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Synthesis of imidazolate bridged dinuclear Cu(II)–Fe(III) porphyrins

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Abstract

Reaction of octaethylporphyriniron(III) perchlorate, Fe(oep)ClO_4, or an iron capped porphyrin perchlorate, Fe(C_2cap)ClO_4, with a copper(II) imidazolate complex, CuIm, gives the imidazolate bridged dinuclear monoadducts, [Fe(oep)CuIm]ClO_4 or [Fe(C_2cap)CuIm]ClO_4, which are characterized by variable temperature magnetic susceptibility as spin coupled intermediate spin and admixed intermediate spin systems, respectively.

Introduction

The absence of facile synthetic routes to simple monoimidazole or monoimidazolate complexes of iron(III) porphyrins is a long standing problem [1] in the porphyrin and heme protein areas due to the propensity of iron(III) porphyrins to form the thermodynamically favored bisadduct in preference to a monoadduct [2]. The difficulty in producing monoadducts of iron(III) porphyrins has hindered efforts to prepare simple spin state analogs of horseradish peroxidase [3] and cytochrome *c′* [4], to evaluate the factors that govern spin state selection in heme proteins, and to produce dinuclear Cu(II)–Fe(III) porphyrin adducts, which are of interest as cytochrome *c* oxidase models [5]. Recent work in this lab has concentrated on synthetic pathways do dinuclear complexes of iron(III) porphyrins that rely on steric control of the axial ligation of iron(III) porphyrins [6].

This investigation focuses on routes to five-coordinate Cu(II)–Im–Fe(III) porphyrin complexes via the axial ligation of iron(III) octaethylporphyrin or an iron(III) ‘capped’ porphyrin with a copper imidazolate complex, CuIm (see Fig. 1)**. The copper chelate CuIm was used in similar reactions to prepare dinuclear complexes from Zn(tpp) [7], Co(tpp) [8], Mn(tpp) [9] and Cr(tpp)Cl [10]. As expected for the reaction of an iron porphyrin with an unhindered nitrogenous base, the reactions of CuIm with the iron porphyrins Fe(tpp) and Fe(tpp)$B_{11}CH_{12}$ produced only trinuclear complexes [11]. The present strategy for insuring formation of the monoadduct relies on blocking one of the porphyrin iron binding sites. This is accomplished in the case of Fe(oep)$^+$ by close stacking of the porphyrin planes and in the case of Fe(C_2cap)$^+$, by the presence of the covalently bound ‘capping’ benzene ring.

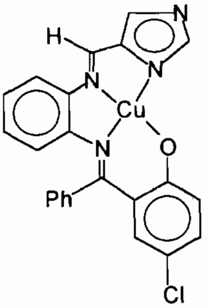

Fig. 1. Structure of copper imidazolate complex, CuIm.

Experimental

General

Visible spectra were obtained on a computer controlled Perkin-Elmer Lamda 4 UV–Vis spectrometer. IR spectra were obtained on a Perkin-Elmer model 1750 FT IR instrument. ESR spectra were recorded on polycrystalline samples at 80 K on a Varian E9 spectrometer. The magnetic susceptibilities were measured between 80 and 295 K on a computer controlled Faraday system as described previously [12]. The experimental data were fitted to the appropriate theoretical equations by a non-linear least-squares fitting program, GraFit, as described previously [13]. All reactions were done in a Vacuum Atmospheres dry box under an atmosphere of helium. Tetrahydrofuran was

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**Abbreviations used in this article: oep, tpp and C_2cap are the dianions of octaethylporphyrin, tetraphenylporphyrin and C_2capped porphyrin, respectively.

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distilled from sodium/benzophenone. The starting materials, $Fe(oep)ClO_4$ [14], $Fe(C_2cap)ClO_4$ [15] and CuIm [16], were prepared as described previously. The iron(III) porphyrins were recrystallized from chloroform. Elemental analysis was performed by MHW laboratories.

Synthesis of dinuclear complexes

The complexes $Fe(oep)(CuIm)ClO_4$ and $[Fe(C_2cap)(CuIm)]ClO_4$ were synthesized by the addition of an equivalent of CuIm to the iron porphyrin in THF and precipitated by the addition of heptane as described below for the preparation of $Fe(oep)(CuIm)ClO_4$. To a solution of $Fe(oep)ClO_4$ (0.100 g, 0.13 mmol) in THF (20 ml) was added a solution of CuIm (0.060 g, 0.13 mmol) in THF (10 ml). The resulting solution was filtered and 1 ml of heptane was added. The product precipitated within 2 h and was collected by filtration. *Anal.* Calc. for $[Fe(oep)(CuIm)]ClO_4 \cdot 2THF \cdot 1/2CHCl_3$: C, 59.48; H, 5.31; N, 8.74. Found: C, 59.98; H, 5.62; N, 8.41%. Calc. for $[Fe(C_2cap)(CuIm)]ClO_4 \cdot 2THF \cdot 1/2CHCl_3$: C, 60.24; H, 3.70; N, 6.28. Found: C, 59.96; H, 4.75; N, 5.99%.

Results and discussion

The use of the octaethylporphyrin ligand to induce monoligation to its Fe(III) complex was first illustrated by the formation of monoadducts of 2-methylimidazole and 3-chloropyridine with $Fe(oep)ClO_4$. Isolation of monoadducts in these reactions were attributed by Scheidt *et al.* to a face to face dimerization of the porphyrin rings as a result of favorable π–π overlap, which consequently blocks one axial binding site [17]. The use of the 'capped porphyrin' ligand to induce monoadduct formation has not previously been observed for its iron(III) complex. However, in the case of iron(II), the presence of the 'capping' benzene is sufficient to block one face of the porphyrin from approach by 1-methylimidazole; consequently, the reaction of $Fe(C_2cap)$ with 1-methylimidazole produced $Fe(C_2cap)$(1-methylimidazole) [18]. The formation of the dinuclear monoadducts of $Fe(oep)^+$ and $Fe(C_2cap)^+$ with CuIm in the present study are attributed to these same steric constraints inherent in the porphyrin ligands.

Reaction of the purple complexes $Fe(oep)ClO_4$ and $Fe(C_2cap)ClO_4$ with CuIm (1:1) in tetrahydrofuran in a dry box yielded brown solids which were formulated as the imidazolate bridged heterodinuclear complexes, $[Fe(oep)CuIm]ClO_4$ and $[Fe(C_2cap)CuIm]ClO_4$, respectively, by elemental analysis and spectroscopic data (see Fig. 2). A [CuIm]/[Fe(por)X] ratio of close to one is needed to avoid formation of $[Fe(oep)(CuIm)_2]ClO_4$ for the reaction of $Fe(oep)ClO_4$ with CuIm. Both dinuclear complexes are air stable as solids but decompose in solution to $[Fe(oep)]_2O$ and $Fe(C_2cap)OH$ or $[Fe(C_2cap)]_2O$ which were identified on the basis of their UV–Vis spectra. IR data for both complexes exhibit shifts in the perchlorate bands from their positions in the starting materials which are consistent with displacement of ClO_4^- by CuIm [19]. For $[Fe(C_2cap)CuIm]ClO_4$, a comparison of the UV–Vis spectra of the starting complex (404, 516) and product (412, 512) revealed a red shifted Soret and a blue shifted visible band on formation of the adduct, features that are attributable to the formation of monoimidazole adducts of iron(III) tetraphenylporphyrins [20]. Little change occurs in the UV–Vis spectrum of $Fe(oep)ClO_4$ upon formation of the monoadduct with either 2-methylimidazole or 3-chloropyridine [17]. Therefore it is not surprising that the UV–Vis spectrum of $[Fe(oep)CuIm]ClO_4$ (392, 534 nm) is also similar to that of $Fe(oep)ClO_4$.

In addition to the analysis and spectral data, magnetic characterization of the complexes is consistent with their formulations as Fe(III)–Cu(II) dinuclear species. The magnetic exchange pathway in these complexes consists of the d_{z^2} magnetic orbital of iron, the imidazolate π system and the $d_{x^2-y^2}$ orbital of copper. Orbital symmetry arguments [9, 11] predict that this pathway should promote antiferromagnetic exchange when the d_{z^2} orbital of iron is occupied (high spin, admixed intermediate spin, or intermediate spin) and ferromagnetic exchange when it is not (low spin). Following these arguments, antiferromagnetic exchange is predicted for the complexes prepared in this work since all examples of five-coordinate iron(III) porphyrin complexes characterized to date have been found to be high spin, intermediate spin, or admixed intermediate spin.

The values of the magnetic moment over the range 80–295 K for $[Fe(oep)CuIm]ClO_4$ (Fig. 3) suggest that the spin state of the iron in this complex is close to pure intermediate spin, $S=3/2$. As predicted and as observed for the isoelectronic high spin Mn(II) complex, Mn(tpp)CuIm [9], the interaction between Fe(III) and Cu(II) atoms in $[Fe(oep)CuIm]ClO_4$ is antiferromagnetic. The data were analyzed by the theoretical equation derived from the Heisenberg spin exchange Hamiltonian.

$$\hat{\mathcal{H}} = -2JS_{\mathrm{Fe(III)}}S_{\mathrm{Cu(II)}}$$

The solid line in Fig. 3 ($J=-20$ cm^{-1}, $g=2.00$, $N\alpha=150\times10^{-6}$ cm^3/mol) represents the best fit of the susceptibility data for this complex to the theoretical equation for the case of interacting $S=1/2$ and $S=3/2$ spins.

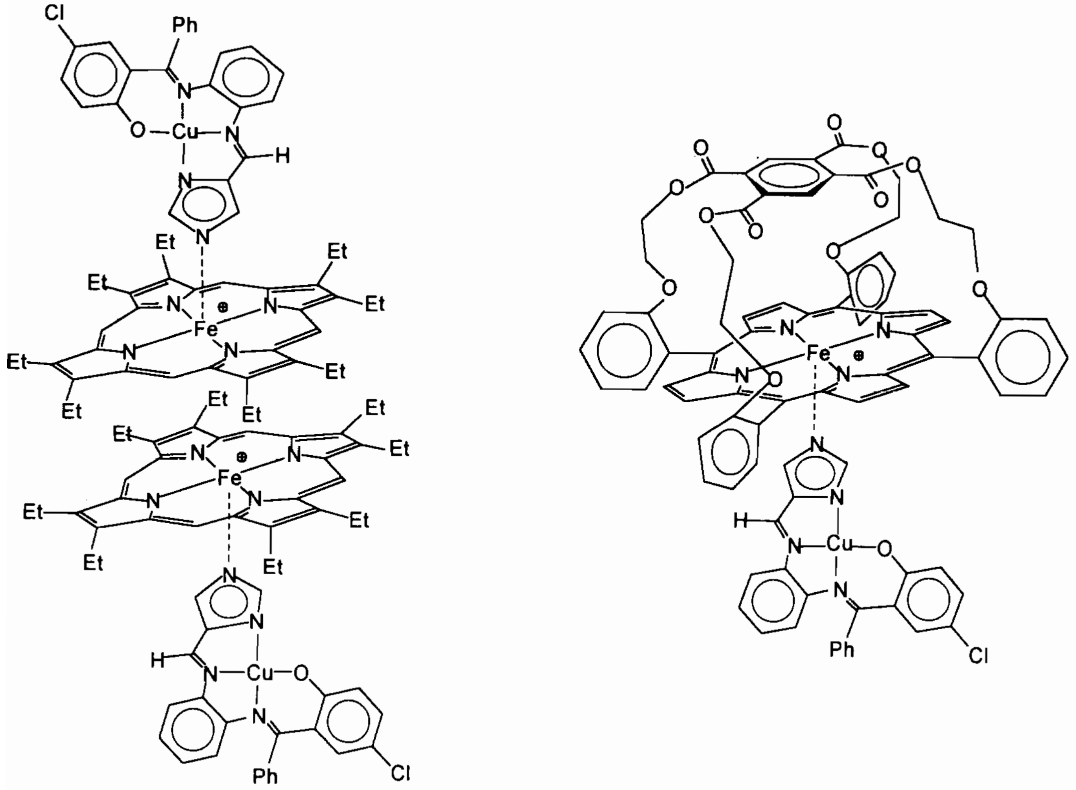

Fig. 2. Line drawings of adducts of CuIm with Feoep$^+$ and FeC$_2$cap$^+$.

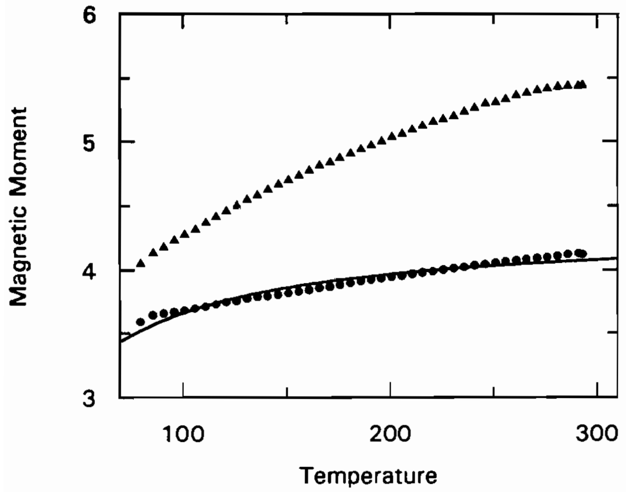

Fig. 3. Plot of magnetic moment vs. temperature for [Fe(oep)-CuIm]ClO$_4$ (●) and [Fe(C$_2$cap)CuIm]ClO$_4$ (▲).

$$\chi=\frac{Ng^2\beta^2}{kT}\,\frac{2+10\exp(4J/kT)}{3+5\exp(4J/kT)}+N\alpha$$

In the above equation, J is the coupling constant, g is the gyromagnetic ratio of the electron, N is Avogadro's number, β is the Bohr magneton, k is Boltzmann's constant and $N\alpha$ is the temperature independent paramagnetism. Magnetic exchange between the iron atoms of the π–π dimer was not taken into consideration in the present analysis as these interactions are known to be quite small ($-J\sim 1$ cm^{-1}) and are not important in this temperature region [17].

The starting complex Fe(oep)ClO$_4$ has been determined to be an admixed intermediate spin system while Fe(oep)Cl has been characterized as pure high spin [14]. Stabilization of the admixed state in Fe(oep)ClO$_4$ is attributed to extreme axial distortions caused by the weakly coordinating perchlorate anion. In the present study, replacement of the perchlorate anion by the bulky CuIm ligand appears to enhance these distortions and stabilize the ^{4}T as the ground state for the adduct, producing the pure intermediate spin state for iron in this complex.

The magnetic moment of [Fe(C$_2$cap)CuIm]ClO$_4$ varies from 4.1 BM at 80 K to 5.5 BM at 295 K (Fig. 3), which suggests an admixed intermediate spin state for the iron atom. The Fe(III)–Cu(II) interaction is antiferromagnetic as indicated by the increase in magnetic moment with increasing temperature. The data could not be fit to either the above equation for interacting $S=1/2$, $S=3/2$ spins or to the equation for interacting $S=1/2$, $S=5/2$ spins. However, the calculations place an upper limit on $-J$ of 50 cm^{-1}. Analysis of this system by a modified Maltempo model [21], as well as other magnetic investigations, are currently in progress.

For comparison with its CuIm adduct, ESR and variable temperature magnetic susceptibility data were also obtained for $Fe(C_2cap)ClO_4$. Unlike $Fe(tpp)ClO_4$, which is an admixed intermediate spin system, data collected in this work support a pure intermediate spin state assignment for $Fe(C_2cap)ClO_4$. Both the ESR (see Fig. 4), which exhibits a $g_\perp$ of 3.96 and a $g_\parallel$ of 1.94 at 77 K, and the average magnetic moment of 4.1 BM between 80 and 295 K support this spin state assignment [22]. Three structural factors that have been associated with the intermediate spin state in iron(III) porphyrins are found in $Fe(C_2cap)ClO_4$, a weakly bound axial ligand, a hindered approach to the iron atom and electron releasing substituents [23]. The data for this species are very similar to those for Fe(tpp)-$[C{=}C(p-ClC_6H_4)_2]Cl$ [24], $Fe(4\text{-}OCH_3tpp)ClO_4$ [25] and Fe(oetap)Cl [12], which have also been characterized as intermediate spin species. Complexation of $Fe(C_2cap)ClO_4$ by CuIm induces a change for the iron(III) atom from essentially pure intermediate spin to admixed intermediate spin. This spin state change could result from movement of the iron away from the porphyrin plane toward the more strongly donating imidazole nitrogen. This movement would be expected to lessen the interaction between the iron and the four strong field porphyrin nitrogen atoms which would in turn cause a lessening of the crystal field strength and result in a higher spin state for iron.

Magnetic interactions arising between intermediate spin and admixed intermediate spin Fe(III) and Cu(II) may have some relevance as biological models of the enzyme cytochrome *c* oxidase. The magnetic moment data for the enzyme have traditionally been interpreted as arising from a strong coupling ($-J > 200$ cm^{-1}) between a high spin cytochrome a_3^{3+} and $Cu_U(II)$ pair to give a $S = 2$ system. However, synthetic efforts to mimic such strong coupling have not proven successful. The present data suggest that intermediate or admixed intermediate spin iron(III) weakly coupled to copper(II) could produce a magnetic moment in the same range as that observed for the enzyme.

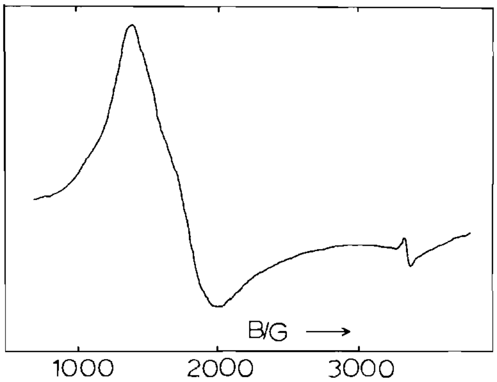

Fig. 4. ESR spectrum of $Fe(C_2cap)ClO_4$ in the solid state at 77 K.

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