Low-spin, Five-co-ordinate, π-Acid Complexes of Iron(II) Porphyrins

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Summary The ligands, benzyl isocyanide, tri-n-butylphosphine, and triethyl phosphite form five-co-ordinate adducts with Fe^{II}(Cap),† which are shown to be low-spin ($S = 0$).

The effects of the binding of axial ligands such as carbon monoxide, phosphines, phosphites, and isocyanides to iron(II) porphyrins are of particular interest in the examination of the electronic state of iron. Sterically hindered bases, *e.g.*, 2-MeIm,† form five-co-ordinate iron(II) porphyrins such as Fe^{II}(Por)(2-MeIm),† which have been fully characterized[2] and shown to be high spin ($S = 2$). However, the five-co-ordinate diatomic molecule adducts of Fe^{II} porphyrins lead to low-spin ($S = 0$) iron(II) complexes. Currently the known examples of low-spin five-co-ordinate iron(II) porphyrins are Fe(TPP)(NO)†[3,4] ($S = \frac{1}{2}$) and Fe(TPP)(CO),[5] ($S = 0$). We have expanded the list to include five-co-ordinate Fe^{II}(Cap) complexes of tri-n-butylphosphine, triethyl phosphite, and benzyl isocyanide ligands. The complex Fe^{II}(Cap), first prepared by Baldwin[1] and coworkers, is uniquely suited for five-co-ordination, since it allows only the addition of one large axial base in the position outside the cap. Spectrophotometric titration[6] (Figure) of Fe(Cap) with base shows that the benzyl isocyanide, tri-n-butylphosphine, and triethyl phosphite ligands form monomeric, 1:1 base adducts of the type Fe^{II}(Cap)(B).† The equilibrium constants are listed in the Table. It is apparent from the equilibrium constants, K^B,† that these ligands resemble CO in binding strongly to Fe^{II}(Cap). The Evans' n.m.r. method[7] for determining magnetic susceptibility was employed to show that the complexes Fe(Cap)[$P(Bu^n)_3$], Fe(Cap)[$P(OEt)_3$], and Fe(Cap)($PhCH_2NC$) are diamagnetic, low-spin ($S = 0$) iron(II) complexes in toluene solution at 35 °C under N_2.

Table. Equilibrium constants for the reaction Fe^{II}(Por) + B ⇌ Fe(Por)(B).

Porphyrin[a]	Ligand	T/°C	log K^B /l mol^{-1}
Fe(Cap)	$P(Bu^n)_3$[b]	23·1	4·66 ± 0·05
	$P(OEt)_3$[b]	23·1	3·24 ± 0·05
	$PhCH_2NC$[b]	23·1	5·44 ± 0·10
Fe(DeutDME)†[c]	CO[d]	25·0	4·30 ± 0·07
Fe(TPP)	CO[e]	20·0	4·82 ± 0·2

[a] Solvent was toluene unless otherwise noted. [b] See also ref. 6. [c] Solvent was benzene. [d] See M. Rougee and D. Brault, *Biochem. Biophys. Res. Comm.*, 1973, **55**, 1364. [e] See ref. 5.

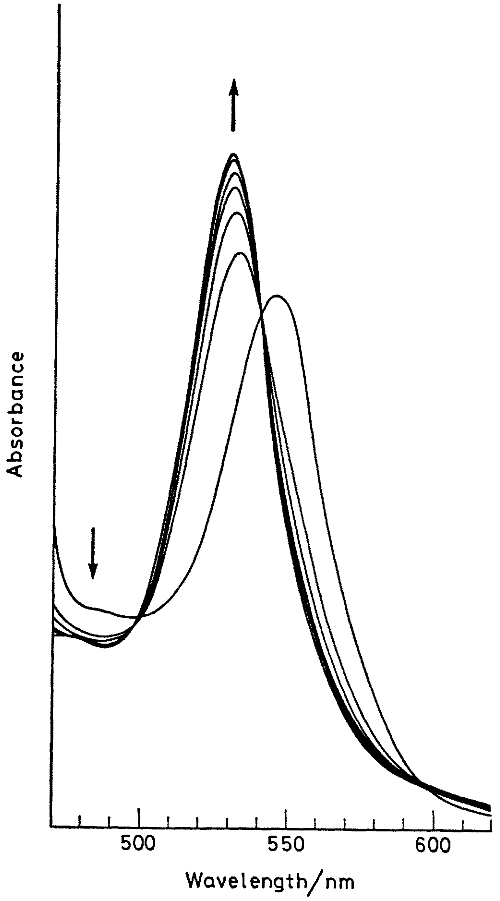

Figure. Optical spectral changes on the addition of benzyl isocyanide ($4·8 \times 10^{-2}$ M in toluene) to a $5·0 \times 10^{-5}$ M solution of Fe(Cap) in toluene at 23·1 °C. The final benzyl isocyanide concentration is $2·9 \times 10^{-3}$ M.

The isocyanide, phosphine, and phosphite ligands are known[8,9] for their good π-acid (π-electron accepting) properties. A π-back bonding argument has been used[3,5] to explain the low-spin nature of the complexes Fe^{II}(TPP)(NO) and Fe(TPP)(CO). This same π-bonding concept can easily be extended to the phosphine, phosphite, and isocyanide adducts of Fe^{II}(Cap).

Although the addition of a single nitrogenous base such as imidazole to iron(II) porphyrins does not cause the formation of a low-spin adduct, the addition of π-acid ligands does further destabilize the d_{z^2} orbital of the iron(II) porphyrin and produce low-spin ($S = 0$) complexes. These results support the view[5] that ligands with synergic σ and π bonding properties are required to produce low-spin five-co-ordinate iron(II) porphyrins. The covalent binding from a nitrogen ligand such as imidazole is not sufficient to yield a five-co-ordinate, low-spin iron(II) porphyrin. The similarity between the bonding of CO and

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† Abbreviations used: Cap = dianion of capped porphyrin (see ref. 1); 2-MeIm = 2-methylimidazole; Por = dianion of any porphyrin; TPP = dianion of *meso*-tetraphenylporphyrin; K^B = the equilibrium constant for the base addition, M(Por) + B ⇌ M(Por)B; B = any Lewis base ligand; DeutDME = dianion of deuteroporphyrin IX dimethyl ester.

other π-acid ligands to iron(II) porphyrins may be important in obtaining a fuller understanding of the contribution of π-bonding of small diatomic molecules to natural haem proteins. Although to our knowledge no five-co-ordinate PR_3 or CNR complexes of 'flat' iron(II) porphyrins such as Fe(TPP) have been reported, on the basis of the results presented here it should be possible to prepare these presumably diamagnetic five-co-ordinate complexes.

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