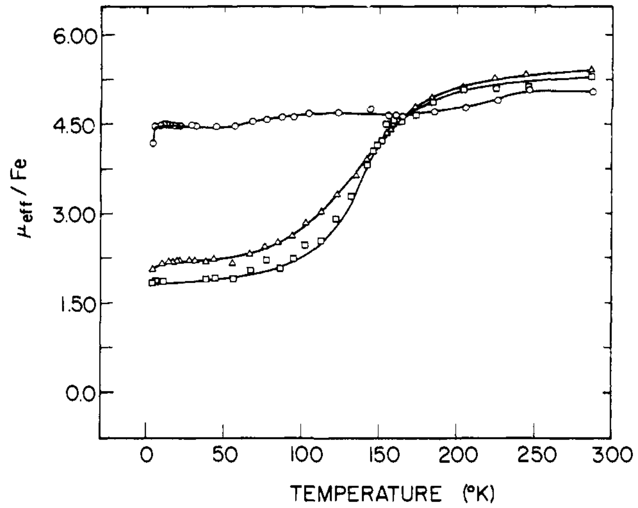

Figure 2. Effective magnetic moment per iron ion (μ_{eff}/Fe) vs. temperature curves for [$Fe_{0.5}Cr_{0.5}$(3-OCH_3-SalEen)$_2$]PF_6: Δ, original microcrystalline solid; ○, microcrystalline solid ground in ball mill; □, ground sample recrystallized by evaporating a methanol solution to dryness.

for the transformation. We have found that the most pronounced effect of grinding is observed for a doped sample. Figure 2 shows the results for [$Fe_{0.5}Cr_{0.5}$(3-OCH_3-SalEen)$_2$]PF_6. The original microcrystalline sample shows a gradual but complete transition. When the same sample is ground in a ball mill, a large fraction of the sample does *not* undergo the transition and a plateau develops. Recrystallization of this ground sample from methanol gives a sample that behaves as the original sample.

Acknowledgment. We are grateful for funding from NIH grant HL13652.

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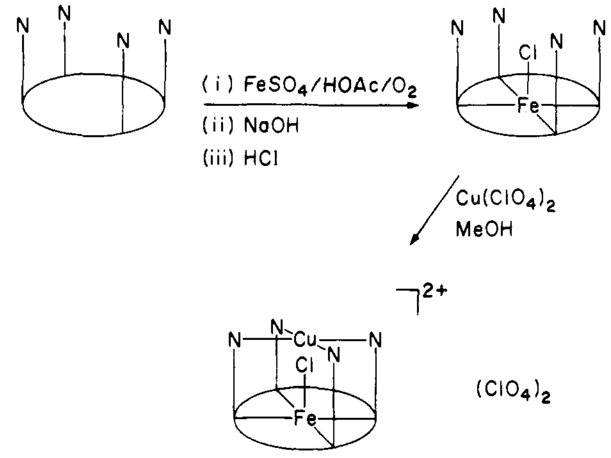
Toward Synthetic Models for Cytochrome Oxidase: a Binuclear Iron(III) Porphyrin-Copper(II) Complex

Sir:

The structure and function of the active site of cytochrome *c* oxidase has been the subject of much investigation and controversy over the past 40 years.[1] More recent ESR,[2] magnetic susceptibility,[3] and mcd[2,4] measurements have indicated the presence of a strongly magnetically coupled Fe(III)-Cu(II) center at the cytochrome a_3 active site in the fully oxidized enzyme. Because of the problems involved in studying the natural enzyme, and the paucity of available information on simple binuclear systems containing different metal ions, there has been considerable recent interest in the synthetic analogue approach to the active site structure of cytochrome *c* oxidase.[5-9]

Scheme I



(1)

We have reported[8] the synthesis and some preliminary studies on a binuclear model consisting of a porphyrin with a covalently attached tetrapyridine ligand system, *meso*-$\alpha,\alpha,\alpha,\alpha$-tetra(*o*-nicotinamidophenyl)porphyrin, (P)-(N_4). We now report synthetic, structural, and magnetic data for the Fe(III)-Cu(II) mixed metal system, [Fe(P)-Cl-Cu(N_4)](ClO_4)$_2$.

Insertion of Fe into the porphyrin to give Fe(P)Cl-(N_4)[10] was achieved by the ferrous sulfate-acetic acid method,[11] followed by treatment of the crude reaction mixture sequentially with aqueous NaOH and 0.01 N HCl. Treatment of a chloroform-methanol (9:1) solution of this compound with a methanolic solution of cupric perchlorate (1 mol) and recrystallization from aqueous acetonitrile gave the dihydrate [Fe(P)-Cl-Cu(N_4)](ClO_4)$_2$·2H_2O[12] (**1**) (Scheme I).

After many unsuccessful attempts, single crystals of **1** were isolated as small, poorly formed brown blocks, most of which were twinned, and none of which diffracted well. Despite the poor quality of the crystals, we were able to obtain X-ray diffraction data as follows: space group $P4/n$; $Z = 2$; cell dimension $a = 15.96$ (1), $c = 14.36$ (1) Å. Intensity data were collected on a Picker FACS1 4-circle diffractometer using graphite-monochromated Mo Kα radiation and θ-2θ scan technique. Of the 1980 unique reflections collected up to 2θ maximum (Mo Kα) of 40°, only 720 (36%) with $I > 2\sigma(I)$ were considered to be observed. The structure was solved by direct methods and refined by full-matrix least squares. The anions were not clearly resolved and are disordered around the fourfold axis. A second water molecule was also unresolved. The current residuals R and R' are 0.214 and 0.234 for the limited number of data and 93 variables.[13,14]

A perspective view of the cation is shown in Figure 1. It has fourfold symmetry with the Fe, Cu, and Cl atoms lying on the fourfold axis. The Cu is coordinated to the four pyridine nitrogens, and the chloride ion lies midway between the Fe and Cu atoms. The exceptionally long Cu-Cl and Fe-Cl bonds (average 2.47 (5) Å) indicate weak bridging between the two metals. The Fe atom is located essentially in the mean plane of the porphyrin and is octahedrally coordinated with a water molecule occupying the sixth coordination site (Fe-O = 2.09

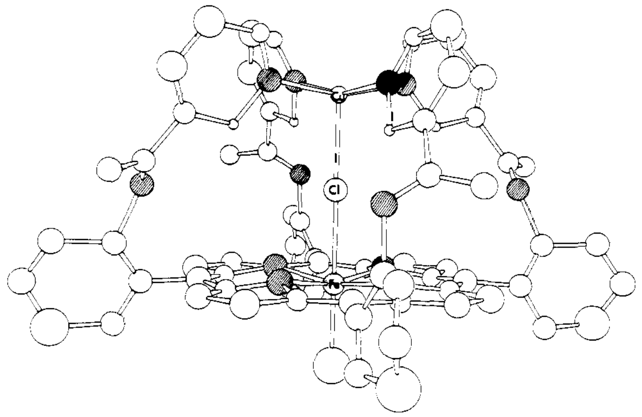


Figure 1. A perspective view of the $[Fe(P)\text{-}Cl\text{-}Cu(N_4)]^{2+}$ cation. Selected bond distances (in ängstroms) are as follows: Fe-N_p, 2.01 (7); Fe-OH_2, 2.081 (13); Fe-Cl, 2.55 (5); Cu-Cl, 2.41 (5); Cu-N_{py}, 2.16 (6); Fe-mean porphyrin plane, 0.04 (3).

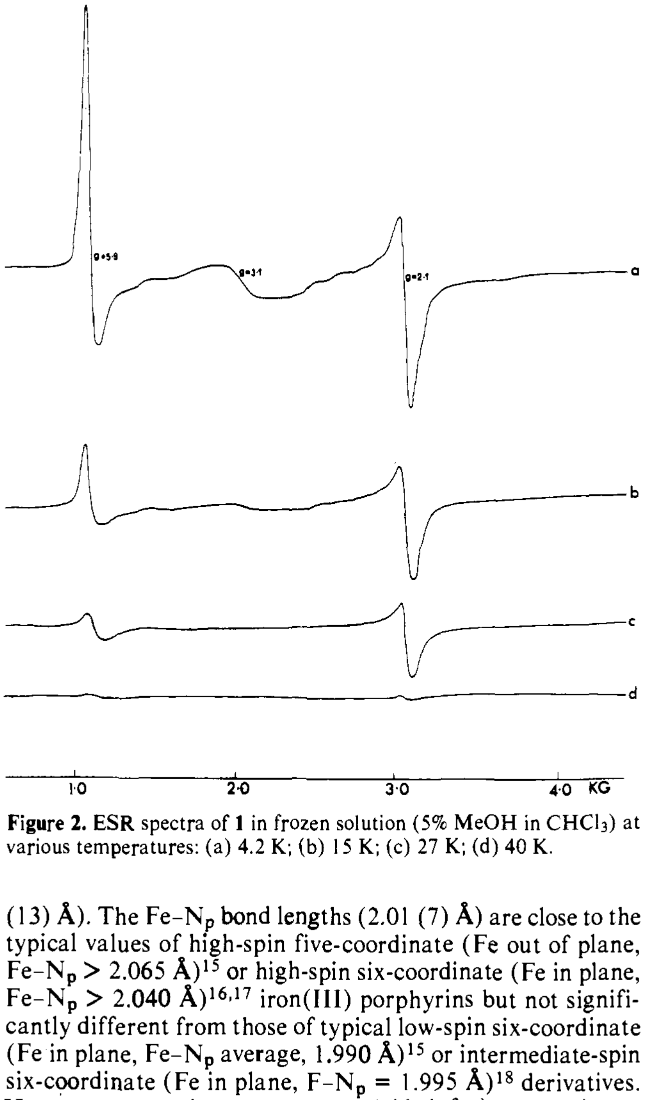


Figure 2. ESR spectra of **1** in frozen solution (5% MeOH in $CHCl_3$) at various temperatures: (a) 4.2 K; (b) 15 K; (c) 27 K; (d) 40 K.

(13) Å). The Fe–N_p bond lengths (2.01 (7) Å) are close to the typical values of high-spin five-coordinate (Fe out of plane, Fe–N_p > 2.065 Å)[15] or high-spin six-coordinate (Fe in plane, Fe–N_p > 2.040 Å)[16,17] iron(III) porphyrins but not significantly different from those of typical low-spin six-coordinate (Fe in plane, Fe–N_p average, 1.990 Å)[15] or intermediate-spin six-coordinate (Fe in plane, F–N_p = 1.995 Å)[18] derivatives. However, magnetic measurements (vide infra) are consistent with a fully or partially occupied $3d_{x^2-y^2}$ orbital on the iron in **1**, i.e. either high-spin ($S = {}^5\!/_2$) or quantum mechanically mixed ($S = {}^3\!/_2, {}^5\!/_2$)[16,19-22] spin state.

The ESR spectrum of **1** in frozen solution (5% MeOH-$CHCl_3$ or DMF) (Figure 2) or as a powder at 4.2 K shows a $g \sim 6$ signal characteristic of high-spin iron(III) porphyrins[23] and a signal at $g \sim 2$ typical of $S = {}^1\!/_2$ Cu(II) ions in a tetragonal field, although the $g_{\parallel}$ components are poorly resolved. The

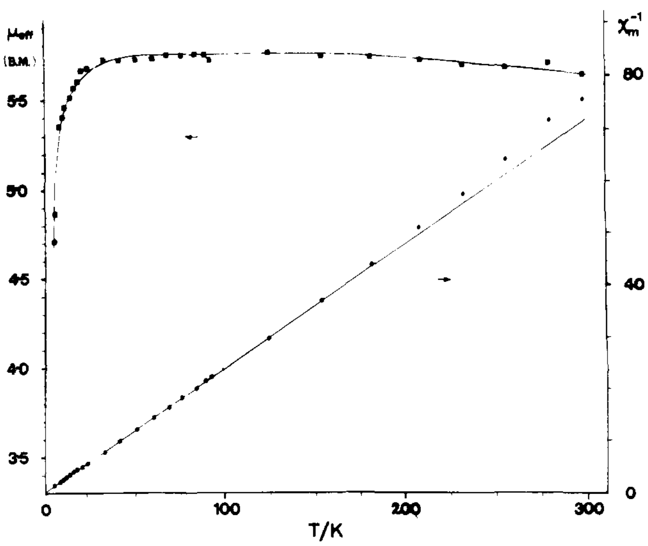


Figure 3. Magnetic moment and reciprocal susceptibility per binuclear molecule vs. temperature plots for **1**.

line widths are remarkably temperature dependent, and no signals are observable above ~40 K, indicating significant dipolar relaxation broadening.[24] An additional broad signal at $g \sim 3.1$ with more extreme temperature dependence, seen only in the frozen solution spectra, is attributed to dimer formation;[25] this tendency of **1** to aggregate in solution is clearly seen in the visible spectrum where the Soret band in the solid state (KBr disk, 427 nm) exhibits a concentration-dependent blue shift in solution[26] (CH_2Cl_2, 403 nm; DMF, 10^{-4} M, 405, and 10^{-5} M, 425 nm; CH_2Cl_2-MeOH, 10^{-4} M, 402, 10^{-5} M, 412, and 5×10^{-6} M, 416 nm). The fact that ESR signals are observed for both Fe and Cu in this system argues against a purely dipolar relaxation mechanism operating in cytochrome *c* oxidase to account for its ESR inactivity.[27]

The magnetic susceptibility of **1** was determined over the temperature range 300-4.2 K using a Faraday balance. A plot of μ_{eff} (per binuclear molecule) vs. T (K) is shown in Figure 3. The moment increases gradually from 5.61 μ_B at 300 K to a plateau value of ~5.74 μ_B in the region 200-50 K. Below 20 K the moment decreases rapidly, reaching 4.71 μ_B at 4.42 K. The $1/\chi$ vs. T plot in the range 100-4.2 K shows Curie-Weiss behavior with a small θ value (≈ 2 K), whereas, above 200 K, it shows approximate linear behavior but with an increased slope; i.e., μ_{eff} decreases. This unusual magnetic behavior cannot be explained simply in terms of a $-2J\bar{S}_1 \cdot \bar{S}_2$ exchange coupled Hamiltonian. The calculated dependence of μ_{eff} and $1/\chi$ on J has been described previously for ($S_1 = {}^5\!/_2$, $S_2 = {}^1\!/_2$) coupling (with $\bar{g} = 2.0$)[28] and some experimental results have recently been reported for binuclear Mn(II)-Cu(II) Schiff-base complexes.[29,30] In a two-level system of this kind, population of the $S' = 3$ and $S' = 2$ levels would occur in the case of zero J yielding $\mu_{eff} = 6.16$ μ_B and Curie behavior. For large J (>-200 cm^{-1}) only the $S' = 2$ level is populated and a temperature-independent μ_{eff} value of 4.90 μ_B is predicted. Intermediate values of J (negative) lead to a reduction in μ_{eff} at 300 K from 6.16 μ_B, the moment then further decreasing and leveling out at 4.90 μ_B as the temperature is decreased. The corresponding $1/\chi$ vs. T graphs all pass through zero at 0 K, being linear in the low temperature region when only the $S' = 2$ state is populated. The present data clearly do not conform to this simple model. The decrease in μ_{eff} below 20 K is generally reminiscent of large zero-field splitting effects common to [iron(III)(porphyrin)X] complexes. Inclusion of a $DS^2_{z(1)}$ term into the Hamiltonian does lead to a predicted decrease in μ_{eff} below 4.90 μ_B at low temperature but with little effect at higher temperatures. In an attempt to separate out the contribution to the susceptibility of the Fe(III) moiety we as-

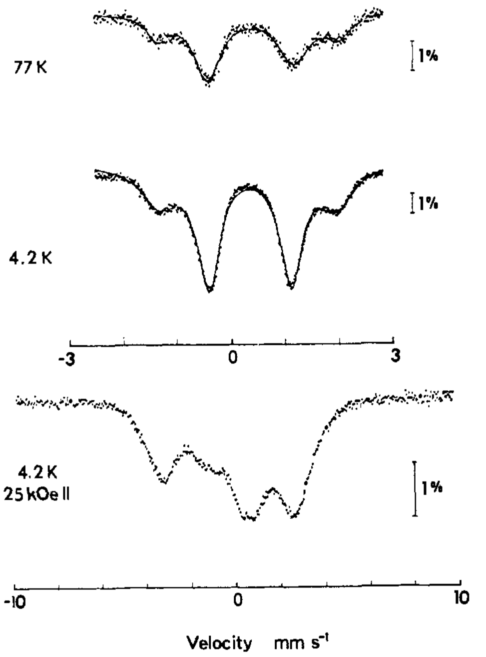


Figure 4. Mössbauer spectra of **1** at various temperatures. Solid lines in the zero-field spectra are fits which yield the parameters in Table I.

sumed zero Fe(III)-Cu(II) coupling and subtracted a Curie component (1.90 μ_B) for Cu(II) from the observed susceptibility.[31] The resulting curve was then compared with that measured separately on the copper-free derivative of **1**, Fe(P)Cl-(N_4).[32] In each case the moment decreases rapidly at low temperatures, but the shapes of the μ_{eff} vs. T curves at higher temperatures (>20 K) differ in detail. Incorporation of Cu(II) into the Fe(P)Cl-(N_4) moiety therefore changes the magnetic state of the Fe(III) center significantly, but at this stage of the analysis the relative contributions of zero-field splitting and exchange coupling have not been clearly defined.

Mössbauer effect results described below show that the electronic properties of **1** are further complicated by the apparent coexistence (at least on the Mössbauer time scale) of two electronic states of iron, one of which is probably of intermediate spin, $S = 3/2$, and the other high spin, $S = 5/2$. The μ_{eff} vs. T behavior shown in Figure 3 is quite similar to that displayed by Fe(TPP)ClO_4·0.5 *m*-xylene, a complex which has a spin-mixed $S = 3/2, 5/2$ ground state, but which shows only one quadrupole doublet in the Mössbauer spectra (4.2-300 K) with parameters typical of intermediate-spin iron(III).[21,33,34] The magnetic behavior of **1** could arise from an uncoupled pair of Fe(III) (mixed spin $S = 3/2, 5/2$; $\mu_{eff} \sim 5\ \mu_B$) and Cu(II) ($S = 1/2$; $\mu_{eff} \sim 1.9\ \mu_B$). The Mössbauer results would then require the presence in the bulk sample of a significant concentration of a structural isomer of **1** containing Fe(III) ($S = 5/2$) and Cu(II) ($S = 1/2$), e.g., an isomer in which the chloride ion is outside the "pocket", [Cl-Fe(P)-Cu(N_4)](ClO_4)$_2$. However, the magnitude of μ_{eff}, the relative intensities, and temperature dependence of the Mössbauer lines do not favor this interpretation. We feel that the data are more indicative of some form of spin equilibrium situation where the contributions from zero-field split $S = 5/2$ and $S = 3/2$ (or mixed spin $S = 3/2, 5/2$) centers vary with temperature. Relating this to structural or chemical features is not easy, although we note that the room temperature structural features of **1** are similar to those of high-spin six-coordinate iron(III) porphyrins.[17] These effects may be attributed to structural alterations as the temperature is lowered so that the Fe-N and Fe-Cl distances tend toward the $S = 3/2$ values. Indeed the very long Fe-Cl and Cu-Cl distances in **1** at room temperature evidence a potential exchange pathway between the two metals via the chloride ion. As the temperature is lowered a strengthening of one or other of the metal-Cl bonds is expected. This is seen in the infrared spectrum of **1** (polythene disk) which shows a considerable (~10-fold) enhancement of the intensity of the Fe-Cl stretching frequency at 375 cm^{-1} as the temperature is lowered from 300 to 200 K (cf. FeTPPCl which shows <2-fold enhancement). Likewise the solid state (KBr disk) visible spectrum of **1** shows a blue shift of 6 nm in the β band as the temperature is lowered from 300 to 150 K, reflecting a change in the electronic environment at the iron.

Table I. Mössbauer Parameters of **1**

T, K		ΔE, mm s^{-1}	δ,[a] mm s^{-1}	Γ,[b] mm s^{-1}	area, %
4.2	doublet 1	1.51	0.34	0.51, 0.50	65
	doublet 2	3.27	0.31	0.82, 0.79	35
77	doublet 1	1.58	0.37	0.60, 0.72	80
	doublet 2	3.31	0.32	0.47, 0.53	20
300		evidence of 2 doublets			
4.2	25 kOe applied field	maximum splitting, 6.40 mm s^{-1} (~200 kOe)			

[a] Relative to α-Fe. [b] Full width at half maximum height.

Despite the complexities of the magnetic properties of **1** it is possible to conclude that it does not mimic the magnetic features of the Fe-Cu couple in the fully oxidized or resting form of cytochrome oxidase which has been shown[2,3] to exhibit Curie behavior described earlier for $J > -200$ cm^{-1}, i.e., $\mu_{eff} \sim 4.9\ \mu_B$.

The Mössbauer spectra of **1** are shown in Figure 4. The zero-field spectra are interpreted in terms of two doublets which are clearly evident at low temperatures and still detectable at 300 K despite poor resolution. The quadrupole splitting and isomer shift values are given in Table I. The parameters for doublet 1 are in the range expected for $S = 5/2$ iron(III) and are very similar in magnitude to those displayed by six-coordinate iron(III) porphyrins such as [Fe(TPP)-(H_2O)$_2$]ClO_4.[18,35] The parameters for doublet 2 are close to those observed recently in intermediate spin, $S = 3/2$, iron(III) porphyrins.[18,19,21] The spread of the lines in the 25-kOe applied field spectrum corresponds to a field of ~200 kOe which is similar to that observed for the $S = 3/2$ complexes, but considerably reduced from a saturated hyperfine field of ~550 kOe expected for high-spin iron(III) porphyrins. Variation in intensities of the lines as a function of temperature shows that the high-spin and intermediate-spin Fe(III) centers exist in approximate ratio 2:1 at 4.2 K, rising to ~4:1 at 77 K.

The copper-free derivative of **1**, Fe(P)Cl-(N_4), shows a quite different Mössbauer behavior.[32] At 4.2 K, the spectrum consists of two doublets whose δ and ΔE values (0.41, 0.24 and 1.16, 1.89 mm s^{-1}, respectively) are similar to those recently reported for high-spin six-coordinate derivatives.[17] At 77 K and above, one asymmetric doublet (δ 0.43, ΔE = 1.35 mm s^{-1}) is observed, and the applied field spectrum corresponds to an internal field of 490 kOe, which further corroborates the $S = 5/2$ spin state assignment.

Thus, the Mössbauer studies on **1** and its copper-free derivative show, as did the susceptibility studies, that incorporation of Cu(II) into the tetrapyridyl ligand system considerably affects the electronic state of the iron(III) in the porphyrin. It is known from other studies that the Mössbauer properties of iron porphyrins which have electronic ground states near to a "crossover" position are very sensitive to minor variations in the axial ligands and even in lattice solvate molecules.[16,34] Finally, we note that the Mössbauer characteristics of well-behaved Fe(III)-Cu(II) exchange-coupled complexes (e.g., the binucleating Schiff-base type[29,36]) are not yet known and are required for understanding of such a coupled system where zero-filled and other effects are minimal.

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Supplementary Material Available: Tables of structural parameters and intermolecular bond lengths and angles of $[Fe(P)-Cl-Cu(N_4)](ClO_4)_2$ (3 pages). Ordering information is given on any current masthead page.

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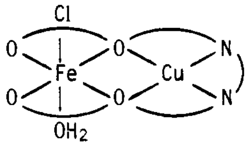
(36) Surprisingly, one such binucleated [Fe(III)–Cu(II)] Schiff-base complex



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