Mössbauer Spectroscopic Studies of Carbonyl Haemochromes; Correlations with Reactivity

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Summary Mössbauer spectra of several bis(piperidine) and carbonylpiperidine haemochromes suggest that replacement of the axial amine by carbon monoxide causes pronounced changes in the iron–porphyrin bonding, *i.e.* causes a substantial *cis*-effect.

Connor and Straub[1] have recently published Mössbauer data for several iron(II) derivatives of the type [Fe(pmxpp)(L)CO] [pmxpp = dianion of tetra(p-methoxyphenyl)porphyrin; L = an amine], and have attributed differences in parameters between these complexes and the corresponding [Fe(pmxpp)(L)$_2$] species solely to changes in iron–axial ligand bonding. We report Mössbauer measurements on [Fe(p)(pip)$_2$] and [Fe(p)(pip)CO] [p = dianions of protoporphyrin IX (pp), tetraphenylporphyrin (tpp), octamethyltetrabenzoporphyrin (omtbp), and phthalocyanine (pc); pip = piperidine], which indicate a pronounced *cis*-effect, whereby replacement of an axial amine by CO is accompanied by large changes in iron–porphyrin bonding. This study also offers the first opportunity to correlate reactivity of a series of closely related iron(II) porphyrins[2–4] with electronic structure of the central metal atom.

The diamagnetic complexes were prepared as described previously[3–5] and gave correct analyses. Mössbauer parameters are given in the Table. Signs of V_{zz}, the principal component of the electric field gradient (e.f.g.), and magnitudes of the asymmetry parameter η, were determined from spectra taken at 4·2 K in longitudinal magnetic fields of 4·5—5·2 T, as discussed elsewhere.[6]

Table. Mössbauer parameters (mm s^{-1}) for the complexes.

Complex	T/K	δ[a]	ΔE_Q[b]	Γ_1	Γ_2
[Fe(pc)(pip)$_2$]	295	0·28	2·34	0·25	0·27
	115	0·36	2·25	0·26	0·26
	4·2	0·34	+2·24	0·27	0·27
[Fe(tpp)(pip)$_2$][c]	300	0·42	1·52		
	77	0·50	1·44		
	4·2	0·51	+1·52		
[Fe(pp)(pip)$_2$][d]	295	0·42	1·43		
	77	0·49	1·42		
[Fe(omtbp)(pip)$_2$][e]	115	0·53	0·89	0·32	0·34
[Fe(pc)(pip)CO]	295	0·11	1·57	0·27	0·25
	115	0·16	1·51	0·28	0·27
	4·2	0·17	+1·48	0·29	0·29
[Fe(tpp)(pip)CO]	295	0·18	0·53	0·24	0·24
	115	0·25	0·47	0·27	0·28
[Fe(pp)(pip)CO]	295	0·18	0·62	0·29	0·27
	115	0·26	0·57	0·26	0·27
[Fe(omtbp)(pip)CO]	295	0·23	0·20	0·27	0·28
	115	0·30	0·17	0·29	0·29
	4·2	0·32	+0·24	0·26	0·26

[a] Relative to metallic iron. [b] Signs refer to the sign of V_{zz} and were determined from Mössbauer–Zeeman spectra; in every case η = *ca.* 0. [c] Ref. 7. [d] Ref. 14. [e] Recorded for a frozen solution.

Trends in both isomer shift, δ, and quadrupole splitting, ΔE_Q, in the [Fe(p)(pip)$_2$] complexes, as p is varied, parallel those found[7] in the corresponding bis(pyridine) derivatives, and which have been related[7] to σ and π donor strengths of the porphyrins. For [Fe(tpp)(pip)$_2$][8] and [Fe(pc)(pip)$_2$], V_{zz} is positive and $\eta = 0$. Positive, axially symmetric e.f.g.s have also been reported for [Fe(p)(py)$_2$] (p = pc,[9] tpp,[10] or omtbp;[5] py = pyridine) and are almost certain to obtain in all bis(amine) iron(II) porphyrins. Upon carbonylation, δ decreases by *ca.* 0·2 mm s^{-1} and ΔE_Q by *ca.* 0·7—1·0 mm s^{-1}, the trends in both parameters as p varies being qualitatively the same as in the bis(amine) complexes. For [Fe(p)(pip)CO] p = pc, tpp, or omtbp, we find $V_{zz} > 0$ and $\eta = 0$. The effectively axial symmetry is consistent with the linear Fe–C–O arrangement found in [Fe(tpp)(py)CO].[11] For carbonylhaemoglobin and carbonylmyoglobin, V_{zz} is known to be positive, although this has not previously been established experimentally for simple protein-free carbonyl haemochromes.[1]

Connor and Straub[1] have attributed the decrease in δ upon carbonylation in such complexes to a decrease in *d*-electron density on the iron, arising from strong Fe$\rightarrow$CO π-bonding and the weaker Fe$\leftarrow$CO σ-bonding than Fe$\leftarrow$amine σ-bonding, but this argument fails to explain the large decrease in ΔE_Q. The major contribution to the e.f.g. in these complexes comes from an imbalance of electron densities in the iron 3*d* valence orbitals.[12] If lattice contributions are ignored, V_{zz} is given approximately by equation (1),[13] where the n_i values are effective populations of the appropriate 3*d* orbitals, and *k* is as defined in ref. 13. As d_{xy} is non-bonding, n_{xy} will make an essentially constant

$$V_{zz} = k[n_{x^2-y^2} - n_{z^2} + n_{xy} - \tfrac{1}{2}(n_{xz} + n_{yz})] \qquad (1)$$

contribution to V_{zz} and can be ignored. It is clear, since $V_{zz} > 0$, that stronger back π donation, which would decrease n_{xz} and n_{yz}, and weaker forward σ donation, which would decrease n_{z^2}, would both serve to increase V_{zz}, contrary to what we observe.

Piperidine is a non-π-bonding ligand whilst CO is a good π acceptor. Hence, differences in iron–axial ligand π-bonding must make V_{zz} larger in the carbonyl complexes, and some other mechanism is needed to account for the smaller V_{zz}'s found. It is unreasonable to assume that CO is so much stronger a σ donor than piperidine as to overcome this effect of iron d_π depletion and additionally produce a lowering of ΔE_Q of $\geqslant$ *ca.* 0·7 mm s^{-1}. We therefore conclude that carbonylation is accompanied by substantial changes in iron–porphyrin bonding. The very large decreases in ΔE_Q make it seem likely that there is both a significant decrease in p $\rightarrow$ Fe σ donation (to diminish $n_{x^2-y^2}$) and an increase in p $\rightarrow$ Fe π donation to help compensate for the Fe $\rightarrow$ CO back bonding. Thus, the porphyrins appear to be acting as 'electron sinks,' whereby they are able to modify both their σ- and π-bonding characteristics towards iron in order to accommodate the requirements of the axial ligands. Such an ability may well be responsible in part for the diverse functions in which metalloporphyrins participate in biological systems.

Kinetic studies[2–4] of the carbonylation of bis(amine)iron(II) porphyrins in solution are consistent with the mechanism shown in equation (2). For these bis(piperidine) complexes k_1, the rate constant for dissociation of an axial amine,

$$L_2Fe(p) \underset{+L,\ k_{-1}}{\overset{-L,\ k_1}{\rightleftharpoons}} LFe(p) \underset{-CO,\ k_{-2}}{\overset{+CO,\ k_2}{\rightleftharpoons}} LFe(p)(CO) \qquad (2)$$

decreases in the order[4] omtbp $>$ pp $\sim >$ tpp $>$ pc. This is the same order in which δ decreases and ΔE_Q increases (Table). This suggests that enhanced electron density in the iron d_π orbitals enhances piperidine lability. Similarly in the carbonyl complexes, Fe $\rightarrow$ CO back bonding, as reflected in ν(CO) values,[4] also decreases in the order omtbp $>$ tpp $>$ pc, the same order as available d_π density decreases as deduced from δ and ΔE_Q values. However, the decarbonylation rate constant k_{-2} shows little variation as p is changed, possibly reflecting accommodation of charge by the synergic CO ligand.

The equilibrium constants, K, for the overall carbonylation reactions[4] do not correlate directly with the Mössbauer parameters. This is not unexpected since K includes rate constants defining the reactivity of the transient five-coordinate intermediates, and will be sensitive to structural differences (*e.g.*, iron in or out of the porphyrin plane) in these intermediates.

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