smallest couplings of this type yet observed,[1-6] and it is consistent with a long H–H bond. The H–H bond length for **3Os** from T_1 measurements is about 1.2 Å,[14] and so that of **2Os** should be a little shorter than this. The HD complex was prepared by heating an acetone solution of **2Os** under 1 atm of D_2 at 50 °C for 2 h. H–D couplings have not been observed in spectra of isotopomers of **3Os**.[3a] We have not been successful in the preparation of the complexes **1Os** and **2Ru**.

The reason for the unexpectedly short H–H bonds in complexes **2** may not be discovered until crystals suitable for diffraction studies are obtained. Perhaps the unevenly substituted diphosphine $Et_2PCH_2CH_2PPh_2$ enhances or reduces the distortions to octahedral coordination observed in the phosphorus atom positions of **1Fe** determined by X-ray diffraction,[3b] or perhaps the breaking of the H–H bond in the exchange process involves a concerted movement of the phosphorus atoms that is selectively hindered in the case of the $Et_2PCH_2CH_2PPh_2$ ligand.[15] An explanation involving a preferred orientation of the H–H ligand with respect to a P–M–P axis as observed for **1Fe** in the solid state is probably not appropriate for the dynamic behavior of the complex in solution, where the H_2 ligand is spinning rapidly. It is interesting to note that the dinitrogen complex *trans*-$[Fe(N_2)H(Et_2PCH_2CH_2PPh_2)_2]BPh_4$ has $\nu(N_2)$ = 2100 cm^{-1},[16] which is intermediate between the stretching frequencies of the corresponding $Ph_2PCH_2CH_2PPh_2$ and $Et_2PCH_2CH_2PEt_2$ complexes.[3a]

Acknowledgment. The financial support of this project by NSERC Canada and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Johnson-Matthey Co. is thanked for the loan of osmium salts, and the Chemistry Department, York University, is thanked for assistance in obtaining low-temperature NMR spectra.

Registry No. **1Fe·BPh$_4$**, 113088-85-0; **2Fe·BPh$_4$**, 113088-87-2; **2Os·BF$_4$**, 113088-89-4; **3Fe·BPh$_4$**, 108150-67-0; **3Os·BF$_4$**, 113088-90-7; *trans*-$FeHCl(Et_2PCH_2CH_2PPh_2)_2$, 113088-91-8; $[Os_2Cl_3(PEt_2Ph)_6]Cl$, 113088-92-9; *cis*-$OsCl_2(Et_2PCH_2CH_2PPh_2)_2$, 113088-93-0; *trans*-$OsH_2(Et_2PCH_2CH_2PPh_2)_2$, 113088-94-1; $[Fe(\eta^2\text{-}HD)D(Et_2PCH_2CH_2PPh_2)_2]BPh_4$, 113088-96-3; $[Os(\eta^2\text{-}HD)D(Et_2PCH_2CH_2PPh_2)_2]BF_4$, 113088-98-5; H_2, 1333-74-0.

Supplementary Material Available: A description of the preparation of the complexes, simulated and observed NMR spectra of **2Os**, and table of activation parameters for the exchange processes (7 pages). Ordering information is given on any current masthead page.

Department of Chemistry and Scarborough Campus
University of Toronto
Toronto, Ontario M5S 1A1, Canada

Maria T. Bautista
Kelly A. Earl
Robert H. Morris*

Received November 23, 1987

---

(14) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Sella, A., submitted for publication.

(15) A reviewer has suggested the possibility that the H_2 ligand is asymmetrically bonded to the metal in complexes **2**.

(16) Bautista, M. T.; Morris, R. H., unpublished results.

New Synthetic Route to Oxo-Bridged Chromium(III) Dimers from Dihydroxo-Bridged Precursors. Crystal Structure and Characterization of the $[\{Cr(tmpa)(NCS)\}_2O]^{2+}$ Cation

Sir:

Although numerous binuclear transition-metal complexes with near-linear M–O–M central units have been reported,[1-3] the only two chromium(III) representatives to be characterized in the solid state are the basic rhodo ion[4] $[(NH_3)_5Cr]_2O^{4+}$, prepared originally by Jorgensen[5] through the aerobic oxidation of chromous ion in concentrated aqueous ammonia, and $[Cr(TPyEA)(NCS)]_2O^{2+}$, isolated recently[6] from a similar reaction of a Cr(II) precursor with O_2 in acetonitrile (TPyEA = tris(2-pyrazol-1-ylethyl)amine). A third member of the oxo-bridged chromium(III) series, $[(H_2O)_5Cr]_2O^{4+}$ (aqua dimer), follows easily from the oxidation of chromous ion by 1,4-benzoquinone in aqueous acidic solution[7] but exhibits facile hydrolysis to $Cr(H_2O)_6^{3+}$ catalyzed by hydrogen ion,[8] anions,[9] and reductants,[10] preventing the isolation of the crystalline complex.

The distinctive substitutional and redox reactivities of the aqua dimer[8-10] and basic rhodo[11] ions prompted our interest in the impact of Cr(III)–O–Cr(III) dimer electronic structure on the rates and mechanisms of these processes. Unfortunately, oxo-bridged chromium(III) complexes generally are *not* accessible through the reactions of Cr(II) precursors with O_2 and other oxidizing agents, such that the systematic study of these intriguing compounds depends upon the development of a nonoxidative synthetic approach. We report here an efficient preparative route to crystalline $N_4LCrOCrN_4L$ compounds with either bidentate (bpy) or tripodal tetradentate (tmpa, tris(2-pyridylmethyl)amine) aromatic amine ligands, based on the nucleophilic displacement of OH$^-$ from readily prepared, dihydroxo-bridged Cr(III) precursors by a variety of monodentate incoming groups (L). The aerobic oxidation of $Cr(tmpa)(ClO_4)_2$ in aqueous ethanol affords a dihydroxo-bridged precursor, $[(tmpa)Cr(OH)_2Cr(tmpa)](ClO_4)_4\cdot 4H_2O$ (I),[12] which is easily prepared in 20-g lots. When 0.841 mmol of the slightly soluble, purple diol I was allowed to react with 33.7 mmol of NaSCN (20-fold excess) in 200 mL of vigorously stirred, boiling water for 1 h, a 60% yield of $[\{Cr(tmpa)(NCS)\}_2O](ClO_4)_2\cdot 0.5H_2O$ (II) formed (eq 1) as a dark brown-green, microcrystalline precipitate; the product is sparingly soluble in water but very soluble in acetonitrile and methanol.

$$[(tmpa)Cr(OH)_2Cr(tmpa)]^{4+} + 2SCN^- \rightarrow [Cr(tmpa)(NCS)]_2O^{2+} + H_2O \quad (1)$$

Anal. Calcd for $[\{Cr(tmpa)(NCS)\}_2O](ClO_4)_2\cdot 0.5H_2O$: Cr, 10.14; C, 44.54; H, 3.64; N, 13.67. Found: Cr, 10.19; C, 44.57; H, 3.39; N, 13.60. The homogeneity of II was confirmed by aqueous cation exchange chromatography on SP-Sephadex C-25 resin,[7] from which the complex eluted as a single band with 0.5 M NaBr, ahead of $Cr(H_2O)_6^{3+}$, which was included as an ionic charge marker.

X-ray diffraction analysis[13] of $[\{Cr(tmpa)(NCS)\}_2O](NCS)_2$ (III) revealed the cation (Figure 1) to be a centrosymmetric dimer having a linear Cr–O–Cr bridge and distorted octahedral N_5O coordination about Cr. Owing to the limited bite of the tmpa ligand, the trans N–Cr–N′ angles (range 160.8 (1)–173.65 (7)°) and some of the cis N–Cr–N′ angles (range 79.75 (9)–101.1 (2)°) deviate substantially from the ideal values. The Cr–N(3) distance is significantly longer than the other four Cr–N distances, consistent with a trans effect arising from the tightly bound oxo group. Unambiguous trans effects were not observed in the parent basic

---

(1) Griffith, W. P. *Coord. Chem. Rev.* **1970,** *5,* 459.

(2) Cotton, F. A.; Najjar, R. C. *Inorg. Chem.* **1981,** *20,* 1866.

(3) Baumann, J. A.; Meyer, T. J. *Inorg. Chem.* **1980,** *19,* 345.

(4) Yevitz, M.; Stanko, J. A. *J. Am. Chem. Soc.* **1971,** *93,* 1512.

(5) Jorgensen, S. J. *J. Prakt. Chem.* **1882,** *25,* 321.

(6) DiVaira, M.; Mani, F. *Inorg. Chem.* **1984,** *23,* 409.

(7) Holwerda, R. A.; Petersen, J. S. *Inorg. Chem.* **1980,** *19,* 1775.

(8) Johnston, R. J.; Holwerda, R. A. *Inorg. Chem.* **1983,** *22,* 2942.

(9) Johnston, R. J.; Holwerda, R. A. *Inorg. Chem.* **1985,** *24,* 3181.

(10) Johnston, R. J.; Holwerda, R. A. *Inorg. Chem.* **1985,** *24,* 3176.

(11) Gafford, B. G.; Holwerda, R. A. *Inorg. Chem.* **1988,** *27,* 210.

(12) Anal. Calcd for I: Cr, 8.75; C, 36.38; H, 3.90; N, 9.43. Found: Cr, 8.73; C, 36.54; H, 3.77; N, 9.27. UV–visible (H_2O): 261 nm (ϵ 15 700 M^{-1} cm^{-1}), 385 (226), 540 (262). Gafford, B. G.; Holwerda, R. A., manuscript in preparation.

(13) Crystallography: $Cr_2S_4ON_{12}C_{40}H_{36}$, monoclinic, $P2_1/c$, a = 11.3212 (8) Å, b = 14.805 (1) Å, c = 12.658 (1) Å, β = 97.82 (1)°, V = 2101.8 (5) Å^3, D_{calcd} = 1.474 g/cm^3, D_{obsd} = 1.45 (1) g/cm^3, Z = 2. The structure was solved by direct methods using 2231 unique reflections ($I > 3\sigma(I)$) collected at 297 (1) K with Mo Kα radiation (0.71073 Å) to 2θ = 46° on an Enraf-Nonius CAD-4 diffractometer. All H atoms were located on difference maps but were not refined. Refinement with all non-H atoms anisotropic yielded R_F = 0.038, R_{wF} = 0.052, and GOF = 1.64. The largest peak in a final difference map was 0.25 e/Å^3. Complete crystallographic details will be published elsewhere.

0020-1669/88/1327-1126$01.50/0

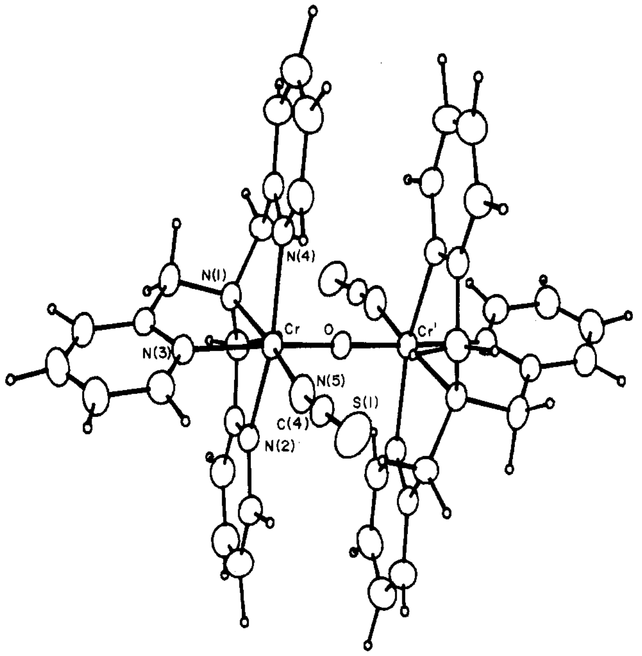

Figure 1. View of the $[\{Cr(tmpa)(NCS)\}_2O]^{2+}$ cation in III. Selected interatomic distances (Å) and angles (deg) are as follows: Cr–O = 1.8001 (4), Cr–N(1) = 2.072 (2), Cr–N(2) = 2.070 (2), Cr–N(3) = 2.121 (2), Cr–N(4) = 2.078 (2), Cr–N(5) = 2.004 (3); Cr–O–Cr' = 180, N(1)–Cr–N(2) = 81.01 (9), N(1)–Cr–N(3) = 81.02 (9), N(1)–Cr–N(4) = 79.75 (9), N(1)–Cr–N(5) = 169.9 (1), N(2)–Cr–N(3) = 85.02 (9), N(2)–Cr–N(4) = 160.8 (1), N(2)–Cr–N(5) = 101.1 (2), N(3)–Cr–N(4) = 92.40 (9), N(3)–Cr–N(5) = 89.3 (1), N(4)–Cr–N(5) = 97.9 (2), Cr–N(5)–C(4) = 168.3 (3), N(5)–C(4)–S(1) = 178.6 (3), O–Cr–N(5) = 95.54 (7).

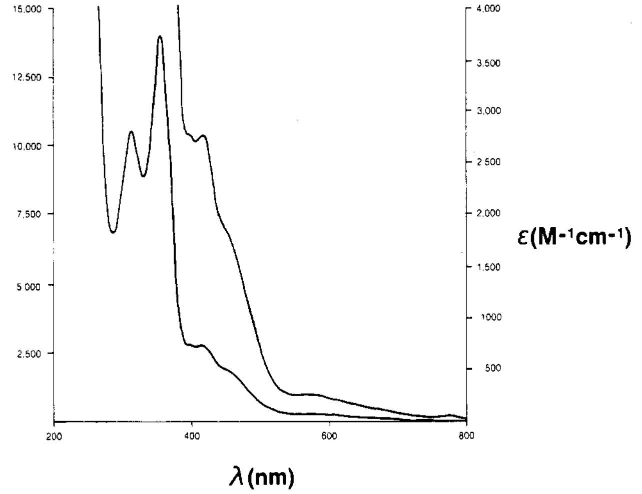

Figure 2. UV–visible spectrum of $[\{Cr(tmpa)(NCS)\}_2O](ClO_4)_2\cdot 0.5H_2O$ in CH_3CN. Right-hand ordinate corresponds to the expanded trace.

rhodo ion[4] and $[Cr(TPyEA)(NCS)]_2O^{2+}$ ion[6] within the reported esd's of the Cr–N distances. The Cr–O distance in III (1.800 Å) is slightly shorter than those reported for the $[(NH_3)_5Cr]_2O^{4+}$ (1.821 Å)[4] and $[Cr(TPyEA)(NCS)]_2O^{2+}$ (1.815 Å)[6] ions.

The rich UV–visible spectrum of oxo-bridged dimer II in acetonitrile (Figure 2) exhibits features at 256 nm (ε 25 000 M^{-1} cm^{-1}), 313 (10 800), 355 (14 100), 368 sh (11 200), 398 sh (2750), 417 (2740), 457 sh (1780), 567 plateau (250), and 773 (58). The most intense near-UV band at 355 nm may be compared with the analogous maxima of $[(NH_3)_5Cr]_2O^{4+}$, $[(H_2O)_5Cr]_2O^{4+}$, and $[Cr(TPyEA)(NCS)]_2O^{2+}$ at 334,[14] 347,[7] and 336 nm,[6] respectively. Strong bands near 850 cm^{-1} in the infrared spectrum of II (Figure 3), attributable to the asymmetric Cr–O–Cr stretching vibration,[15,16] confirm the oxo-bridged structural assignment.

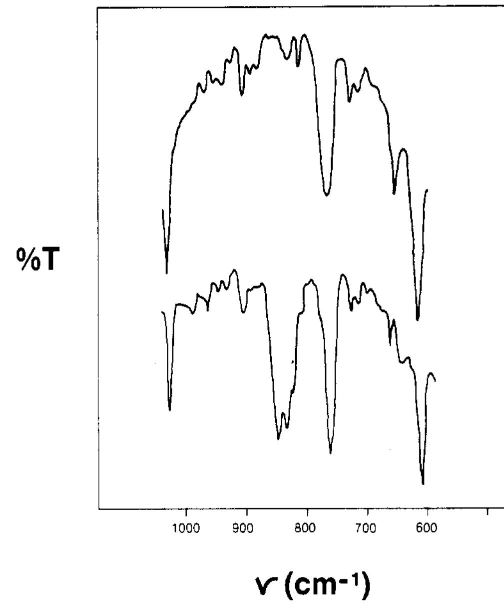

Figure 3. KBr pellet infrared spectra of $[\{Cr(tmpa)(NCS)\}_2O](ClO_4)_2\cdot 0.5H_2O$ (lower trace) and $[\{Cr(tmpa)(NCS)\}_2OH](ClO_4)_3\cdot 6H_2O$ (upper trace).

Unlike the aqua dimer, II is highly resistant to acid hydrolysis. Indeed, the oxo-bridged complex is transformed into needles of a maroon, hydroxo-bridged derivative, $[\{Cr(tmpa)(NCS)\}_2OH](ClO_4)_3\cdot 6H_2O$ (IV), upon boiling in 1.00 M $HClO_4$, followed by slow cooling to room temperature. Anal. Calcd for IV: Cr, 8.49; C, 37.28; H, 4.03; N, 11.44. Found: Cr, 8.51; C, 37.19; H, 3.22; N, 11.29. UV–visible (H_2O): 262 nm (ε 19 400 M^{-1} cm^{-1}), 327 (8700), 524 (410). Spectrophotometric measurements in CH_3CN confirmed that the conversion of II to IV is complete upon the uptake of 0.5 mol of H^+ (HNO_3)/mol of Cr. As expected, IV lacks the asymmetric Cr–O–Cr infrared stretching band (Figure 3) but may be reversibly converted back to II in neutral, aqueous solution. A spectrophotometric titration[17] of II carried out in the range pH 1–10 defined the pK_a of conjugate acid IV as 2.05 ± 0.10 (25.0 °C, I = 0.1 M ($NaNO_3$)), in marked contrast to the pK_a value of 7.63 reported for $[(NH_3)_5Cr]_2OH^{5+}$[14] and the failure of the aqua dimer to protonate even in 1 M $HClO_4$.[8] Compound II is sensitive to base-catalyzed oxo bridge cleavage above pH 10; a blue monomeric product, $[Cr(tmpa)(OH)_2]^+$, is formed within 1 h at 50 °C in 0.1 M NaOH.

Whereas the aqua dimer exhibits a totally irreversible, one-electron reduction wave with $E_{1/2}$ = +0.52 V vs SHE (25.0 °C in H_2O, I = 0.1 M ($HClO_4$)), resulting in oxo-bridge fragmentation,[10] the cyclic voltammogram of II in CH_3CN[18] shows no reductive electrochemistry in the range +1.5 to −2.0 V vs SHE (with initial cathodic sweep). However, a nearly reversible (peak-to-peak separation = 71 mV; sweep rate = 50 mV/s, anodic to cathodic peak current ratio = 1.0) one-electron wave corresponding to the *oxidation* of II to $[(tmpa)(SCN)Cr^{III}OCr^{IV}(SCN)(tmpa)]^{3+}$ was observed at $E_{1/2}$ = +1.17 ± 0.01 V vs SHE (25.0 °C, I = 0.1 M (TBAP)). The absence of cathodic peaks in steady-state voltammograms besides that due to the reduction of the Cr(III)–O–Cr(IV) species to II suggests that the mixed-valence dimer does not readily decompose to other electroactive species.

Although ring opening/closing equilibria that interconvert dihydroxo- and single hydroxo-bridged chromium(III) dimers are

---

(14) Schwarzenbach, G.; Magyar, B. *Helv. Chim. Acta* **1962**, *45*, 1425.

(15) Hewkin, D.; Griffith, W. *J. Chem. Soc. A* **1966**, 472.

(16) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley: New York, 1970.

(17) Holwerda, R. A.; Clemmer, J. D. *Inorg. Chem.* **1982**, *21*, 2103.

(18) Pt working electrode, Au auxiliary electrode, and SCE reference electrode in 0.1 M aqueous $NaNO_3$; 1 mM solute. $E_{1/2}$ was calculated as $(E_{pa} + E_{pc})/2$, and is independent of sweep rate in the range 10–200 mV/s. Potentials were referenced to SHE with an internal (hydroxyethyl)ferrocene calibrant; see ref 10 for details.

well documented,[19,20] this behavior has not been previously exploited to prepare linear oxo-bridged Cr(III) dimers. Our observation of single hydroxo bridge displacement by two thiocyanate ions in $[(\mathrm{tmpa})\mathrm{Cr(OH)_2Cr(tmpa)}]^{4+}$ opens the door to the synthesis of an extensive class of $[(\mathrm{tmpa})(\mathrm{L})\mathrm{Cr^{III}OCr^{III}}(\mathrm{L})(\mathrm{tmpa})]$ complexes through direct nucleophilic attack by a variety of incoming groups (L) on an easily obtained chromium(III) diol precursor. For example, the oxo-bridged compounds with L = $\mathrm{Cl^-}$ and $\mathrm{CN^-}$ are obtained in excellent yield by refluxing NaCl and NaCN, respectively, with I in acetonitrile, the solvent of choice to avoid dimer hydrolysis side reactions.[21] The generality of nonoxidative Cr(III)-O-Cr(III) complex synthesis is indicated by the conversion of another chromium(III) diol with aromatic amine ligands, $[(\mathrm{bpy})_2\mathrm{Cr(OH)_2Cr(bpy)_2}](\mathrm{ClO_4})_4\cdot 2\mathrm{H_2O}$ (V), to oxo-bridged dimers through nucleophilic attack by pseudohalide incoming groups. Dark brown compounds with elemental analyses corresponding to $[\{\mathrm{Cr(bpy)_2(SCN)}\}_2\mathrm{O}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (VI)[22] and $[\{\mathrm{Cr(bpy)_2(N_3)}\}_2\mathrm{O}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (VII)[23] are obtained from V[24] and NaSCN or $\mathrm{NaN_3}$ by the same procedure used to synthesize II. Oxo-bridged dimers VI and VII exhibit Cr-O-Cr asymmetric stretching bands at 855, 845, and 835 and 850, 825, and 810 $\mathrm{cm^{-1}}$, respectively, and UV-visible spectra ($\mathrm{CH_3CN}$) dominated by a single, extremely intense peak: 301 nm (VI) (ϵ 52 300 $\mathrm{M^{-1}\,cm^{-1}}$) and 300 nm (VII) (ϵ 56 000 $\mathrm{M^{-1}\,cm^{-1}}$).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of research at Texas Tech University.

Supplementary Material Available: Positional and thermal parameters for $[\{\mathrm{Cr(tmpa)(NCS)}\}_2\mathrm{O}](\mathrm{NCS})_2$ (4 pages). Ordering information is given on any current masthead page.

---

(19) Christensson, F.; Springborg, J. *Acta Chem. Scand., Ser. A* **1982**, *36*, 21.

(20) Springborg, J.; Toftlund, H. *Acta Chem. Scand., Ser. A* **1976**, *30*, 171.

(21) Gafford, B. G.; Holwerda, R. A., work in progress.

(22) Anal. Calcd for $[\{\mathrm{Cr(bpy)_2(SCN)}\}_2\mathrm{O}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$: Cr, 9.64; C, 46.80; H, 3.18; N, 12.99. Found: Cr, 9.63; C, 46.81; H, 2.91; N, 12.83.

(23) Anal. Calcd for $[\{\mathrm{Cr(bpy)_2(N_3)}\}_2\mathrm{O}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$: Cr, 9.94; C, 45.94; H, 3.28; N, 18.75. Found: Cr, 9.91; C, 46.58; H, 3.03; N, 18.79.

(24) Josephsen, J.; Schaffer, C. E. *Acta Chem. Scand.* **1970**, *24*, 2929.

Department of Chemistry
and Biochemistry
Texas Tech University
Lubbock, Texas 79409
Boyd G. Gafford
Robert A. Holwerda*

Department of Chemistry
Rutgers, The State University
of New Jersey
New Brunswick, New Jersey 08903
Harvey J. Schugar
Joseph A. Potenza

Received September 30, 1987

Pentacoordinate Iron-Sulfur Complexes. Structure and Spectroscopic and Electrochemical Properties of Phenoxy- and Thiophenoxy-Bridged Binuclear Complexes

Sir:

The importance of iron-sulfur compounds in biochemical processes has been known for many years since they are the active center of many iron-sulfur proteins and also have been related to the function of redox enzymes. The simulation of the active sites of rubredoxin, 2Fe- and 4Fe-ferredoxins, etc, by synthesizing iron-sulfur compounds, has become an important branch of inorganic chemistry. Among the many kinds of iron-sulfur compounds, 5-coordinate dinulcear thiolato-bridged systems with 1,2-dithiolene ligands have been known[1] while the structurally related phenoxy-bridged analogue is scarce in the literature. We wish to report here a comparison of structures and ^{1}H NMR, Mössbauer, magnetic, and electrochemical properties of two pentacoordinate thiophenoxy- and phenoxy-bridged diiron complexes $(\mathrm{Et_4N})_2[\mathrm{Fe_2(XSC_6H_4)_4}]$ (X = S or O). Differences induced by oxygen or sulfur atom at the bridging position are revealed for the first time.

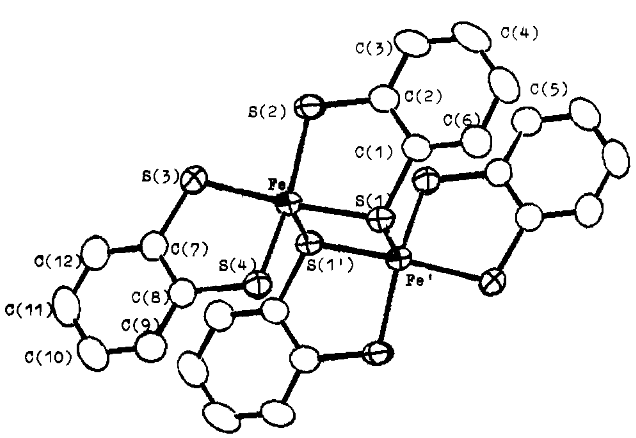

Figure 1. Structure of the anion of $(\mathrm{Et_4N})_2[\mathrm{Fe_2(BDT)_4}]$.

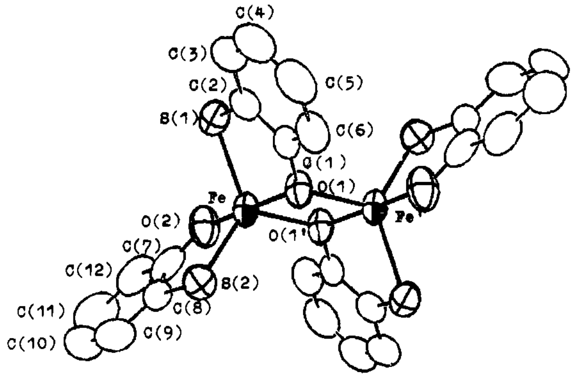

Figure 2. Structure of the anion of $(\mathrm{Et_4N})_2[\mathrm{Fe_2(MP)_4}]\cdot 2\mathrm{CH_3CN}$.

Results and Discussion. Compounds $(\mathrm{Et_4N})_2[\mathrm{Fe_2(XSC_6H_4)_4}]$ (**1**, X = S, $\mathrm{C_6H_4S_2}^{2-}$ = $\mathrm{BDT^{2-}}$; **2**·$2\mathrm{CH_3CN}$, X = O, $\mathrm{C_6H_4OS^{2-}}$ = $\mathrm{MP^{2-}}$) were obtained from reaction of anhydrous $\mathrm{FeCl_3}$ with $\mathrm{Na_2BDT}$ (**1**) or $\mathrm{Na_2MP}$ (**2**) in ethanolic solution on addition of $\mathrm{Et_4NBr}$ and recrystallization from $\mathrm{CH_3CN}$.[1f,2] Although both anions of **1** and of **2** have 5-coordinate iron atoms bridged by X atoms of two individual 1,2-dithiolene ligands (X = S in **1**, X = O in **2**), they have quite different structures mainly due to different hybridizations of bridging atoms as shown in Figures 1 and 2. The oxygen atom in **2** is sp^2 hybridized with bond angles around bridging O(1) being 118.3, 125.6, and 101.7° (average 115.2°). In contrast, the sulfur atom is sp^3 hybridized at the bridge in **1** (bond angles around bridging S(1) are 105.6, 103.3, and 83.6°

---

(1) (a) Kanatzidis, M. G.; Coucouvanis, D. *Inorg. Chem.* **1984**, *23*, 403. (b) Schultz, A. J.; Eisenberg, R. *Ibid* **1973**, *12*, 518. (c) Schrauzer, G. N.; Mayweg, V. P.; Finck, H. W.; Heinrich, W. *J. Am. Chem. Soc.* **1966**, *88*, 4604. (d) Balch, A. L.; Dance, I. G.; Holm, R. H. *Ibid.* **1968**, *90*, 1139. (e) Balch, A. L. *Ibid.* **1969**, *91*, 6962. (f) Weng, L. H.; Kang, B. S. *Jiegou Huaxue* **1987**, *6*, 94. (g) Hamilton, W. C.; Bernal, I. *Inorg. Chem.* **1967**, *6*, 2003.

(2) Anal. Calcd for **2**·$2\mathrm{CH_3CN}$ ($\mathrm{Fe_2S_4O_4C_{44}H_{62}N_4}$): Fe, 11.75; S, 13.49. Found: Fe, 12.18; S, 13.51. Crystal data: M_r = 950.97, a = 11.580 (2) Å, b = 16.731 (6) Å, c = 12.869 (2) Å, β = 98.07(2)°, V = 2468.6 Å^3, monoclinic system, space group $P2_1/n$, Z = 2, D_{calcd} = 1.279 g/cm^3. Of the 4707 independent reflections (Enraf-Nonius CAD-4 diffractometer, Mo K_α, λ = 0.71069 Å, $1° \leqslant \theta \leqslant 25°$, Lp and empirical absorption corrections), 2242 reflections with $I > 3\sigma(I_0)$ were used and gave a final R (R_w) = 0.069 (0.077). The SDP program package was used for the calculations. The coordinate of the Fe atom was taken from a Patterson map; the other non-hydrogen atoms were located by subsequent difference Fourier syntheses and least-squares refinements.

0020-1669/88/1327-1128$01.50/0