J. Am. Chem. Soc. **1984**, *106*, 1127–1128

as evidenced by the IR spectrum. The ^1H NMR spectrum (CD_2Cl_2 with added Et_4NBH_4) of **3** shows a doublet at δ 5.10 (J_{PH} = 1.0 Hz), a multiplet followed by a singlet centered at 7.31, and a doublet at 14.89 (J_{PH} = 4.0 Hz) with relative areas 5:15:1. The spectral data thus indicate that **3** is the trans isomer also. As reported previously,[16] reaction of **1** with excess $NaBH_4$ in THF yields $CpMo(CO)_2(PPh_3)CH_3$ (**5**). However, treatment of **3** with $NaBH_4$ does not lead directly to **5**; this reaction is under further study.

Although anionic formyl complexes are known to be potent hydride donors, the neutral complexes are apparently less active (as might be expected).[4] However, hydride transfer does occur from CpRe(NO)(CO)CHO to benzaldehyde,[19] although the reaction appears to require acid catalysis. Formyl complex **3** behaves as a hydride donor to $Ph_3C^+BF_4^-$ and is converted to **1** in 70% yield.

Formyl complex **3** is labile in solution at room temperature, converting cleanly to $CpMo(CO)_3H$ within a few minutes (as also suggested by the observations of Gladysz[17]). Added triphenylphosphine slows, but does not stop, this conversion; the inhibiting effect of Et_4NBH_4 is not yet understood. Since we have determined that **3** has trans stereochemistry, it appears that a formyl group must be regarded as a trans labilizing ligand in this series also.[20]

Work is in progress to define the chemistry of **2** and **3**, as well as related systems, further.

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A Sulfur-Bridged Iron(III) Porphyrin–Copper(II) System: Relevance to Cytochrome *c* Oxidase

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The properties of the active site of the resting form of cytochrome *c* oxidase (CcO) must be accounted for in terms of a unit containing a copper(II) atom and an iron(III) heme.[1] Strong ligand-mediated antiferromagnetic coupling between these metal atoms has been proposed[2–6] to explain the magnetic properties of the CcO active site. Potential model compounds[7–12] involving imidazolate and oxide bridging ligands have not successfully reproduced these magnetic properties.

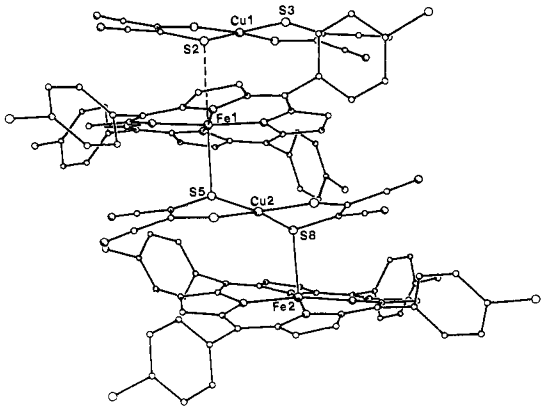

Figure 1. View of the metal-containing anionic unit of **2**. Atoms have been drawn as spheres of arbitrary radius.

EXAFS studies of CcO have suggested that the iron/copper active site pair may be bridged by thiolate sulfur.[13] We have described[14] a trinuclear complex (**1**) involving two $Fe(TPP)^+$ (TPP = *meso*-tetraphenylporphyrin) moieties coupled to $Cu(MNT)_2^{2-}$ (MNT^{2-} = *cis*-1,2-dicyano-1,2-ethylenedithiolate). Although single crystals were not obtained for **1**, EXAFS studies[15] favored sulfur atom bridges between iron(III) and copper(II). Appreciable antiferromagnetic coupling was not observed for **1**. Instead, the lack of a significant EPR signal at 77 K was interpreted as due to an extreme broadening of the copper(II) signal by rapidly relaxing $S = {}^3/_2$ iron.

A slight change in synthetic conditions[16] has permitted isolation of $(TBA)\{[Fe(p\text{-}Cl_4TPP)]_2[Cu(MNT)_2]_2\}\cdot 3C_6H_6$ (**2**) as a crystalline compound. Single-crystal X-ray diffraction[17] has established (Figure 1) that **2** contains a pair of $Fe(p\text{-}Cl_4TPP)^+$ units that sandwich a $Cu(MNT)_2^{2-}$ anion. This anion is bound strongly to both Fe1 and Fe2 through cis sulfur atoms S5 and S8 (Fe2–S8 = 2.444 (2), Fe1–S5 = 2.549 (2) Å). Six-coordination about Fe1 is completed by a weak bond to S2 (Fe1–S2 = 2.956 (2) Å) of an additional $Cu(MNT)_2^-$ anion, but Fe2 is five-coordinate

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(16) Under N_2 atmosphere, 80.6 mg (0.10 mmol) of $Fe(p\text{-}Cl_4TPP)$ ($p\text{-}Cl_4TPP$ = *meso*-tetra(*p*-chlorophenyl)porphyrin) and 67.4 mg (0.12 mmol) of $(TBA)[Cu(MNT)_2]$ (TBA^+ = tetra-*n*-butylammonium ion) were mixed in 50 mL of benzene and stirred for 6 h. Filtration removed the excess $(TBA)_2[Cu(MNT)_2]$ product. Vapor diffusion of *n*-heptane into the filtrate for 1 month (under N_2 atmosphere) yielded a mixture of crystals: (a) the major product, ostensibly the Fe–Cu–Fe trimer analogous to that previously reported; (b) some $(TBA)[Cu(MNT)_2]$ and/or $(TBA)_2[Cu(MNT)_2]$; (c) approximately 10% yield of the tetranuclear derivative **2** described in this Communication, as efflorescent dark brown crystals. Magnetic and Mössbauer data for **2** are not presently available for comparison with the properties of **1**, although such studies are planned. Solution spectra of **1** and **2** are qualitatively similar.

(17) For **2** ($C_{138}H_{102}N_{17}S_8Cu_2Fe_2Cl_8$), a = 13.378 (3) Å, b = 17.356 (2) Å, c = 28.918 (7) Å, α = 104.05 (2)°, β = 99.62 (2)°, γ = 98.38 (2)° at −130 °C. Space group $P\bar{1}$, $Z = 2$, μ(calcd) = 9.2 cm^{-1}. A small (0.42 mm × 0.46 mm × 0.30 mm) crystal yielded 16078 unique observed ($I > 2\sigma(I)$) reflections on the R3m/E diffractometer. The refinement (individual anisotropic thermal parameters for most non-hydrogen atoms, idealized phenyl and benzene rings with isotropic thermal parameters, no H atoms) of 1042 parameters (using the R3m/E SHELXTL software) converged at R = 0.063, R_w = 0.069, GOF = 1.72.

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(Fe2–S3′ = 3.641 (3) Å is the closest ligand atom contact trans to S8).

The structural determination provides unambiguous identification of the copper oxidation states in **2**. For Cu(MNT)$_2^{2-}$, Cu(II)–S(av) = 2.276 (1) Å,[18] a value very close to Cu2–S(av) = 2.261 (1) Å in **2**. For the Cu(MNT)$_2^-$ anion, Cu(III)–S(av) = 2.170 (4) Å,[19] and Cu1–S(av) = 2.180 (1) Å in **2**. As might be expected, the bridging interactions involving sulfur atoms bound to Cu1 are long compared to those originating at Cu2. For both copper complex anions, these bridging interactions result in tetrahedral distortions.

Scheidt and Reed[20] have outlined the structural parameters expected for $S = {}^3/_2$ ferric porphyrins. Fe–N$_p$ bond lengths should be similar to those of low spin derivatives, due to depopulation of the $d_{x^2-y^2}$ orbital. Five-coordinate complexes should exhibit Fe–Ct$_p$ values greater than 0.11 Å (the maximum known for $S = {}^1/_2$ complexes) and less than 0.39 Å (the minimum known for $S = {}^5/_2$ complexes), while six-coordinate $S = {}^3/_2$ complexes must exhibit very long axial bonds.

The five-coordinate Fe2 atom is presumably structurally similar to the iron(III) atoms in **1**. The Fe2–Ct$_p$ distance of 0.22 Å (Fe2–Ct$_N$ = 0.20 Å) observed in **2** falls within the range of 0.11–0.39 Å for five-coordinate $S = {}^3/_2$ ferric porphyrins. The Fe2–Ct$_N$ distance is less than the corresponding distances of 0.26 and 0.28 Å in two mixed-spin ($S = {}^3/_2, {}^5/_2$) five-coordinate ferric porphyrin complexes.[21,22] Since high-spin ferric porphyrins usually exhibit much larger Fe(III)–Ct$_N$ distances (average 0.40 Å),[20] the short Fe2–Ct$_N$ distance in **2** must reflect a higher proportion of $S = {}^3/_2$ character for Fe2 relative to the two admixed spin systems referred to above. As expected for a predominantly intermediate-spin porphyrin, the bonding between Fe2 and the porphyrin nitrogen atoms is strong (Fe2–N$_p$(av) = 1.976 (4), Ct$_N$–N$_p$(av) = 1.966 Å), and the porphyrin core shows significant S_4 ruffling.

The spin state of the six-coordinate Fe1 atom is more difficult to infer from the metric results. Fe1 is clearly not high spin, since this would require a much larger Ct$_N$–N$_p$ value[20] than the average of 1.975 Å observed (Fe1–N$_p$(av) = 1.978 (4) Å). At the same time, the Fe1–Ct$_N$ distance of 0.12 Å is outside the range of 0.00–0.09 Å found for $S = {}^1/_2$ six-coordinate ferric porphyrin complexes.[20] The only structurally characterized $S = {}^3/_2$ ferric porphyrin complex[23] exhibits an iron(III) atom precisely in the plane of the porphyrin core and longer Fe(III)–N$_p$ distances (Fe–N$_p$(av) = 1.995 (3) Å) than those characteristic of Fe1. Nevertheless, Fe1 may also involve a significant degree of intermediate-spin character, on the basis of the short Fe1–N$_p$ distances and the fact that the Fe1–S bond lengths in **2** are much longer than previously known Fe(III)–S bond lengths in ferric porphyrin systems.[20,24,25]

Finally, Powers and Chance[13] reported Fe(III)–S = 2.60, Cu(II)–S = 2.18, and Fe–Cu = 3.75 Å in CcO. The structure of **2** involves similarly long Fe(III)–S linkages and metal–metal distances (Fe2–Cu2 = 3.921 (1), Cu2–Fe1 = 3.857 (1), Fe1–Cu1 = 4.060 Å) that are strikingly close to the Fe–Cu distance reported for the resting enzyme. These similarities, together with the likely intermediate-spin character for iron(III) in **2**, lend support to the suggestion[14] that an intermediate-spin state for Fe(III) in the fully oxidized form of CcO may have much to do with the intriguing magnetic properties of that enzyme.

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Supplementary Material Available: Table I, containing a listing of the atomic coordinates and equivalent isotopic thermal parameters for **2** (3 pages). Ordering information is given on any current masthead page.

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Conversion of Thiourea Dioxides to Dioxygen

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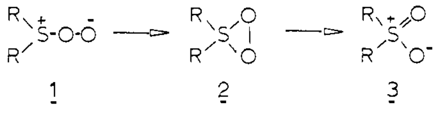
The oxygen atom transfer[1] reaction of 1,2- and 1,3-dipoles[2] containing one or more oxygen atoms has received considerable recent attention. Prominent among these reactive intermediates are persulfoxides, **1**, which result from the action of singlet oxygen on sulfides[3] or hydrogen peroxide on fluoro derivatives of trialkoxysulfuranes.[4] It has been shown that **1** (R = alkyl) can transfer an oxygen atom to sulfides to give sulfoxides and more rapidly converts sulfoxides to sulfones. If **1** is derived from a trialkoxysulfurane it is electrophilic enough to epoxidize alkenes.[4] In the absence of oxidizable reagents, **1** is ultimately converted into the sulfone, **3**, possibly via the electrocyclization product, the hypervalent thiadioxirane **2**. From studies of the solvent effects on efficiency of oxygen atom transfer the primary species present seems to be **1**.[3,5] However, when **1** (R = Ph) is generated via the sulfurane route in the presence of a triplet energy acceptor such as 9,10-dibromoanthracene, chemiluminescence of the latter is observed.[6] This suggests that **3** is derived from **2** in a triplet state. Clearly, the reaction surface connecting **1** and **3** is most unique.



We thought that the reaction above could be reversed, **3** → **2** → O$_2$. If **3**, by proper substitution, were made less stable than **2**, since an electron acceptor substituent with an energetically low-lying unoccupied molecular orbital (LUMO) of the π-type attached to sulfur stabilizes a tricoordinate hypervalent sulfurane bonding array >, a possible reaction might be the sequence **4** → **5** → **6**. In this communication we describe our observations on this strategy using an imidazolium or a dimethylamino group to adjust the carbonium ion substituent LUMO energy.

It has been reported that diaminocyclopropenium[8] and dihydrodiazepinium[9] salts may be lithiated by alkyllithium reagents[8] to give substituent stabilized lithiocarbenium ions which readily undergo SE reactions with weak electrophiles. Following these

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