 174.7(3); S(3)–Mo(1)–C(3), 172.7(3).

to pale yellow over 30 min.⁹ The ν_{CO} resonances in the IR spectrum concomitantly move to lower energy, 1899 (vs), 1784 (vs) cm^{-1} . The ν_{CO} pattern is consistent with face-capping tridentate ligation by RTt^- . This bonding mode is confirmed by the 1H NMR spectrum. There are two distinct resonances for the CH_3 protons which integrate 9:3. The CH_2 protons also exhibit two signals of intensity 6:2. Both CH_2 resonances are quartets resulting from $^2J_{BH} = 4.0$ Hz. The spectrum is consistent with a C_3 symmetry about Mo with three equivalent thioethers. Clearly, on the NMR time scale, the complex is not fluxional so as to equilibrate all four thioether arms through a ligand exchange mechanism. Such dynamic equilibration has been observed for the pyrazole groups in poly(pyrazolyl)borates including $[Bpz_4]_2Zn$.¹⁰ The ^{11}B NMR singlet at $\delta -17.5$ is shifted only 1 ppm upfield from that of the free ligand. Such a minor shift suggests that the charge distribution at B does not change appreciably upon complexation to the $Mo(CO)_3$ fragment. That the negative charge remains localized on B is supported by the position of the ν_{CO} resonances. $(ttcn)Mo(CO)_3$, the neutral thioether analog of $(RTt)Mo(CO)_3^-$, has ν_{CO} 1925 (vs), 1815 (vs) cm^{-1} . The 25–30 cm^{-1} shifts to lower energy observed with the additional charge on $(RTt)Mo(CO)_3^-$ are only about one-fourth that expected for complexes which place the charge at the metal.¹¹ The molecular structure of $[Bu_4N][(RTt)Mo(CO)_3]$ as determined by X-ray diffraction confirms the tridentate, face-capping nature of the ligand, Figure 1.¹² Bond angles around the Mo atom define a pseudooctahedral coordination sphere. The average Mo–S distance of 2.571 Å is significantly longer than that in $(ttcn)Mo(CO)_3$ (2.520 Å).¹³ The average $\angle Mo-S-CH_3$ of 111° and $\angle Mo-S-CH_2$ of 112° support pyramidalization at S. Additionally, the trigonal faces defined by the three sulfur atoms and the carbonyl carbons are twisted with respect to one another by *ca.* 6.1° .

[†] Kansas State University.

[‡] University of Delaware.

(1) (a) Lancaster, J. R., Ed. *The Bioinorganic Chemistry of Nickel*; VCH Publishers: New York, 1988; Chapter 8–10, 13, 14. (b) Ragsdale, S. W. *Crit. Rev. Biochem. Mol. Biol.* **1991**, *26*, 261–300. (c) Lindahl, P. A.; Kojima, N.; Hausinger, R. P.; Fox, J. A.; Teo, B. K.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3062.

(2) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979.

(3) (a) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141. (b) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.

(4) For example: (a) Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068. (b) Wiegardt, K.; Schmidt, W.; Herrmann, W.; Kuppers, H.-J. *Inorg. Chem.* **1983**, *22*, 2953.

(5) (a) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170. (b) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17. (c) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(6) Abbreviations: the general form of the ligand, $RB(CH_2SCH_3)_3^-$, is abbreviated RTt^- , where Tt represents the potentially tridentate $B(CH_2SCH_3)_3$ fragment and R may be H, alkyl, etc. In the present case, R is defined as CH_2SCH_2 . We thank a reviewer for helpful suggestions regarding this nomenclature. pz, pyrazole; ttcn, 1,4,7-trithiacyclononane; tacn, 1,4,7-triazacyclononane.

(7) $[Bu_4N][RTt]$: 1H NMR ($CDCl_3$) δ 3.24 (m, NCH_2 , 8 H), 2.05 (s, SCH_3 , 12 H), 1.76 (q, $^2J_{BH} = 4.0$ Hz, BCH_2 , 8 H), 1.63 (m, CH_2 , 8 H), 1.45 (m, CH_2 , 8 H), 1.01 (t, CH_3 , 12 H); ^{13}C NMR ($CDCl_3$) δ 58.9 (s, NCH_2), 35.2 (q, $^1J_{BC} = 40.0$ Hz, BCH_2), 24.0 (s, CH_2), 20.5 (s, SCH_3), 19.8 (s, CH_2), 13.7 (s, CH_3).

(8) Kennedy, J. D. In *Multinuclear NMR*; Mason, J. Ed.; Plenum Press: New York, 1987; Chapter 8.

(9) Anal. Calcd for $C_{27}H_{56}BMoNO_3S_4$: C, 47.78; H, 8.10; N, 2.15; S, 18.68. Found: C, 47.85; H, 8.33; N, 2.07; S, 18.92. 1H NMR (acetone- d_6): δ 3.44 (m, NCH_2 , 8 H), 2.31 (s, SCH_3 , 9 H), 1.88 (s, SCH_3 , 3 H), 1.83 (m, CH_2 , 8 H), 1.60 (q, $^2J_{BH} = 4.0$ Hz, BCH_2 , 6 H), 1.43 (m, CH_2 , 8 H), 1.29 (q, $^2J_{BH} = 4.0$ Hz, BCH_2 , 2 H), 0.97 (t, CH_3 , 12 H).

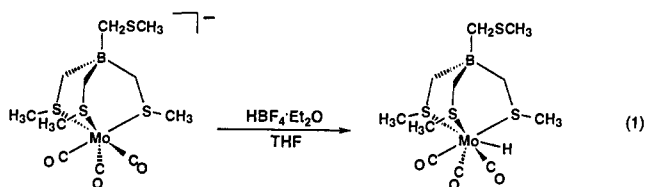
(10) Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 3148.

(11) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 114.

(12) Crystal data for $[Bu_4N][(RTt)Mo(CO)_3]$: $C_{27}H_{56}BMoNO_3S_4$; yellow blocks, monoclinic, $P2_1/c$, $a = 21.975(5)$ Å, $b = 13.487(3)$ Å, $c = 24.462(5)$ Å, $\beta = 92.63(2)^\circ$, $V = 7242(3)$ Å³, $Z = 8$; $R = 5.93$, $R_w = 6.43$.

(13) Ashby, M. T.; Lichtenberger, D. L. *Inorg. Chem.* **1985**, *24*, 636.

Protonation of $[\text{Bu}_4\text{N}][(\text{RTt})\text{Mo}(\text{CO})_3]$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in THF results in immediate formation of the air-sensitive Mo hydride, eq 1. This reaction is characterized by the diagnostic



shift to higher energy of ν_{CO} 2000 (vs), 1910 (vs) cm^{-1} . Shifts of similar magnitude are observed upon protonation of $\text{CpMo}(\text{CO})_3^-$, which yields $\text{CpMo}(\text{CO})_3\text{H}$.¹⁴ The ^1H NMR spectrum confirms the Mo atom as site of protonation ($\delta -4.47$).

Reaction of 2 equiv of $[\text{Bu}_4\text{N}][\text{RTt}]$ with $[\text{Fe}(\text{H}_2\text{O})_6][\text{BF}_4]_2$ over several hours in THF results in clean formation of $(\text{RTt})_2\text{Fe}$ as a microcrystalline, emerald green solid.¹⁵ The compound is soluble in chlorinated hydrocarbons. It is stable to both oxygen and moisture. The electronic spectrum displays two d-d bands at 627 ($\epsilon = 46 \text{ M}^{-1} \text{ cm}^{-1}$) and 441 nm (79). These are assigned to the transitions $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$, respectively. These data yield calculated values of $D_q = 1763 \text{ cm}^{-1}$ and $B = 420 \text{ cm}^{-1}$.¹⁶ Using Fe^{II}L_2 complexes as a benchmark, the ligand field strength of RTt^- is somewhat less than those of both ttcn ($D_q = 2067 \text{ cm}^{-1}$) and tacn (1894 cm^{-1}), which form low-spin complexes. The temperature-dependent ^1H NMR spectrum contains a total of four broad lines for two inequivalent CH_3 and CH_2 environments. The intensities are consistent with three magnetically equivalent thioether arms per borate bound to Fe. At 27 °C, the chemical shifts of the unbound thioether protons are close to those for the free ligand, while those bound to the Fe exhibit contact shifts of 6–7 ppm to lower field. The magnetic moment of $(\text{RTt})_2\text{Fe}$ was measured in CDCl_3 using Evans' NMR method.¹⁷ The solution magnetic moment is temperature dependent, with a value of $1.8 \mu_B$ at 27 °C. This significant deviation from zero (for a fully low-spin electronic state) is responsible for the appearance of the ^1H NMR spectrum. The magnetic behavior is indicative of a spin-crossover equilibrium between the $^1A_{1g}$ and $^5T_{2g}$ electronic states.¹⁸ Such equilibria have been observed for $[\text{R}(\text{Bpz})_3]_2\text{Fe}$ complexes, for which the room temperature magnetic moments are dependent upon the identity of the B substituents.¹⁹ For example, $[\text{Bpz}]_2\text{Fe}$ is diamagnetic at room temperature, while $[\text{HB}(\text{Me}_2\text{pz})_3]_2\text{Fe}$ is high spin ($5.22 \mu_B$).

The molecular structure of $(\text{RTt})_2\text{Fe}$ has been confirmed by X-ray diffraction, Figure 2.²⁰ The molecule contains two tridentate borate ligands resulting in a S_6 -coordination environment of virtual O_h symmetry. The Fe atom occupies a crystallographic inversion center which renders *trans* thioether arms

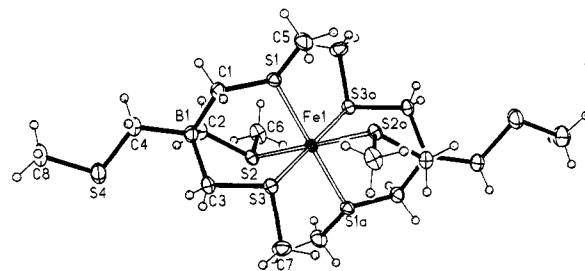


Figure 2. Molecular structure of $(\text{RTt})_2\text{Fe}$. Thermal ellipsoids are drawn at the 35% probability level. Selected bond lengths (Å) and angles (deg): Fe(1)–S(1), 2.295(1); Fe(1)–S(2), 2.311(1); Fe(1)–S(3), 2.303(1); S(1)–Fe(1)–S(2), 87.2(1); S(1)–Fe(1)–S(3), 88.2(1); S(2)–Fe(1)–S(3), 87.7(1).

metrically equivalent. The bond angles about Fe are all very close to those in an idealized octahedron. The average Fe–S distance of 2.303(2) Å is significantly longer than that in the corresponding cationic $(\text{ttcn})_2\text{Fe}^{2+}$ prepared by Wieghardt (2.250 Å).²¹ Again, all the thioethers are pyramidalized, with the angle between the $\text{CH}_2\text{--S--CH}_3$ plane and the Fe–S vector (\angle_{av}) equal to 121.0°. The disposition of the thioethers is such that each SCH_3 vector is canted in the same direction. Presumably, this minimizes steric interactions between *cis* ligands: the opposite orientation would result in overcrowding between CH_3 groups of adjacent thioethers. Each methyl group "caps" a single *cis* sulfur ($\text{S} \cdots \text{CH}_3$, 3.29 Å), with a dihedral angle, $\text{CH}_3\text{--S--Fe--S}_{\text{cis}}$, of less than 2°. This orientation of the methyl groups may protect the ligand kinetically from reactions at the coordinated S.

Cyclic voltammetry performed on CH_2Cl_2 solutions of $(\text{RTt})_2\text{Fe}$ shows a reversible one electron couple at +535 mV (vs SCE). We assign this to the metal-centered oxidation, $\text{Fe}^{2+}/\text{Fe}^{3+}$. $(\text{ttcn})_2\text{Fe}^{2+}$ displays a reversible couple at a much higher potential, +1.39 V, which Wieghardt has attributed to ligand-based oxidation.²¹ The less positive potential of our complex is consistent with its overall electroneutrality. For example, $E_{1/2}$ for Fc^+/Fc is only 55 mV lower than that for $(\text{RTt})_2\text{Fe}^+ / (\text{RTt})_2\text{Fe}$.

In summary, we have prepared a new poly(thioether)borate analogous to the ubiquitous poly(pyrazolyl)borates. RTt^- may be conveniently synthesized and, therefore, contrasts the poly(thioether) macrocycles which are more arduous to prepare. RTt^- serves as a powerful monoanionic ligand capable of forming 1:1 and 2:1 adducts with $\text{Mo}(\text{CO})_3$ and Fe^{2+} , respectively, in which three thioether arms facially complex the metal, leaving one arm unbound. The chelate provides a ligand field which is somewhat weaker than ttcn , as evidenced by the electronic spectrum and spin state of Tt_2Fe . We are currently preparing derivatives of RTt^- , for example $\text{B}(\text{CH}_2\text{SPh})_4^-$ ($\text{R}'\text{Tt}^{\text{Ph}-}$), and MeTt^- to vary systematically the electronic and steric parameters of the thioethers.

Acknowledgment. The financial support of Kansas State University is greatly appreciated.

Supplementary Material Available: Structure determination summary, atomic coordinates, bond lengths and bond angles for $[\text{Bu}_4\text{N}][(\text{RTt})\text{Mo}(\text{CO})_3]$ and $(\text{RTt})_2\text{Fe}$ (19 pages); observed and calculated structure factors (34 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfiche version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(21) Wieghardt, K.; Küppers, H.-J.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 3067.

(14) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(15) Anal. Calcd for $\text{C}_{16}\text{H}_{40}\text{B}_2\text{FeS}_6$: C, 33.89; H, 7.16; S, 46.48. Found: C, 33.93; H, 7.12; S, 45.28. ^1H NMR (CDCl_3 , 27 °C): δ 7.73 (br, SCH_3 , 9 H), 7.55 (br, BCH_2 , 6 H), 1.88 (br, SCH_3 , 3 H), 0.90 (br, BCH_2 , 2 H).

(16) Assuming $C = 4B$, D_q and B were calculated as in: Dabrowiak, J. C.; Merrell, P. H.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 1979.

(17) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. A correction for the superconducting solenoidal field must be made, see: Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791.

(18) Full temperature-dependent magnetic data will be published elsewhere.

(19) Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 3158.

(20) Crystal data for $(\text{RTt})_2\text{Fe}$: $\text{C}_{16}\text{H}_{40}\text{B}_2\text{FeS}_6$; green plates, triclinic, $P\bar{1}$, $a = 8.472(18)$ Å, $b = 8.4609(14)$ Å, $c = 10.3262(21)$ Å, $\alpha = 74.568(14)^\circ$, $\beta = 71.215(15)^\circ$, $\gamma = 87.002(15)^\circ$, $V = 675.06(21)$ Å³, $Z = 1$; $R = 3.68$, $R_w = 5.25$.