Formation Constants of Some Pyridine–Metalloporphyrins

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MANY metalloporphyrins in nonaqueous solution form 1 : 1 or 2 : 1 pyridine complexes.[1] The stoicheiometry and formation constants of the reaction can be obtained from changes in the metalloporphyrins' characteristic absorption spectra upon complexation.[1,2] These parameters are reported for several porphyrins containing various transition-metal ions at 25° in chloroform solutions. All titrations showed isosbestic points, and constants calculated at different wavelengths agreed within 15%.

The basicity towards protons of the metal-free porphyrins studied follows the order mesoporphyrin > hæmatoporphyrin > mesotetrapyridylporphine.[3] Formation constants for the monopyridine-zinc(II), -copper(II), and dipyridine-nickel(II) porphyrins increased as the porphyrins basicity decreased. This trend was also observed in aqueous solution for dipyridineiron(II) porphyrins.[4] The rationalization was that electron-withdrawing groups on the porphyrin decrease the electron density at the central nitrogen atoms making the metal atom more electropositive and attractive to extra-planar donor ligands.

TABLE

Formation constants of some pyridine–metalloporphyrins

	log $K_{formation}$[a]		
Metal	Tetrapyridylporphine[b]	Haematoporphyrin[b]	Mesoporphyrin[b]
Zn^{II}	3·76	2·97[c]	2·47
Cu^{II}	−1·1	−2·1[c]	—
Ni^{II}	2·7	1·5[c]	—
$Co^{III}Cl$	—	3·9	—
$Fe^{III}Cl$	0·7	0·9	—
$Mn^{III}Cl$	0·40	0·34	0·54
VO^{II}	−0·92	−1·0[c]	—

[a] All units L/M except Ni^{II} entries of $(L/M)^2$; [b] All compounds gave satisfactory analytical data; [c] Dimethyl ester derivatives. All others non-esterified.

However, the formation constants for the mono-pyridine-VO^{II}, -$Mn^{III}Cl$, and -$Fe^{III}Cl$ complexes are relatively independent of the porphyrins basicity. This effect could be due to these particular metal ions lying significantly above and not in the plane of the four central nitrogen atoms, thereby being less affected by the porphyrins, inductive behaviour. The crystal structures of several metalloporphyrins show that Cu^{II}, Ni^{II}, and Zn^{II} ions lie in the mean porphyrin plane,[5,6] whereas Fe^{III} is more than 0·3 Å above the central nitrogen atoms. It has been speculated that low-spin Fe^{II} lies in the plane.[6] Theoretical calculations place VO^{II} above the plane.[7] Also, Mössbauer parameters for high-spin Fe^{III} porphyrins are rather independent of porphyrin basicity while the dipyridine-Fe^{II} low-spin parameters depend strongly on the particular porphyrin.[8]

In combination with Miller and Dorough's data, the affinity of pyridine for metal ions in porphyrins follows the order $Co^{III}Cl > Zn^{II} > Cd^{II} > Mg^{II} > Hg^{II}$, $Fe^{III}Cl$, $Mn^{III}Cl > VO^{II} > Cu^{II}$. With the exception of $Co^{III}Cl$, which could involve strong π-bonding, the affinity for pyridine roughly parallels the ease of displacement of the metal ion from the porphyrin by acidic reagents.[9]

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