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(4) Abbreviations: Cap, cap porphyrin; HmCap, homologous cap; $HmCapH_2$, homologous cap porphyrin; 1-MeIm, 1-methylimidazole; 1,2-Me_2Im, 1,2-dimethylimidazole; $P_{1/2}^{O_2}$, O_2 pressure at half saturation.

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(7) Magnetic susceptibilities were determined at 34 °C using the Evans method. At 0.02 M 1-MeIm, Fe(HmCap)(1-MeIm) is the predominant porphyrin species (~90%), whereas at 1.8 M 1-MeIm, it is Fe(HmCap)(1-$MeIm)_2$ (~90%). An error of ±0.2 μ_B has been assigned to the μ_{eff} values.

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The Iron(II) and Cobalt(II) "Cap" and "Homologous Cap" Porphyrins. Base and Oxygenation Equilibria Studies of Relevance to Hemoglobin Cooperativity

Sir:

The topic of Hb[1] cooperativity is of considerable interest, and explanations for this complicated phenomenon are being sought through model complex studies.[2,3] Here we report on base and oxygenation equilibria measurements for the iron(II) and cobalt(II) "cap" and "homologous cap" porphyrins (Figure 1).[4,5] The results obtained show that there are significant differences in the base and dioxygen binding of the two porphyrins, and the implications as to the nature of Hb cooperativity are discussed.

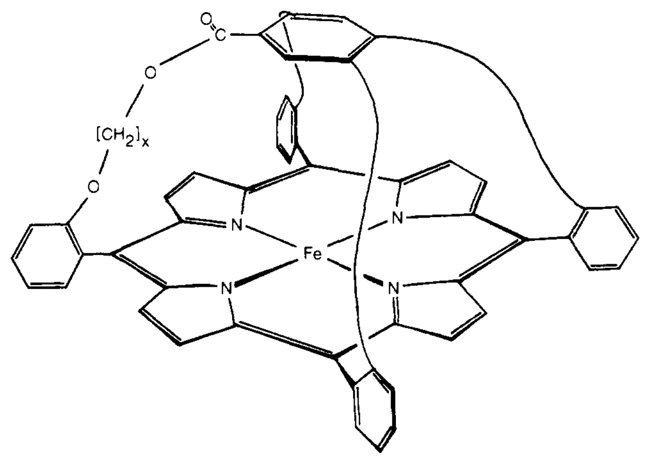

Figure 1. Schematic representations of the "cap" ($x = 2$) and "homologous cap" ($x = 3$) porphyrin complexes.

A lowering in both the dioxygen and carbon monoxide affinities for Fe(porphyrin)B complexes has been observed when the axial base, B, is changed from 1-MeIm to the sterically hindered 2-MeIm or 1,2-Me_2Im; and moreover, these latter complexes are suggested to mimic T-state Hb.[3,6–9] These results have also been used[9] to support the Hoard–Perutz mechanism for cooperativity. This proposes that, in T-state Hb, the protein tertiary structure places greater restraint on the motion of the proximal histidine towards the heme plane as oxygenation occurs. A recent alternative explanation[10] for the R and T states, based on energy minimization calculations, suggests that nonbonding protein-heme interactions in the T state constrain the porphyrin to a "domed" configuration. The additional energy required to "undome" the porphyrin upon oxygenation is reflected in the lower T-state dioxygen affinity. A similar proposal has also been advanced by Hoffman.[11]

Table I summarizes base and dioxygen equilibria data for the "cap" and "homologous cap" systems as well as for some other representative model complexes. Discussing firstly, the "cap" systems, it is apparent that both Fe(Cap)(1-MeIm) and Fe(Cap)(1,2-Me_2Im) have considerably lower dioxygen affinities compared with their "picket-fence" porphyrin[3] analogues. However, both the iron "cap" and "picket-fence" porphyrins show comparable reductions in $K_B^{O_2}$ on substituting 1,2-Me_2Im for 1-MeIm as the axial base. Similar observations may be made for the cobalt complexes although,

Table I. Base and Oxygenation Equilibria Data in Toluene

species	base	log K^B (±0.05)[a]	$P_{1/2}^{O_2}$ at 0 °C, Torr	ref
Fe(Cap)	1-MeIm	2.90	4.5	this work
	1,2-Me_2Im	3.06	930	this work
	t-$BuNH_2$	2.50	0.27[d]	this work
Fe(HmCap)	1-MeIm	3.31	(120–180)	this work
	1,2-Me_2Im	3.61	880[d]	this work
	t-$BuNH_2$	2.23	575[d]	this work
Co(Cap)	1-MeIm	2.32	5.9×10^4, 140[e]	this work
	1,2-Me_2Im	1.84	(2000–4000)[e]	this work
Co(HmCap)	1-MeIm	2.28	(>5000)[e]	this work
	1,2-Me_2Im	1.93	*f*	this work
FeTpivPP(4CIm)PP			0.042	9
FeTpivPP	1,2-Me_2Im	4.5[b]	4.5	9
FeTPP	2-MeIm	4.1[c]		14
CoTpivPP	1-MeIm	4.2[b]	26.6	9, 22
	1,2-Me_2Im	3.2[b]	152	9, 22
CoT(*p*-OCH_3)PP	1-MeIm	3.37[c]	3.87×10^3	23, 24
	1,2-Me_2Im	2.79[c]		23

[a] At 23.1 ± 0.1 °C unless otherwise stated. [b] At 20 °C. [c] At 25 °C. [d] At −63 °C. [e] At −78 °C. [f] The dioxygen affinity was too small to estimate.

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surprisingly, Co(Cap)(1-MeIm) is an even worse dioxygen binder than the simple model complex CoT(p-OCH_3)PP(1-MeIm), The presence of oxygen-oxygen stretching bands in the infrared spectra of the Co and Fe dioxygen complexes attributable to $\nu_{^{16}O_2}$ and $\nu_{^{18}O_2}$ confirms that oxygenation has occurred.[12]

There are several possible factors which could produce the lower dioxygen affinities found for the "cap" complexes, and they include the following: (1) unfavorable steric interactions between the bound dioxygen and porphyrin cap, (2) an increase in the conformational strain energy of the "cap" porphyrin upon oxygenation, (3) the absence of stabilizing solvent or environmental interactions for the bound dioxygen, and (4) electronic substituent effects. Previous studies,[13,14] however, have shown that factor 4 has relatively little effect on dioxygen binding to cobalt(II) and manganese(II) para-substituted tetraphenylporphyrins.

In order to further clarify the situation, the "homologous cap" porphyrin complexes were investigated. The unusual properties of Fe(HmCap) are more fully discussed in an accompanying communication, but it should be noted that both Fe(HmCap)B and Co(HmCap)B (B = 1-MeIm or 1,2-Me_2Im) are significantly worse dioxygen carriers than the corresponding "cap" compounds. This surprising result then strongly suggests that factor 2 above is primarily responsible for the variation in dioxygen affinities; factors 1 and 3 are less likely explanations, since the environments of the bound dioxygen in both the "cap" and "homologous cap" complexes should be similar, and also the size of the dioxygen binding pocket in the latter should be greater than in the former.

For measurements of base addition constants (K^B), Fe(Cap) has a great advantage over other ferrous porphyrins because K^B can be determined directly, instead of having to be estimated.[15] The data in Table I shows Fe(Cap) to be a poorer base binder compared with Fe(HmCap) and other related model complexes. A similar situation exists for cobalt, although, in this case, both Co(Cap) and Co(HmCap) have comparable K^B values. It is noteworthy that, for 1-MeIm and 1,2-Me_2Im binding to Fe(Cap) and Fe(HmCap), the latter sterically hindered base is the better ligand. This has also been noted[7] for another model system. For cobalt porphyrin complexes, however, the reverse is found. These trends may be attributed to the following factors: (a) the greater basicity of 1,2-Me_2Im compared with 1-MeIm and (b) the greater porphyrin-axial base steric interactions for the cobalt complexes, which have a shorter P_c to metal distance.[16]

As shown in Figure 1, the "cap" and "homologous cap" porphyrins differ only in that the latter contains an extra methylene group in each of the porphyrin straps. Yet, there are pronounced differences in both the base and dioxygen binding properties of their complexes. These differences appear to be intimately associated with the nature of the cap and with the porphyrin system's ability to accommodate the conformational changes which occur upon addition of base and dioxygen.[19-22]

For the extrapolation to Hb cooperativity, it is apparent that the above discussion is closely related to the porphyrin "doming" concept mentioned[10] earlier. This work strongly supports the viability of such a mechanism, although it does not necessarily require that the porphyrin be constrained to a "domed" configuration. It would be sufficient for the nonbonding protein-heme interactions in T-state Hb to oppose the porphyrin conformational changes which occur upon oxygenation. A more complete understanding of the "cap" and "homologous cap" porphyrin systems must await the elucidation of their respective structures and at present we are attempting to grow suitable crystals for X-ray analysis.

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(1) Abbreviations: Hb, hemoglobin; Cap, cap porphyrin; HmCap, homologous cap porphyrin; TPP, *meso*-tetraphenylporphyrinato; TpivPP, *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-$o$-pivalimidophenyl)porphyrinato; Tripiv(4CIm), *meso*-tri(α,α,α-o-pivalimidophenyl)-β-3-(N-imidazolyl)propylamidophenylporphyrinato; T(p-OCH_3)PP, *meso*-tetra(p-methoxyphenyl)porphyrinato; 1-MeIm, 1-methylimidazole; 2-MeIm, 2-methylimidazole; 1,2-Me_2Im, 1,2-dimethylimidazole; t-BuNH_2, *tert*-butylamine; K^B, the equilibrium constant for the base addition, M(porphyrin) + B $\rightleftharpoons$ M(porphyrin)B; $K_B^{O_2}$, the equilibrium constant for the uptake of dioxygen, M(porphyrin)B + O_2 $\rightleftharpoons$ M(porphyrin)BO_2; $P_{1/2}^{O_2}$, the O_2 pressure at half saturation; P_c, the 24-atom porphyrinato plane.

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Optically Active Poly(triphenylmethyl methacrylate) with One-Handed Helical Conformation

Sir:

It has been pointed out that a vinyl polymer obtained from an achiral monomer, $CH_2{=}CXY$, can not be optically active to a measurable extent even if it is highly isotactic.[1,2] The basis for this reasoning is that, except for the carbon atoms located near the ends of the polymer chain, each asymmetric carbon which is formed in the process of the polymerization becomes "pseudo" asymmetric after the polymer grows to a long chain. This is also recognized in the vinyl polymers which have asymmetric terminal groups deriving from optically active

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