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Spin Conversion in Manganese(II) Porphyrin Systems

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Four- and five-coordinate manganese(II) porphyrin complexes, Mn(porp) and Mn(porp)L (where porp = the dianion of 5,10,15,20-tetraphenylporphyrin (TPP) and 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) and L = a neutral or anionic, axial ligand) are high spin ($\mu_{eff} = 5.9–6.3\ \mu_B$), with the metal being out of the porphyrin plane [1–4]. In-plane geometry and formation of six-coordinate species have been predicted to require a change to intermediate or low spin [5, 6], and the existence of any such species to date, ignoring low-spin Mn(TPP)(NO)L species [7] where oxidation state formalism is problematic, has been seriously questioned [3], including the reported isolation of $Mn(TPP)py_2$ (py = pyridine) the magnetic moment of which (6.02 μ_B) corresponds to a high-spin d^5 complex [8]. We followed the literature procedure for synthesis of this complex [8] and isolated only Mn(TPP)py [3].

Attempts to force six-coordination within TPP or OEP systems have been unsuccessful [6], and we find also that, even with a strong base such as piperidine ($pK_a = 11.3$ [9]), solution spectrophotometry (see below) shows formation of only Mn(porp)pip species at up to 10 M piperidine (neat ligand). We report here data for the toluene solution equilibria of equation (1) involving an octamethyltetrabenzoporphyrin system (Fig. 1), and demonstrate the required spin conversion during formation of $Mn(OMBP)pip_2$ from Mn(OMBP)pip in the L = pip system.

$$\underset{\mathbf{1}}{\mathrm{Mn(OMBP)}} \underset{}{\overset{+\mathrm{L},K_1}{\rightleftharpoons}} \underset{\mathbf{2}}{\mathrm{Mn(OMBP)L}} \overset{+\mathrm{L},K_2}{\rightleftharpoons} \underset{\mathbf{3}}{\mathrm{Mn(OMBP)L_2}} \qquad (1)$$

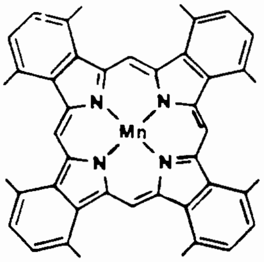

Fig. 1. Structural diagram of Mn(OMBP).

Complex **1**, synthesized by a standard procedure [10] has a magnetic moment in the solid state ($\mu_{corr} = 5.1\ \mu_B$ at 25 °C), which is somewhat low for a purely high-spin $S = 5/2$ state; this may result from stacking in the solid state [11], or possibly an admixed $S = 5/2$, $3/2$ state [12, 13]. Of note, the metal-in-plane phthalocyanine complex MnPc exists as an $S = 3/2$ intermediate spin state with $\mu_{eff} = 4.33\ \mu_B$ at 20 °C [14]; OMBP shows resemblances to Pc [15], and a more in-plane structure compared to Mn(TPP) and Mn(OEP) could make the $d_{x^2-y^2}$ level somewhat less accessible and give rise to the admixed state [13]. Ligand binding to **1** in toluene was readily studied by UV–Vis spectroscopy, and K_1 and K_2 determined by standard methods using the Hill equation [2, 15] (see Fig. 2)

$$\log Y/(1 - Y) = n \log[\mathrm{L}] + \log K \qquad (2)$$

where $Y = (A_0 - A)/(A - A_\infty)$, and A, A_0 and A_∞ are the absorbances at a specific [L], at [L] = 0, and for a limiting spectrum of fully formed five- or six-coordinate species, respectively.

Complex **1** in toluene obeys Beer's Law up to a concentration of $\approx 10^{-5}$ M, where a monomer is assumed to be present [3]; non-linearity in the absorbance versus concentration plot at higher concentrations almost certainly reflects aggregation phenomena [11, 16]. Pyridines, imidazoles and O-donors form only Mn(OMBP)L species, as with Mn(TPP) and Mn(OEP), but addition of piperidine to Mn(OMBP) gives 'two sets' of spectrophotometric titration data; the K_1 and K_2 values are sufficiently separated to allow for their determination using non-overlapping titrations. Figure 2 shows the spectra of **1**, fully formed **2** and close to fully formed **3** (L = pip); intermediate spectra are obtained by varying [pip]. The Hill plots for both stages yield lines of slope (n) 1.0 ± 0.1 (Fig. 2) and the K values given in Table 1. In neat *N,N'*-dimethylacetamide (DMA) solution, the manganese is present as Mn(OMBP)DMA (Table 1), and there is no evidence of aggregation at 10^{-3} M.

The five-coordinate complexes (L = py, pip, DMA) are readily isolated from toluene solutions,

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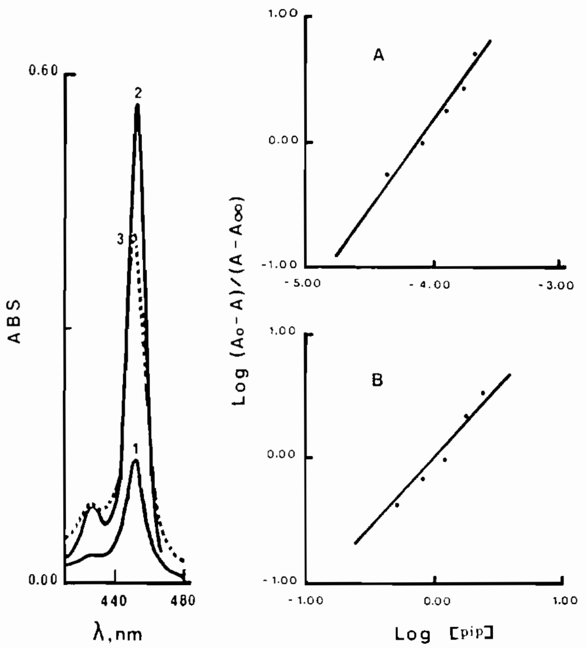

Fig. 2. UV–Vis spectrophotometric titration data for addition of piperidine to ~10^{-5} M Mn(OMBP) (**1**) in toluene; Mn(OMBP)pip (**2**) measured at [pip] = 10^{-2} M; spectrum (3) approximates to that of Mn(OMBP)pip_2 (**3**) and is measured at [pip] ~ 7 M (toluene/piperidine, 3:7 vol./vol.). Intermediate spectra at intermediate piperidine concentrations lead to the Hill plots shown at the right for absorbance data at 453 nm: (A) 1 + pip $\rightleftharpoons$ 2; (B) 2 + pip $\rightleftharpoons$ 3). Addition of py and DMA to 1 shows formation of only Mn(OMBP)L (L = py, DMA); spectral changes are similar to those shown for 1 → 2 but slight blue shifts are evident in the Soret maximum region.

TABLE 1. Data for axial ligand (L) binding to some four-coordinate metalloporphyrins[a]

Metalloporphyrin	L	log K_1	log K_2
Mn(OMBP)	pip	4.1	0.02
	py	2.6	< -2.0[b]
	DMA	1.8	< -2.0[b]
Zn(OMBP)[c]	py	5.6	
Zn(TPP)[c]	py	3.8	
Co(OMBP)	pip	4.9	0.8
Co(PpDME)[d]	pip	3.8	−0.7
Co(OEP)[e]	pip	3.3	
Co(OMBP)	py	4.3	0.4
Co(PpDME)[d]	py	3.8	
Co(OEP)[e]	py	2.9	

[a] In toluene at 25 °C; data for Mn(OMBP) and Co(OMBP) [10] from the present work; error in log K_1 is ±0.2, and in log K_2 is ±0.05. [b] No detection of Mn(OMBP)L_2 in neat L. [c] From ref. 17. [d] From ref. 18. [e] From ref. 19.

and have magnetic moments in the range 5.0–5.5 μ_B that are largely independent of temperature from 109–308 K; solutions of these species (maintained by addition of L at an appropriate concentration) gave essentially the same moments when measured by the Evan's method [20]; these values, like that for **1**, are somewhat below the high-spin values and could again result from an admixed $S = 5/2$, 3/2 state. Even a neat pyridine solution of **1** contains only species **2** (L = py), as monitored by UV–Vis, and has a moment of 5.2 μ_B. With piperidine, however, at higher [pip], the moment measured in toluene solution decreases as more Mn(OMBP)pip_2 is formed, and in neat piperidine when the Mn(OMBP)pip_2:Mn(OMBP)pip ratio ≈10:1 the moment is ≈3.3 μ_B, reasonably consistent with conversion in the bis(piperidine) species to the intermediate $S = 3/2$ state. Unfortunately, work-up procedures from such solutions thus far have led to isolation of only the five-coordinate complex, due to either a decrease in [L] or a lower solubility of **2** within the equilibria outlined in eqn. (1).

The OMBP ligand provides an extremely weak σ-donor field (much weaker than OEP and TPP) as evidenced by Mössbauer data [21], and this leads in general to stronger axial ligand binding at a metalloporphyrin centre [17, 19]. This is exemplified for OMBP by data for some Zn(II) and Co(II) systems (Table 1), noting that the σ-donor basicity trend is OEP > PpDME (the dimethyl ester of protoporphyrin IX) > TPP > OMBP [17–19, 21]. The K_1 and K_2 data were again obtained from spectrophotometric titrations that gave excellent Hill plots. The expected trend of increased axial ligand bonding with axial ligand basicity within a given metalloporphyrin [19] is also evident. The d^7 Co(II) systems are known to be low spin in both five- and six-coordinate species [22]. Spin conversion in d^5 systems has been discussed in detail for Fe(III) porphyrin systems, where considerable structural as well as magnetic data are available, and it is clear that the spin state and stereochemistry are controlled in the expected way by the field strength and number of axial ligands, which determine the relative energies of the d_{z^2} and $d_{x^2-y^2}$ levels [12, 13]. The $S = 3/2$ ground state is invariably considered to result from the d-orbital population $(d_{xy})^2(d_{xz}, d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^0$ [13]. We believe that in Mn(OMBP)pip_2, the d_{z^2} level lies above that of $d_{x^2-y^2}$. This best rationalizes the magnetic data for the various Mn(II) porphyrin systems, especially the fact that the spin conversion is noted only with the most basic axial ligand (raises d_{z^2}) and the weakest σ-donor (lowers $d_{x^2-y^2}$) and strongest π-donor porphyrin [15, 21]. Such an unusual inversion of energy levels also holds for Fe(OMBP)$(CO)_2$, but not for Fe(TPP)$(CO)_2$ or FePc$(CO)_2$ [21], and implies distorted octahedral structures for both Mn(OMBP)pip_2 and Fe(OMBP)$(CO)_2$ containing shorter axial than equatorial bonds. Attempts to elucidate d-orbital population by detailed ESR studies are in progress on both the Mn(OMBP)pip_2 species and the five-coordinate complexes Mn(OMBP)L (L = pip, py) which show frozen solution spectra at 77 K atypical of the other, purely high-spin Mn(porp)L species [3].

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