Spin-state Change in Bis(2-methylimidazole)tetratolylmesoporphyrinatoiron(III) Induced by Ligand-mediated Interaction with a Copper(II) Complex

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Summary Interaction of the low-spin species bis(2-methylimidazole)tetratolylmesoporphyrinatoiron(III) [(TTP)Fe(2-MeIm)$_2$] with Cu(acac)$_2$ (Hacac = acetylacetone) in chloroform leads to the high-spin species (TTP)Fe–2-MeIm–Cu(acac)$_2$; spectral evidence indicates that magnetic interaction between the Cu^{II} and the Fe^{III} is weak.

THE dioxygen-binding active centre in cytochrome c oxidase is believed to involve Fe^{III} in the high-spin state.[1] A model for the site has recently been suggested in which a porphyrinatoiron(III) species bonds *via* an imidazolate bridge to a copper(II) ion.[2] The presence of haem–haem interactions[3] and Cu^{II}–Fe^{III} couples ($S = 2$ or 3)[4] have also been suggested. The presence of an imidazolate bridge implies that the Cu^{II} induces a spin-state change at the Fe^{III} since haemichromes and analogous compounds (with imidazole-type ligands, at least) are known to be low-spin.[5] Construction of low molecular weight model complexes is not easy because of the difficulty in isolating the porphyrinatoiron(III) imidazolate precursors.[6] Despite this problem, we report that evidence for a spin-state change in solution is forthcoming from the interaction between a Cu^{II} complex and [(TTP)Fe(2-MeIm)$_2$]$^+$ (TTP = tetratolylporphyrin, 2-MeIm = 2-methylimidazole).

Addition of an excess of 2-MeIm to (TTP)FeCl in chloroform gives a low-spin (TTP)Fe(2-MeIm)$_2^+$ species having characteristic electronic absorption bands at 7 500 and 9 000 cm^{-1} (ϵ *ca.* 200 mol^{-1} dm^3 cm^{-1}), not present in high-spin derivatives.[7] Spectrophotometric titration of this solution with Cu(acac)$_2$ (Hacac = acetylacetone) in chloroform leads to formation of a 1:1 complex with virtually complete disappearance of the near-i.r. bands (Figure 1).† The

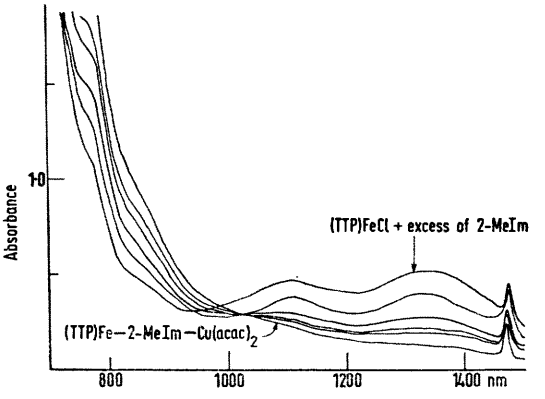


FIGURE 1. Electronic absorption spectra in the near-i.r. region. Effect of adding Cu(acac)$_2$ to a $2{\cdot}76 \times 10^{-3}$ mol dm^{-3} solution of (TTP)FeCl + excess 2-MeIm in chloroform (at room temp.) to a final Cu^{2+}–Fe^{3+} mole ratio 1:1.

e.s.r. spectrum of a 1:2:1 (TTP)FeCl–2-MeIm–Cu(acac)$_2$ chloroform glass at 90 K shows that there are significant changes compared to that of Cu(acac)$_2$ + 2-MeIm alone (ratios 1:1 to 1:100) (Figure 2). At 10 K the same solution gave an e.s.r. signal characteristic of high-spin Fe^{III}, as well as that of the modified Cu^{II} signal.[8]‡

† The many cases of addition of imidazole and substituted imidazoles reported in ref. 5 indicates that the appearance of near-i.r. bands in porphyrinatoiron(III) complexes is a valid means of identifying low-spin Fe^{III} species. It is still not clear whether these are *d–d* or charge-transfer in origin (*e.g.*, see P. O' D. Offenhartz, *J. Chem. Phys.*, 1965, **42**, 3566). The presence of the less-common Fe^{III} $S = 3/2$ spin state after addition of Cu(acac)$_2$ may be excluded since this would be expected to give rise to weak *d–d* bands ($\epsilon \leqslant 20$ mol^{-1} dm^3 cm^{-1}) between 5 000 and 8 500 cm^{-1}.

‡ The $g_{\parallel} = 2{\cdot}00$ component of the Fe^{III} signal is lost under the Cu^{II} signal. A further, very weak signal present, with $g_1 = 4{\cdot}33$, $g_2 = 3{\cdot}58$, and $g_3 = 2{\cdot}84$, is presumably due to traces of the low-spin [(TTP)Fe(2-MeIM)$_2$]Cl complex.

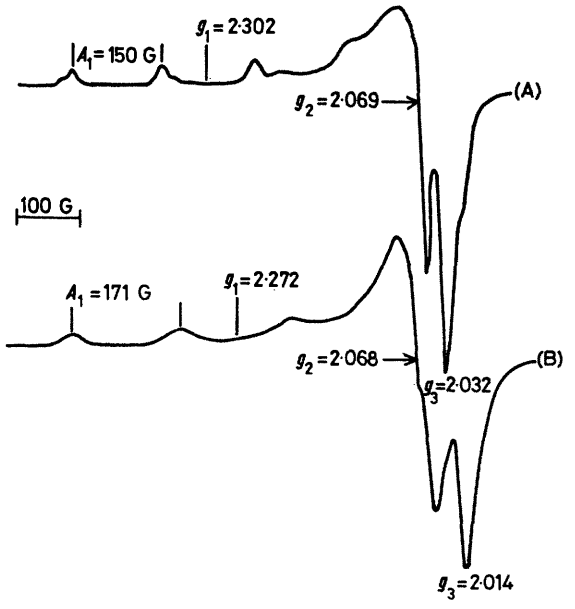
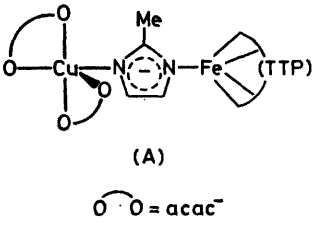


FIGURE 2. E.s.r. spectra ($CHCl_3$, 90 K): (A) $Cu(acac)_2$–2-MeIm (1:1); the spectra of solutions up to ratio 1:100 were virtually identical, except for the intensity of the second signal, due to traces of $Cu(acac)_2$. (B) (TTP)FeCl–2-MeIm–$Cu(acac)_2$; the much higher rhombic character of the signal in (B) and the rather broad A_1 components suggest that an oxygen atom of the $Cu(acac)_2$ lies out of the $Cu(acac)_2$ plane. This often occurs with base adducts of Cu^{II} chelates.

Confirmation that these spectral changes can be due only to further bonding of the 2-MeIm to the $Cu(acac)_2$ comes from the spectra of solutions identical in all respects to those mentioned, but containing 1-methylimidazole (1-MeIm). Addition of a stoicheiometric amount of $Cu(acac)_2$ to (TTP)FeCl + excess of 1-MeIm (*ca.* 25 times, sufficient for all the Fe^{III} to be present as the bis-1-MeIm adduct[5]) left the near-i.r. bands characteristic of low-spin Fe^{III} virtually unchanged in both intensity and wavelength. The e.s.r. spectrum of 1:2:1 (TTP)FeCl–1-MeIm–$Cu(acac)_2$ ($CHCl_3$ glass, 90 K) in the Cu^{II} region was identical to that of the same solution but free of (TTP)FeCl.



(A)

O O = acac⁻

All attempts to separate crystals from the 2-MeIm system have led to precipitation of [(TTP)Fe(2-MeIm)$_2$] Cl contaminated with (presumably) $Cu(acac)_2$(2-MeIm); consequently, a full analysis is not possible. Nevertheless, the spectroscopic results provide convincing evidence that species such as (**A**) are present in chloroform (addition of an organic proton sponge led to no significant changes in the spectra).

The observation of separate e.s.r. signals for the Cu^{II} and Fe^{III} species and the absence of any indication of antiferromagnetically coupled Cu^{II} and Fe^{III} suggests that an imidazolate-bridged Fe^{III}–Cu^{II} unit cannot give rise to the strongly coupled Cu^{II}–Fe^{III} believed to be present in the cyt-a_3-Cu^{II} sub-unit in cytochrome c oxidase.

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