Can μ-Imidazolate Mediate Strong Antiferromagnetic Coupling?

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A re-examination of antiferromagnetic coupling *via* imidazolate bridging ligands in manganese(II) tetraphenylporphyrin complexes suggests that previous reports of strong antiferromagnetic coupling in Mn$^{\mathrm{II}}$(imidazolate)Cu$^{\mathrm{II}}$ systems may be in error.

The importance of magnetic coupling in multimetal proteins has stimulated much interest in exploring the ability of bridging imidazolate ligands to mediate antiferromagnetic coupling in M(imidazolate)M′ systems. The conclusion reached in the majority of recent studies is that imidazolate, whether free or part of a chelating ligand, is a weak to moderate mediator of antiferromagnetic coupling ($|-J| < 90$ cm^{-1}).[1—9] Since all systems involving metalloporphyrins[2] had shown weak or non-detectable coupling, the report[10] of strong antiferromagnetic coupling ($|-J| > 200$ cm^{-1}) in a (tpp)-Mn$^{\mathrm{II}}$(imidazolate)Cu$^{\mathrm{II}}$ system (tpp = tetraphenylporphyrin) came as a surprising exception to a growing consensus. Our development of a new, closely related system which displays only very weak coupling ($-J = 6$ cm^{-1}) suggests a re-evaluation of this apparent exception.

Figure 1 illustrates the new Mn$^{\mathrm{II}}$(imidazolate)Cu$^{\mathrm{II}}$ system we have developed. The competence of the copper(II) chelate, Cuimid to act as an imidazole-like axial ligand to a metalloporphyrin has previously been demonstrated spectroscopically[11,12] and more recently crystallographically.[13] When Cuimid is added anaerobically to a toluene solution of Mn(tpp) the familiar bright green colour of a five-co-ordinate manganese(II) porphyrin[14] is observed [$\lambda_{\max}$ 417, 442(Soret), 535, 576, 617, 652 nm]. The formation of a simple imidazole-like adduct is evidenced not only by the extremely close spectral similarity to Mn(tpp)(1-Meimid) [$\lambda_{\max}$ 417, 442(Soret), 534, 576, 615, 652 in toluene] but also by its behaviour upon exposure to air. The gradual appearance of an intense 475 nm absorption, diagnostic of Mn$^{\mathrm{III}}$ tetraphenylporphyrin derivatives,[15] parallels the behaviour of Mn(tpp)(1-Meimid) in air and rules out an internal redox formulation such as Mn$^{\mathrm{I-II}}$(tpp)(Cu$^{\mathrm{I}}$imid). Of great importance for comparative magnetic work is the capability of replacing the paramagnetic Cu$^{\mathrm{II}}$ in Cuimid with an isostructural, diamagnetic 'control' metal. Ni$^{\mathrm{II}}$ provides this and Mn(tpp)(Niimid) can be prepared and isolated in analogous fashion to the Cu$^{\mathrm{II}}$ system. The spectral characteristics are essentially identical to the Cu analogue [$\lambda_{\max}$ 417, 440(Soret), 535, 575, 616, 652 nm in toluene] and the two crystalline materials differ only in the number of toluene solvate molecules.†

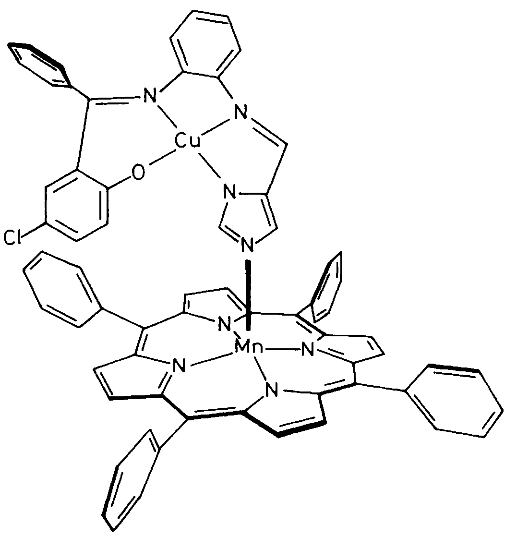

Figure 1. Schematic representation of Mn(tpp)(Cuimid) where Cuimid is the copper(II) Schiff base chelate derived from sequential condensation of 5-chloro-2-hydroxybenzophenone, 1,2-diaminobenzene and imidazole-4-carbaldehyde.[11]

The anaerobically acquired magnetic data for the control system, Mn(tpp)(Niimid)·3 toluene, are shown in Figure 2(a). The nearly temperature independent magnetic moment of 5.8 ± 0.1 μ_B from 300 to 20 K is typical of an $S = 5/2$ system (spin only $\mu = 5.9$ μ_B) and indeed, the data essentially overlay those of Mn(tpp)(1-Meimid).‡ The magnetic data for Mn(tpp)(Cuimid)·toluene are shown in Figure 2(b). The depression of the room temperature moment (5.84 μ_B) below the spin only value (6.13 μ_B) hints at an antiferromagnetic Mn$^{\mathrm{II}}$/Cu$^{\mathrm{II}}$ interaction but compelling evidence comes from the rapid fall-off of magnetic moment with decreasing temperature. The data have been fit to a standard isotropic spin Hamiltonian of the form $H = -2JS_{5/2}\,S_{1/2}$ [solid line, Figure 2(b)] to yield J −6.0 cm^{-1}. The uncertainty in this value of the coupling constant is not more than a few percent and classifies the complex as weakly coupled, not unlike a Mn$^{\mathrm{II}}$(imidazolate)-Co$^{\mathrm{II}}$ porphyrin system investigated earlier (J −5 cm^{-1}).[2]

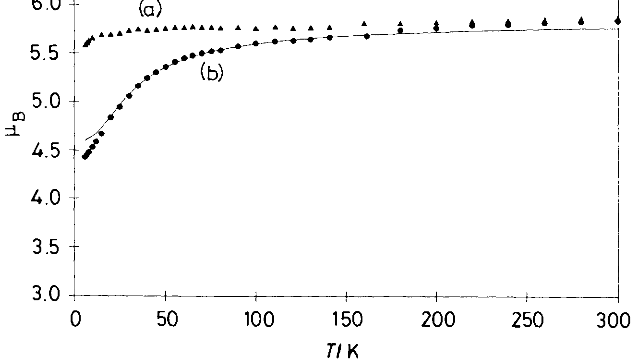

Figure 2. Magnetic moment *vs.* temperature plots for (a) Mn(tpp)(Niimid)·3toluene and (b) Mn(tpp)(Cuimid)·toluene. The solid curve is a theoretical fit with J −6.0 cm^{-1} and $g = 1.90$. Diminishing μ_{eff} at very low temperatures could arise from zero field splitting and/or lattice antiferromagnetic coupling effects. These effects were not treated quantitatively because they are inconsequential when determining the desired intramolecular J.

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† Satisfactory elemental analyses for C, H, N, Mn, Cu, and Ni were obtained and supplied to referees.

‡ Sample prepared according to ref. 14 and run 6-300 K on the same instrumentation, SHE 905 SQUID Susceptometer.

The present result raises the question of whether studies with a different copper imidazolate system could be radically different. The answer is probably no because the orientation of the magnetic orbitals is optimal for maximizing an interaction through the σ-bonding system of the imidazolate bridge and possible bond angle dependence is not expected to be dramatic.[1,3,8,9] The tetragonal stereochemistry at copper places its unpaired electron in a $\sigma^*_{\text{Cu-imid}}$ orbital (*i.e.* $d_{x^2-y^2}$) and there is no evidence that other exchange mechanisms can be nearly as effective as a σ/σ pathway.[1,2] A closer scrutiny of the data of Chunplang and Wilson who report strong antiferromagnetic coupling ($|-J| \geqslant 200$ cm^{-1}) in $\{$Mn(tpp)[Cu(imid)(Himid)dap]$\}$BF$_4$[10] (dap = diacetylpyridine) reveal a number of problems with the formulation and integrity of this complex. Most importantly, the recorded spectrum[16] is indicative of Mn^{III} not Mn^{II}, particularly with respect to the distinctive intensities and splitting of the Soret absorptions at ~380 and 475 nm§ in Mn^{III} tetraphenylporphyrin derivatives.[15] This suggests the possibility of oxidation by the copper(II) complex and/or aerobic oxidation during the lengthy reaction and work-up. Secondly, the temperature dependence of the magnetic moment of the analogous Zn(II) 'control' is not typical of Mn^{II}. The reported decrease from 5.84 μ_B at 300 K to 5.09 μ_B at 20 K is much greater than expected [*cf.* Figure 2(a)]. Thirdly, under strictly anaerobic conditions (glovebox, $O_2 < 1$ p.p.m.) we are unable to find any evidence for the simple ligation of Mn(tpp) by [Cu(Himid)$_2$dap][BF$_4$]$_2$. The visible spectrum of Mn(tpp) with excess of the zinc complex [Zn(Himid)$_2$dap][BF$_4$]$_2$ and excess Proton Sponge in acetonitrile does suggest ligation [λ_{max} 429, 442(Soret), 535, 576, 617 nm] but the same experiment with the copper analogue, [Cu(Himid)$_2$dap][BF$_4$]$_2$ gives the distinctive 475 Soret maximum of Mn^{III} regardless of how quickly or anaerobically the experiment is done. Similar observations are made with Fe(tpp); the zinc complex shows some evidence of binding but the copper complex oxidizes Fe(tpp) to a [Fe^{III}(tpp)(imid)$_2$]$^+$ type species [λ_{max} 420(Soret), 553 nm]. Apparently, [Cu^{II}(Himid)$_2$dap][BF$_4$]$_2$ can be readily reduced in basic solution.

In conclusion, of the three reports[10,17,18] of strong antiferromagnetic coupling *via* bridging imidazolate, one[17] has recently been reinterpreted[5] and the present work raises questions about the second[10] and presumably the third.[18] The competence of [Cu^{II}(Himid)$_2$dap]$^{2+}$ to act as an imidazole-like ligand to metalloporphyrins and to mediate strong magnetic coupling remains to be definitively established.

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§ Some of the λ_{max} quoted in ref. 10 differ by some 20 nm from those apparent in the spectra reproduced in ref. 16.