Ag levels, clear diffraction evidence is seen for other phases. The case for Ag substituting for Cu, rather than for Y or Ba, has already been made above.

Linear coordination of the type found for Cu in $YBa_2Cu_3O_6$ is well-known for Ag(I). We did not find evidence in terms of diffraction intensities (cf. ref 7) for the O-poor compound, which contains Cu in the formal oxidation state of +1. However, on the basis of our electrical and magnetic measurements we cannot exclude the possibility that it is present, with Ag in it, although our synthetic procedure, under flowing O_2, argues against formation of the O-poor material.

Notwithstanding this uncertainty, our results are consistent with the assumption that Ag will preferentially substitute for Cu in the CuO_4 chains. In that case our data suggest that interrupting these chains with AgO_4 groups leads to a decrease in the superconducting fraction of the sample, without a clear effect on T-(onset), which would still be the result of the Ag-free regions of the material (e.g. by electronic interaction with the CuO_5 planes). Also, the temperature interval over which the transition occurs is broadened considerably. We cannot say if these effects are electronic, structural, or a combination of the two.

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Articles

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Synthetic Model Approach to the Active Site of Cytochrome *c* Oxidase: Studies of a Heterodinuclear Iron(III) Porphyrin–Copper(II) Tripeptide Complex

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The reaction in THF of iron(II) *meso*-tetraphenylporphyrin, $Fe^{II}TPP$, with $Cu^{III}(aib_3)$, where aib_3 is the tripeptide of α-amino-isobutyric acid, results in the formation of a neutral heterodinuclear complex, $[Fe^{III}(TPP)Cu^{II}(aib_3)]$ (**1**). Optical, conductance, electrochemical, magnetic, EPR, and Mössbauer data are reported for the dinuclear complex **1**. Isosbestic behavior is exhibited at 600, 525, and 415 nm by solutions of $Fe^{II}TPP$ to which varying amounts of $Cu^{III}(aib_3)$ are added, indicating the formation of **1**. EPR and Mössbauer spectra provide evidence for the presence of a high-spin ($S = ^5/_2$) iron(III) and ($S = ^1/_2$) copper(II) in complex **1**. A weak antiferromagnetic interaction between the iron and copper is evident from the EPR measurements. While the magnetic interaction is weak, electrochemical and conductometric results indicate that the anionic $Cu^{II}(aib_3)^-$ complex is moderately strongly bound to the $Fe^{III}TPP^+$.

Introduction

Cytochrome *c* oxidase, found in mitochondria of all aerobic organisms, is the respiratory enzyme that catalytically reduces O_2 to H_2O with the concomitant release of energy [O_2 + $4H^+$ + $4e^-$ → $2H_2O$ + energy]. Despite extensive studies, the active site structure of cytochrome *c* oxidase remains one of the most enigmatic and controversial problems in chemistry.[1]

Anomalous magnetic and spectroscopic behavior is observed for one iron and one copper site in the fully oxidized enzyme. This behavior has typically been interpreted in terms of a strong antiferromagnetic coupling between Fe(III) and Cu(II) atoms in the oxygen-binding site.[2] Several possible structural models have been advanced to account for the proposed large antiferromagnetic coupling. In most instances a bridging ligand is envisaged between the two metal centers. With this view in mind, several workers have reported[3,4] the synthesis of compounds that are, to varying degrees, potential structural analogues of the oxidized active site. Most of these systems incorporate bridging ligands containing N, O, or S atom(s). We have reported[4] trinuclear $Fe^{III}/Cu^{II}/Fe^{III}$ and tetranuclear $Fe^{III}/Cu^{II}/Fe^{III}/Cu^{III}$ complexes that have

Table I. Mössbauer Data for Iron(III) Porphyrin Complexes

compd	spin state assignt	T, K	δ,[a] mm/s	ΔE_Q, mm/s	ref
1	$S = ^5/_2$	77	0.51	1.04	*c*
$(Fe^{III}TPP)_2[Cu^{II}(MNT)_2]$	$S = ^3/_2$	*b*	0.24	3.13	4a
$Fe^{III}(TPP)OMe$	$S = ^5/_2$	4.2	0.42	0.62	24
$Fe^{III}(TPP)Cl$	$S = ^5/_2$	4.2	0.41	0.46	24
$Fe^{III}(TPP)ClO_4$	$S = ^5/_2, ^3/_2$	77	0.38	3.48	19

[a] Reported relative to metallic iron. [b] Room temperature. [c] This work.

bridging S atoms between the iron(s) and copper(s). Presently, none of the potential synthetic model compounds, including our

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own,[3,4] have successfully reproduced all of the properties of the active site of the natural enzyme.

As the identity of the bridging group of the cytochrome c oxidase is still under debate, the ability of a carboxylate function to serve as a bridge in dinuclear systems is of direct relevance to the controversy. In the present paper we wish to report the characterization of a new heteronuclear (porphyrinato)iron-(III)–copper(II) peptide complex, which appears to contain a μ-carboxylato bridge between iron(III) and copper(II). The system is based on (*meso*-tetraphenylporphyrinato)iron(III), $Fe^{III}TPP^+$ and a copper(II) complex of the tripeptide of α-aminoisobutyric acid, $Cu^{II}(aib_3)^-$.

To date it remains true that no examples of four-coordinate Fe^{III} porphyrin complexes have been observed. In the absence of other anionic ligands or strongly coordinating neutral ligands, $Cu^{II}(aib_3)^-$ will act as an axial ligand for the $Fe^{III}TPP^+$. Examination of space-filling models of $Cu^{II}(aib_3)^-$ indicates that the only reasonable points of interaction are through one or both carboxylate oxygens (each of the amide oxygens and nitrogens are sterically blocked from interaction by the two adjacent methyl groups). Moreover, the strong antiferromagnetic coupling in carboxylate dimers is well documented.[5] To the best of our knowledge, there are no previous reports of a carboxylate-bridged Fe^{III}/Cu^{II} system; therefore, these inveistgations present the first such example in this series.

Experimental Section

$Cu^{III}(aib_3)$ and **1** are both decomposed by light. $Fe^{II}TPP$ and **1** react rapidly with oxygen. Therefore, all of the manipulations were done in the dark and/or under an oxygen-free nitrogen atmosphere where necessary.

$Fe^{II}TPP$ was prepared and purified according to published procedure.[6] The ligand $H_3aib_3 \cdot 2H_2O$ was prepared by the literature method[7] and analyzed. Anal. Calcd for $C_{12}H_{27}N_3O_6$: C, 46.57; H, 8.80; N, 13.58. Found: C, 46.67; H, 8.46; N, 13.71. Solid samples of $Cu^{III}(aib_3)$ were prepared[8] by the following modified method: $CuSO_4 \cdot 5H_2O$ and the
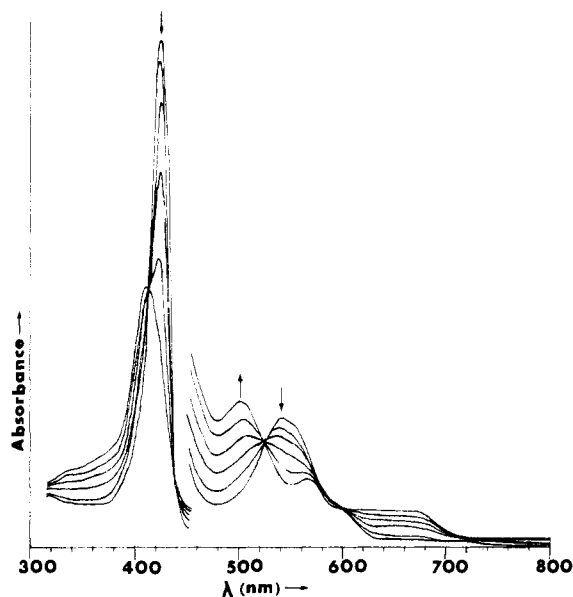
Figure 1. Spectral titration in THF solution obtained by addition of aliquots of $Cu^{III}(aib_3)$ to $Fe^{II}TPP$. $Fe^{II}TPP$ was present initially at a concentration of 6.41×10^{-5} M, and the spectra correspond to $Fe^{II}TPP:Cu^{III}(aib_3)$ ratios of 1.0:0.2, 1.0:0.4, 1.0:0.6, 1.0:0.8 and 1.0:1.0 in order of decreasing absorption at ~ 540 nm.

ligand $H_3aib_3 \cdot 2H_2O$ (1:1.05 equiv) were first dissolved in triply distilled H_2O. Solid $Na_2B_4O_7$ was added in small amounts until the deep red-purple color of the $[Cu^{II}(aib_3)^-]$ complex fully developed (pH ~ 9). This solution was oxidized electrochemically on a reticulated vitreous carbon electrode with 1.0 M $MgSO_4$ as an electrolyte at a constant potential of +0.90 V vs SCE in the dark and under N_2 at ~ 4 °C. After electrolysis the solution was lyophilized. The complex was extracted from the solid residue with dry acetone and chromatographed on silica gel, eluting with dry acetone. The eluent was concentrated, and the desired complex, $Cu^{III}(aib_3)$, was precipitated as a brown powder by addition of dry benzene. The sample was dried thoroughly before use and stored at -20 °C. Its purity was checked by recording the UV–vis absorption spectra. λ_{max}, nm (ϵ): found, 278 (11.43×10^3), 395 (5.01×10^3); reported[9] 278 (11.50×10^3), 395 (5.20×10^3).

Cyclic voltammograms (cv) were obtained by employing platinum working and auxiliary electrodes. The supporting electrolyte, tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$) concentration was 0.1 M. The reference electrode typically consisted of silver wire immersed in 0.1 M $AgNO_3$ in DMSO contained in a small tube fitted with a vicor frit. All values of potential are reported vs. this Ag^+/Ag reference ($E_{1/2}$ = +0.303 V for ferrocene/ferrocenium). The electrochemical equipment has been described previously.[10] The cv's were recorded at room temperature (~ 23 °C) in an inert-atmosphere box. UV–vis spectra were recorded on a Perkin-Elmer 553 spectrophotometer. A specially designed cell with an air-tight reservoir was used for the spectral titrations. Conductances were measured in the drybox by using a Yellow Spring Instruments Model 31 conductivity bridge.

EPR spectra were recorded near liquid He and liquid N_2 temperatures on a Varian E-9 X-band EPR spectrophotometer interfaced to an IBM CM 9000 computer and equipped with a variable-temperature unit. EPR tubes were sealed with septa and wrapped with aluminum foil prior to removal from the drybox, whereupon the solutions were immediately frozen in liquid N_2. An ^{57}Fe enriched sample for Mössbauer spectroscopy was prepared as follows: $(^{57}Fe^{III}TPP)_2O$ was prepared by a literature method[11] using $^{57}Fe_2O_3$ (>90% enriched; Oak Ridge National Laboratory). The μ-oxo dimer was then converted to $^{57}Fe^{II}TPP$ by reduction with ethanethiol.[12] The Mössbauer equipment has been described previously.[13]

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Magnetic susceptibilities in THF solutions were determined by the Evans method.[14] The NMR spectra were recorded on a Bruker 270-MHz or 200-MHz FT-NMR instrument equipped with a variable-temperature probe. The diamagnetic susceptibility of THF and the H_3aib_3 ligand were calculated from Pascal's constants.[15] Literature values for the diamagnetic susceptibility of the hexamethyldisiloxane standard (HMDS)[16] and TPP[17] were used.

Results

Optical Absorption Spectra and Solution Conductivity Behavior. The titration of $Fe^{II}TPP$ with $Cu^{III}(aib_3)$ in THF[18] was followed spectrophotometrically (Figure 1). Three isosbestic points are observed in the titration at 600, 525, and 415 nm, respectively. After the addition of exactly 1 equiv of $Cu^{III}(aib_3)$ no further change in the spectrum is observed with further additions except for a slight increase in absorbance around ~500 nm, which is due to the relatively weak and broad absorption by the excess $Cu^{III}(aib_3)$. The final spectrum of the product is quite similar to that of $Fe^{III}(TPP)OAc$ in THF. The spectrum also bares qualitative resemblance to the spectrum of $Fe^{III}(TPP)ClO_4$ in THF, but there are clear and marked differences. These results argue that the product, **1**, consists of the anion-bound, five-coordinate prophyrin and not the ion-dissociated, solvent-bound form.[19,20] Thus the reaction in solution can be written as
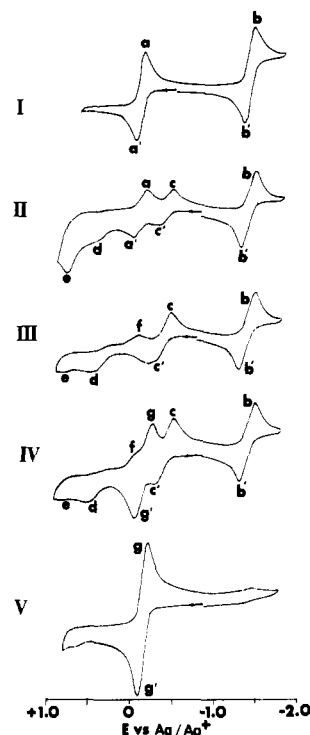
$$Fe^{II}TPP + Cu^{III}(aib_3) \rightarrow Fe^{III}TPPCu^{II}(aib_3).$$
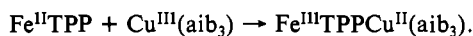
The relatively strong binding of the $Cu^{II}(aib_3)^-$ anion at the axial Fe^{III} site is further supported by electrochemical results (vide infra).

A plot of the absorbance at 500 nm during a titration of $Fe^{II}TPP$ with $Cu^{III}(aib_3)$ gave two linear regions intersecting at 1 equiv of added Cu^{III} complex. Within experimental error there is no indication of curvature in this plot near the equivalence point indicating that the formation constant for the binding between $Cu^{II}(aib_3)^-$ and $Fe^{III}TPP^+$ is greater than 1×10^6.

The above results are in concert with analogous titrations in THF followed conductometrically. For solutions that were initially 1.0 mM in $Fe^{II}TPP$, when titrated with up to 2.0 equiv of added $Cu^{III}(aib_3)$ produced equivalent conductances that were, within experimental error, identical with that of pure THF (<0.2 Ω^{-1} cm^2 equiv^{-1}). This result can be compared with equivalent conductances in THF of 10.4 Ω^{-1} cm^2 equiv^{-1} for $Fe^{III}TPP^+SO_3CF_3^-$ and 19.0 Ω^{-1} cm^2 equiv^{-1} for $Fe^{III}TPP(Im)_2^+SO_3CF_3^-$. The spectral and conductometric titration demonstrate that the electron transfer between the $Cu^{III}(aib_3)$ and the $Fe^{II}TPP$ is complete and that, once formed, the $Cu^{II}(aib_3)^-$ binds strongly to the $Fe^{III}TPP^+$ axial position.

Electrochemistry. The reaction of $Fe^{II}TPP$ with $Cu^{III}(aib_3)$ was followed by cyclic voltammetry.[21] The cv of pure $Fe^{II}TPP$ in THF containing 0.1 M (TBA)PF$_6$ shows two reversible waves, one at $E_{1/2} = -0.055$ V for Fe^{II}/Fe^{III} couple and one at $E_{1/2} = -1.380$ V for the formal Fe^{I}/Fe^{II} couple (Figure 2). Addition of aliquots of concentrated $Cu^{III}(aib_3)$ solution results in the changes observed in Figure 2. Initially as the $Cu^{III}(aib_3)$ is added the wave due to the Fe^{II}/Fe^{III} couple (Figure 2, waves a/a') decreases and ultimately disappears at 1.0 equiv of added $Cu^{III}(aib_3)$. Concomi-

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(18) Halogenated solvents such as CH_2Cl_2 and $CHCl_3$ were avoided as they were found to react with $Fe^{II}TPP$.
(19) The observed value of ε at λ$_{max}$ = 502 nm of complex **1** in THF is 10.73 $\times 10^3$ M^{-1} cm^{-1} (±0.35%).
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(21) The qualitative behavior of the electrochemical titration is independent of the initial potential and of initial scan direction as long as the initial potential is negative of peak d in Figure 2. This is true even though the initial potential chosen in Figure 2 is the potential of zero current only at the beginning of the titration.

Figure 2. Cyclic voltammograms at a platinum electrode in 0.1 M (TBA)PF$_6$/THF solutions obtained during the titration of $Fe^{III}TPP$ with $Cu^{III}(aib_3)$. $Fe^{II}TPP$ concentration was initially 7.48 × 10^{-4} M and $Cu^{III}(aib_3)$ was added to give $Fe^{II}TPP$:$Cu^{III}(aib_3)$ ratios of (I) 1.0:0.0, (II) 1.0:0.5, (III) 1.0:1.0, (IV) 1.0:2.0, (V) 0.0:1.0. The scan rate was 100 mV/s.

tantly, a new, quasireversible wave appears at $E_{1/2} = -0.332$ V (Figure 2, waves c/c'), which increases in peak current until 1 equiv of $Cu^{III}(aib_3)$ has been added. Two additional irreversible oxidation waves, labeled d and e in Figure 2, also grow in as the titration to 1 equiv proceeds. The reduction process labeled f is associated with the process d and is absent if the positive scan is reversed prior to the oxidation at d. The potential of the formal $Fe^{I/II}$ couple, waves b/b', is unaffected by the $Cu^{III}(aib_3)$ addition, indicating that, upon reduction to the Fe^{II} form, the axially ligated $Cu^{II}(aib_3)^-$ dissociates. These results are quite typical of other Fe^{III}–porphyrin systems where a moderately tightly bound anion such as Cl$^-$ is lost upon reduction to Fe^{II}.[22]
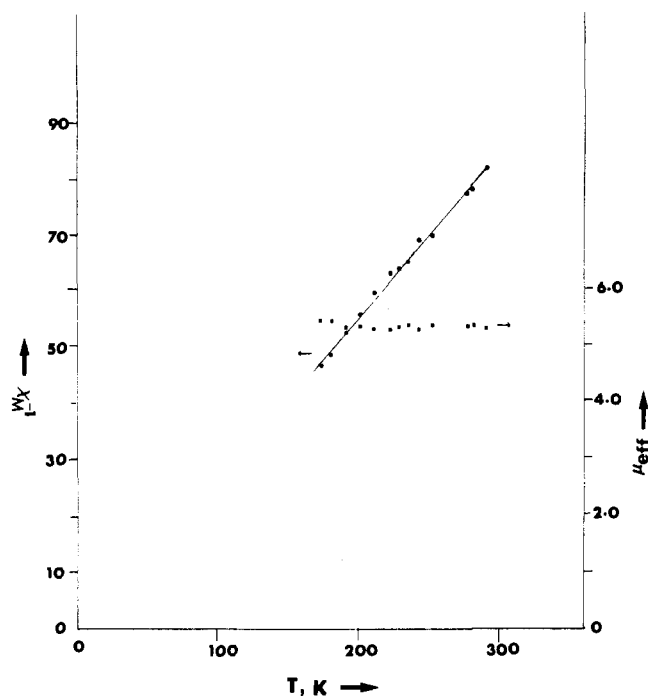
Finally, the first irreversible oxidation at wave d is assigned to the oxidation of the intact complex, $Fe^{III}TPPCu^{II}(aib_3)$.

Magnetic Properties. Changes in magnetic susceptibility were followed during the titration of $Fe^{II}TPP$ (3.127 mM) with $Cu^{III}(aib_3)$ (9.578 mM) by the Evans method.[14] The magnetic moment of the dinuclear complex **1** at room temperature (24 °C) was found to be 5.5 ± 0.2 μ_B (average value of six measurements). This value is lower than the calculated spin-only value of 6.16 μ_B, expected for a totally noncoupled $(S = ^5/_2)–(S = ^1/_2)$ system but higher than 4.90 μ_B, the spin-only value expected for the fully spin-coupled $(S = ^5/_2)–(S = ^1/_2)$ system. If the spin-only susceptibility of the Cu^{II} is subtracted from the observed magnetic moment, a room temperature value of 5.25 ± 0.20 μ_B is obtained. Conversely, the calculated spin-only value for the intermediate spin $(S = ^3/_2)$ Fe^{III} and $(S = ^1/_2)$ Cu^{II} is only 4.24 μ_B.

Because of the thermal, photochemical, and oxygen instability of **1** (vide supra) to date we have been unable to study the solid-state magnetic properties of **1**. We have, however, obtained solution magnetic susceptibilities of **1** in THF over the temperature range from 172 to 290 K. These results are presented in Figure 3. Plots of χ_M^{-1} vs. T show Curie law behavior, and values of μ_{eff} are invariant.

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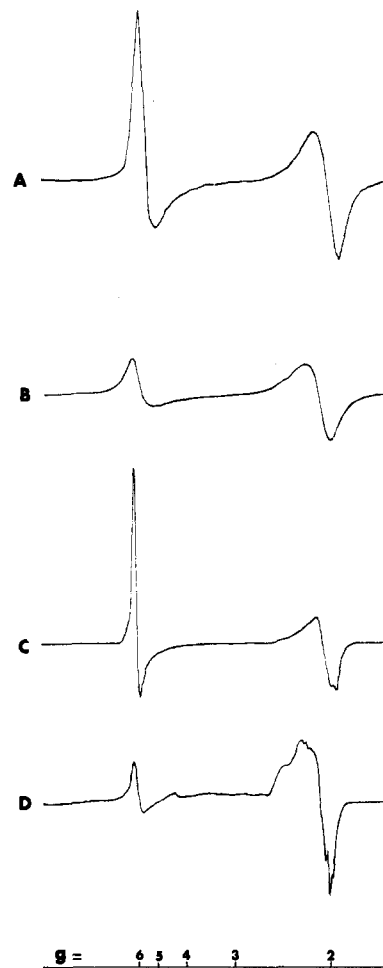
Figure 3. Inverse molar magnetic susceptibility in cgsu (●) and effective magnetic moment (per binuclear complex) in μ_B (■) vs temperature (K) curve for $Fe^{III}(TPP)Cu^{II}(aib_3)$.

EPR Spectroscopy. EPR spectra obtained by the addition of 0.5, 1.0 and 1.5 equiv of $Cu^{III}(aib_3)$ to $Fe^{II}TPP$ were recorded in THF glass near liquid-He temperatures. All of the spectra are identical except in their absolute magnitudes. Figure 4 shows the spectra of **1** in frozen THF glass at 11 and 100 K and solid-state spectra at 17 and 99 K. Both the solid-state and frozen-solution spectra near liquid-He temperature are qualitatively the same except that the magnetically isolated, frozen-solution spectrum is sharper. At higher temperatures the intensity of the $g \sim 6$ signal due to the iron is significantly diminished as would be expected for a typical five-coordinate, $S = {}^5/_2$, ferric porphyrin. Attempts to quantitate the frozen-solution spectrum near liquid-He temperature were unsuccessful due to the fact that even at very low microwave powers there was evidence of signal saturation for the iron signal in **1**. Each spectrum in Figure 4 contains features attributable both to high-spin iron ($S = {}^5/_2$) and copper ($S = {}^1/_2$). The mononuclear $Cu^{II}(aib_3)^-$ complex, however, gives very narrow and well-resolved metal hyperfine and ligand superhyperfine lines.[23] The broadness and absence of hyperfine splitting on the $g \sim 2$ signal in the spectrum of **1** suggests that the iron–copper centers are not magnetically isolated from one another.

Finally, EPR spectra of complex **1** in benzene and toluene glasses near liquid-He temperatures gave results similar to those obtained in THF glass.

Mössbauer Spectroscopy. The 77 K, zero-field Mössbauer spectrum for a ^{57}Fe enriched sample of **1** in frozen THF is shown in Figure 5. The best fit values of the isomer shift, δ, and quadrupole splitting, ΔE_Q, are given in Table I and compared with other known systems. The isomer shift and quadrupole splitting values are in the range of those observed for five-coordinate high-spin iron(III) porphyrins.[24] The spectrum in Figure 5 shows a broad asymmetric pair of quadrupole lines with broad wings (line width left = 1.1 mm s^{-1}, and line width right = 1.0 mm s^{-1}). There is no evidence of paramagnetic hyperfine structure, indicating that the system is rapidly relaxing. It is, however, observed that the left to right asymmetry is affected by the application of a small external magnetic field (1.3 kG), indicating a paramagnetic ground state. There is no strong spin coupling indicated by the Mössbauer

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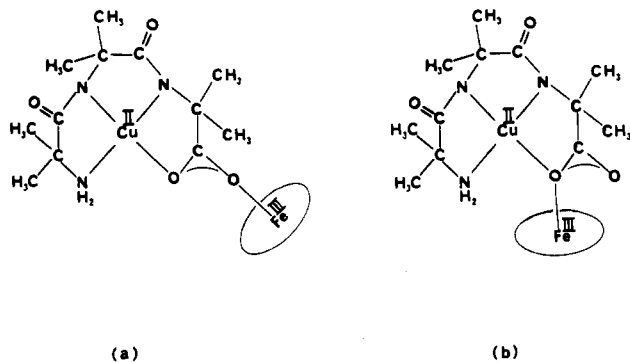
Figure 4. EPR spectra of $Fe^{III}(TPP)Cu^{II}(aib_3)$: (A) in solid state at 17 K; (B) in solid state at 99 K; (C) in THF glass at 11 K; (D) in THF glass at 100 K.
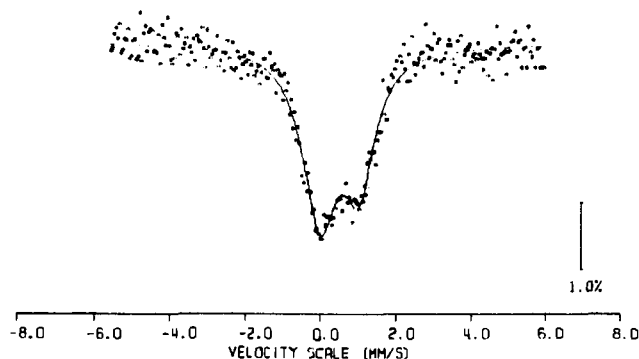
Figure 5. Zero-field Mössbauer spectrum at 77 K of $^{57}Fe^{III}(TPP)Cu^{II}$-$(aib_3)$ in THF relative to Fe^0.

results; however, the argument that the iron ($S = {}^5/_2$) and copper ($S = {}^1/_2$) spins are weakly coupled is consistent with the results.

Stability and Reaction. $Fe^{III}TPPX$ (X = any redox innocent anion), $Cu^{II}(aib_3)^-$ and $Cu^{III}(aib_3)$ are each unreactive toward O_2. $Cu^{III}(aib_3)$ will decompose (minutes) in solution in the presence of visible light, while $Cu^{II}(aib_3)^-$ is photostable. In contrast, complex **1** reacts with both dry O_2 and light.

In the absence of light, solutions of **1** react very rapidly with O_2 on a time scale of seconds or less. The visible spectrum of the resulting solution is indistinguishable from that of the (μ-oxo)ferric porphyrin dimer. The fate of the $Cu(aib_3)$ moiety in this reaction is, at present, unknown; however, whatever the product is, it remains in solution.

In the absence of O_2, solutions of **1** degrade in light but much more slowly than they react with O_2 (tens of minutes). The

(a)   (b)

Figure 6. Possible structures of $Fe^{III}(TPP)Cu^{II}(aib_3)$ (1).

spectrum of the degradation product in solution is again similar to that of the μ-oxo ferric porphyrin dimer. Unlike the degradation with O_2, however, during the degradation by light a fine precipitate forms that presumably contains copper. ·

In the absence of both light and O_2 1 is stable on the time scale of any of the measurements reported herein. There exists, however, a very slow thermal degradation in solution that becomes noticeable over the course of tens of hours. The products resulting from the thermal decomposition appear to be similar to the products obtained from the light-catalyzed decomposition. Our efforts thus far in growing x-ray diffraction quality crystals of 1 have thus far failed and resulted in isolation only of crystals of the (μ-oxo)ferric porphyrin dimer.

Discussion

The results from each of the various physical methods used to study complex 1 are consistent with a linked 1:1 stoichiometry. The most compelling evidence for this stoichiometry comes from the spectral, conductometric, and electrochemical titrations. If one assumes that shifts in the potential of the $Fe^{II/III}$ couple within a series of anionic ligands primarily reflect differences in the binding constant of the $Fe^{III}TPP$ for the anion (rather than relative differences in binding of the anion to $Fe^{II}TPP$ which in all cases is expected to be weak), one can argue, at least qualitatively, that the $Cu^{II}(aib_3)^-$ complex is coordinated to the $Fe^{III}TPP$ more strongly than, for example, ClO_4^-, but less strongly than Cl^-.[25]

The relatively strong axial binding of the $Cu^{II}(aib_3)^-$ anion by the iron is consistent with the $S = {}^5/_2$ spin assignment for the Fe^{III} made from the EPR and Mössbauer results. The EPR and Mössbauer studies also do not indicate any strong exchange coupling between the two metal centers. The solution magnetic susceptibility values over the range from 290 to 172 K also indicates a lack of strong exchange coupling. The fact that these values are consistently lower than expected for a simple uncoupled $S = {}^5/_2$ and $S = {}^1/_2$ ground state thus cannot be explained on the basis of a strongly coupled spin-exchange model nor can it be explained by invoking thermally populated spin states of lower multiplicity for the iron ($S = {}^1/_2$ or ${}^3/_2$). If the low value of the magnetic susceptibilities were due to antiferromagnetic coupling alone the coupling constant would have to be large enough to observe non Curie law behavior in the susceptibilities even over the limited temperature range studied. Similar deviations from Curie law behavior would be expected if a low-lying $S = {}^3/_2$ or ${}^1/_2$ excited state were being thermally populated at room temperature. The possibility of a quantum-mechanical admixed spin state for the iron that is predominantly $S = {}^5/_2$ in character,

however, cannot be ruled out. In fact, this explanation seems to be the one most consistent with the results from each of the various physical measurements.

Consideration of space-filling models of $Cu^{II}(aib)_3^-$ show rather unambiguously that the only sites sterically accessible for binding to the iron are the two oxygens on the terminal carboxylate. There are numerous precedents for either possible mode of bridged binding. Therefore, we can propose the two possibilities presented in Figure 6 as being reasonable from steric considerations. Primarily on the basis of the fact that the coupling between the two metal centers is weak, we marginally favor structure a; however, structure b cannot be ruled out on the basis of our data.

O_2 Reactivity. The observed rapid reactivity of 1 with O_2 is of particular interest. As pointed out earlier neither simple $Fe^{III}PX$ complexes nor $Cu^{II}(aib_3)^-$ alone reacts with O_2. This behavior is not, however, unique. We have observed a similar, albeit more complex, O_2 reaction with the sulfur-bridged trinuclear and tetranuclear FeP/Cu systems previously reported.[4] In the sulfur-bridged systems the (μ-oxo)ferric porphyrin dimer is also a product. In each case the irons are clearly in the ferric form initially, *but* in each case the iron is also linked directly to a redox active copper(II)-containing anion that has an accessible redox couple within a few hundred millivolts of the potential of the $Fe^{II/III}$ couple. We speculate that the copper complex can act as an electron reservoir and thus allow the ferric iron to react with the O_2 at the open Fe^{III} coordination site. Such a reaction could produce the same μ-peroxo intermediate as has been proposed in the reaction of $Fe^{II}P$ with O_2.[26]

$$2Fe^{III}(TPP)Cu^{II}(aib_3) + O_2 \rightarrow$$
$$2Cu^{III}(aib_3) + Fe^{III}TPP-O-O-Fe^{III}TPP$$
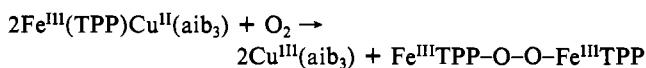
We are presently studying these reactions further and will report on the detailed results in a separate report.

Summary

$Fe^{II}TPP$ and $Cu^{III}(aib_3)$ react in a 1:1 stoichiometry to form a neutral carboxylate-bridged complex. Cyclic voltammetry studies and conductometric and spectral titrations reveal that the iron(III) center binds the copper(II) containing anion relatively strongly. Solution magnetic moment, EPR, and Mössbauer data are all consistent with the presence of a single complex having a weak antiferromagnetic spin interaction between the metal centers.

A kinetically facile mechanism exists for the heterodinuclear complex to react with O_2 despite the fact that the iron is formally in the Fe^{III} form. This reactivity is likely due to the availability of an open coordination site on the iron combined with the existence of the relatively low-potential $Cu^{II/III}$ couple, which acts as electron reservoir.

Finally, the magnetic properties of 1 are very different from those reported for the resting oxidase. The ambiguity in the exact nature of the carboxylate bridge (i.e. one atom vs three atom) prevents us from commenting definitively on the potential relevance of complex 1 to the controversy surrounding the cytochrome c oxidase active site. Whatever the exact mode of binding in 1 is, it produces only a weak magnetic interaction.

(25) Strictly, shifts in potential reflect only relative differences in binding constants between the two oxidation states involved in the couple. Thus if there were significant differences in the binding constant of Fe^{II} for the various ligands, this would effect the argument presented.

(26) Chin, D.; LaMar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 4344.