The Transmission of Electronic Effects in Paramagnetic Metal Complexes: the Proton Magnetic Resonance Spectra of Bis-pyridinoiron(III) Protoporphyrin IX Complexes

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Summary There is a linear relationship between the paramagnetic chemical shifts of the protons of the peripheral methyl groups in low-spin bis-pyridinoiron(III) protoporphyrin IX complexes and the basicity of the co-ordinated pyridine.

THE n.m.r. spectra of paramagnetic complexes have been[1] most helpful in the investigation of the electronic and molecular structures of transition-metal complexes. Recently Caughey and Johnson have shown[2] that the ^{1}H n.m.r. spectra of deuterohemins are dependent on the axial ligand, the latter affecting the "interaction between the porphyrin nitrogens and the iron." We have observed[3] that bis-pyridinoiron(III) protoporphyrin IX complexes are in an equilibrium between two spin-states; a ground-state doublet and an excited-state sextet. At low temperatures *ca.* 200°K, all the complexes are in the low-spin forms, the ^{1}H n.m.r. spectra consist of sharp lines, and the chemical shifts of all protons, especially those of the peripheral methyl groups, (a in Figure 1) are dependent on the axial ligands. This dependence allows us to comment on "interaction between the porphyrin nitrogens and the iron".[2] The paramagnetic shift (*i.e.* the observed chemical shift relative to that in diamagnetic complexes) to low-field for the peripheral methyl groups (a) and to high-field for the *meso*-hydrogens (e) suggests that the origin of the shifts lies in the contact term, with positive spin-density present on the relevant adjacent carbons, as suggested[4] for the low-spin complex cyanohemes. Figure 2 shows that as the ligand basicity increases, the paramagnetic shift of the peripheral methyl hydrogens decreases. (The four methyl groups are not equivalent though two, those which have the largest low-field shift, are nearly so.) The effect on the *meso*-hydrogens is much smaller and has the opposite dependence. The increasing shift of the methyl hydrogens with decreasing basicity, and presumably decreasing electron density on the iron, suggests that the main mechanism for spin delocalisation can be described in terms of charge-transfer from a ligand π-orbital to the iron, becoming less important as the electron-density on the iron increases. Why are the shifts of the *meso*-hydrogens less dependent on the axial ligand? As Eaton and La Lancette have pointed out,[5] if spin-density is present in the ligand nitrogen π-orbital it is impossible to write resonance forms which place spin-density on the carbons adjacent to the *meso*-hydrogens. The spin-density must therefore be transferred

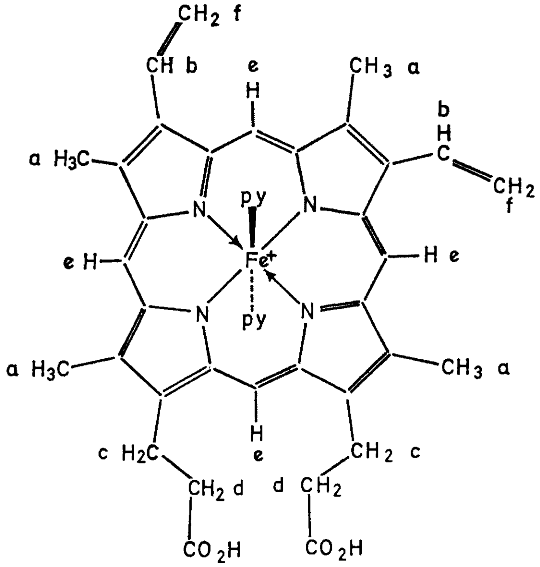

FIGURE 1. *Structural formula of bis-pyridinoiron*(III) *protoporphyrin* IX *complex cations.*

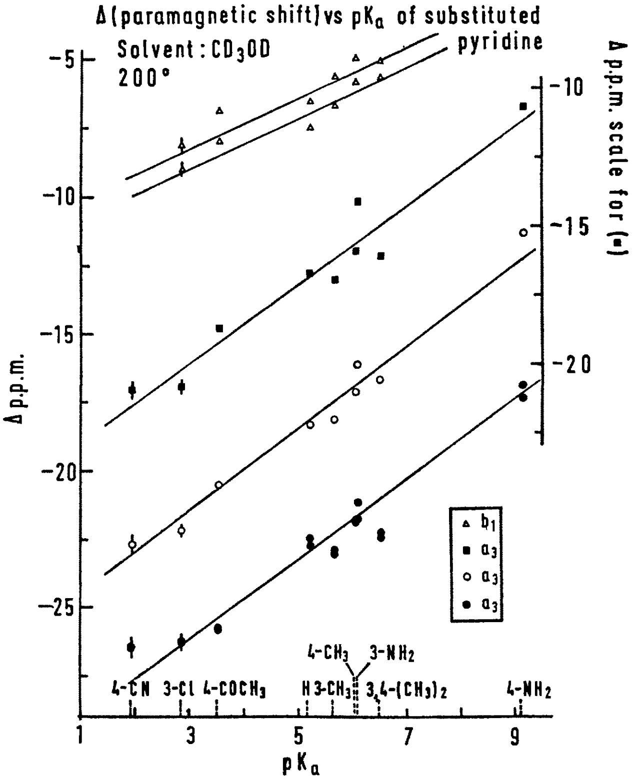

FIGURE 2. Δ(*Paramagnetic shift*) *of the low-field resonances of iron*(III) *photoporphyrin* IX *chloride in* CD_3OD *in the presence of a large excess of substituted pyridines plotted against the* pK$_a$ *of the substituted pyridine* (*measured at* 60 MHz, 200°K). (*Subscripts indicate the number of protons*).

through the σ-orbitals or π-orbitals other than the highest filled.

Using the McConnell formula,[6] $A_{\mathrm{Me}} = Q_{\mathrm{Me}}\rho_{\mathrm{C}}^{\pi}$, with $Q_{\mathrm{Me}} = 2{\cdot}7 \times 10^{7}$ Hz, ρ_{C}^{π}, the spin density on the adjacent carbon as % of one unpaired electron increases from *ca.* 1·5 for the 4-amino pyridine to *ca.* 2·4 for the 4-cyano-derivative for the methyl group which gives rise to the largest low-field shift. The work suggests that, at least in a limited series of complexes, the basicity of a nitrogenous ligand may serve as a useful indication of the changes in electron density on a metal ion with which it is complexed.

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