"Picket Fence Porphyrins." Synthetic Models for Oxygen Binding Hemoproteins

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Abstract: Model iron(II) porphyrin complexes for the active site of myoglobin and oxymyoglobin have been synthesized and fully characterized by Mössbauer, electronic, and infrared spectral analysis, magnetic susceptibility, and X-ray crystallography. The synthesis is reported for the "picket fence porphyrin," *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-pivalamidophenyl)porphyrin, which has great steric bulk creating a nonprotic cavity on one side of the porphyrin. The unsaturated ferrous complex, **1**, reacts with strong field ligands to give six-coordinate, diamagnetic complexes, **2**. The complexes, **2**, react reversibly with oxygen, in solution at 25°. Crystalline diamagnetic dioxygen complexes, **3**, having 1-methylimidazole or 1-*n*-butylimidazole as axial ligands were isolated and characterized. The complex, **3**, contains O_2 bound "end-on" with an Fe–O–O angle of 136 (4)°. A dioxygen complex with tetrahydrofuran as an axial base, **4**, was also prepared and appears to be paramagnetic (2.4 BM). Carbonyl complexes with imidazoles (ν_{CO} = 1965 cm^{-1}) and THF (ν_{CO} = 1955 cm^{-1}) as axial ligands are all diamagnetic. The dioxygen complexes, **3** and **4**, show no ν_{O_2} at 25° but a strong, sharp band is seen at 1385 cm^{-1} at −175°. The complexes are thus described as containing coordinated singlet (Δ) oxygen. The remarkable stability of the complexes, **3** and **4**, and their Mössbauer and spectral properties are discussed.

The interaction of molecular oxygen with hemoproteins is of primary importance in respiratory and metabolic processes. The reversible binding of oxygen in hemoglobin (Hb) and myoglobin (Mb) has long commanded considerable attention while the enzymic reductive activation and consequent utilization of oxygen in the oxidation of small molecules, as in the P_{450} cytochrome monooxygenases, has been investigated more recently. These protein systems rely on the formation of an Fe(II) heme dioxygen complex. In cytochrome oxidase molecular oxygen is reduced in the terminal step of the electron transport chain, a process which may also involve reaction at the heme component of the protein. Clearly a fundamental understanding of molecular oxygen's interaction with heme complexes is necessary to develop a basic comprehension of hemoprotein function. Nevertheless the nature of the coordinate link between iron and dioxygen in these hemoproteins has not been defined at the atomic level. Furthermore the influence of the protein-heme interaction on reversible oxygen binding and on the enzymic activation of molecular oxygen remains obscure. We have addressed and partially clarified these issues by preparing crystalline iron(II) porphyrin-dioxygen[2] complexes.[3] These remarkable oxymyoglobin, MbO_2, models which reversibly bind molecular oxygen in solution or in the solid state at ambient temperature have been definitively characterized by Mössbauer and ir spectra[4] and X-ray crystallographic analysis.[5]

The strategies which led to the synthesis and isolation of these crystalline diamagnetic and paramagnetic dioxygen complexes were based on known structural characteristics of Mb and consideration of the mechanisms for irreversible autoxidation of Fe(II).

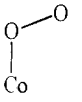
Myoglobin, the oxygen binding protein in muscle tissue responsible for the storage and possible transport of oxygen across membranes, is composed of a 153 residue peptide and an iron(II) protoporphyrin IX complex.[6,7] The ferrous protoporphyrin IX is held within a cleft in the protein principally by noncovalent, largely apolar interactions. The only covalent linkage between porphyrin and protein arises from a coordinate bond between the so-called proximal imidazole of histidine residue F-8 and the Fe(II). In Mb, the deoxy form, Fe(II) is five-coordinate, high spin, with an ionic radius too large to fit within the cavity of the porphyrin.[7] Consequently, the high spin iron atom projects out of the mean plane of the four porphyrin nitrogens toward the proximal imidazole and away from the oxygen binding site. The low spin iron atom of diamagnetic oxymyoglobin is thought to lie in the porphyrin plane. Thus in coordinating dioxygen the iron atom moves into the porphinato plane perhaps pulling along the proximal imidazole.[8] This motion of the proximal imidazole may be transferred through the four Mb like subunits of hemoglobin,[9] contributing to the cooperativity of oxygen binding between the four distant iron porphyrins in Hb.

Proposed structural models for dioxygen binding in HbO_2 and MbO_2 include a sideways, triangular structure, i, by Griffith[10] and an end-on angular bond, ii, by Pauling[11]

i

ii

and by Weiss.[12] The former would necessitate a formal coordination number of seven for MbO_2 or HbO_2, a sterically unfavorable situation at the very least. Structural analogs of the i model have been derived from coordinatively unsaturated d^8 and d^{10} complexes of other transition metals,[13,14] but these are four- or six-coordinate, and none involves a macrocyclic, tetradentate ligand. Three angular dioxygen complexes of cobalt(II),



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iii, have been structurally characterized[15-18] but these are not isoelectronic with the iron(II) dioxygen moiety. Electron spin resonance studies indicate[19] that the one extra electron occupies a π^* orbital of coordinated O_2.

Previous attempts to prepare dioxygen complexes of Fe(II) have led to a number of reports of reversible oxygenation,[20-30] some later shown to be incorrect.[31,32] In none of these cases was a solid dioxygen complex *isolated* and fully

characterized. Most reports of Fe(II) dioxygen complexes have relied substantially on changes in visible absorption spectra as criteria for reversible oxygenation in solution. Such measurements in the presence of an excess of axial ligand must be used with caution because of the now well-recognized facile ligand redox reactions of iron complexes.[33] Thus an excess of an axial ligand such as imidazole can reduce iron(III) porphyrins to the ferrous state producing an illusion of reversible oxygen binding. However, solution equilibria with well-documented stoichiometry, demonstrating dioxygen coordination with varying degrees of kinetic stability, have been reported in the past 2 years.[27-29] Spectral measurements using the natural protoporphyrin IX chromophore[21,27] represent more definitive structural characterization because of comparisons which can be made with the well-studied hemoproteins. Very recently Baldwin[27b] has used a "capped" porphyrin to produce in solution an Fe(II) dioxygen complex whose diamagnetism is established. However, this elegant system has so far not resulted in the isolation of a solid dioxygen complex.

The principal difficulty in preparing ferrous dioxygen complexes arises from the rapid irreversible autoxidation of Fe(II) to Fe(III). Thus six-coordinate iron(II) tetraphenylporphyrin complexes, $Fe(TPP)B_2$ (**1**) (B = imidazole, pyridine, etc.), are rapidly oxidized to the well-characterized, μ-oxo ferric dimer, **3** (Scheme I).[34] Since the rate of this

Scheme I

$$Fe^{II}(TPP)B_2 \longrightarrow Fe(TPP)B \xrightarrow{O_2} (TPP)Fe^{III}\text{-}O\text{-}Fe^{III}(TPP)$$

1 **2** **3**

reaction is depressed[35,36] by excess axial base, B, an intermediate five-coordinate iron(II) complex, **2**, is implicated.

Detailed study by Hammond and Wu[37] of the autoxidation of ferrous chloride in aqueous alcohol led to a rate law second order in Fe(II) and first order in O_2. The overall stoichiometry of the reaction and indications of a potent ox-

$$\frac{-d[Fe(II)]}{dt} = [Fe(II)]^2[O_2]$$

$$4Fe(II) + O_2 \longrightarrow 4Fe(III)$$

idizing intermediate suggested a mechanism of oxidation involving a bimolecular reaction as the rate limiting step (Scheme II). The observed oxidations of ethanol to acetal-

Scheme II

$$Fe(II) + O_2 \rightleftharpoons FeO_2$$

$$FeO_2 + Fe(II) \xrightarrow[\text{limiting step}]{\text{rate}} Fe^{III}OFe^{III} \text{ or } 2Fe^{IV}{=}O$$

$$Fe^{IV}{=}O + Fe(II) \longrightarrow Fe^{III}OFe^{III}$$

dehyde and benzoin to benzil might have been effected by the suggested intermediate $Fe^{III}OOFe^{III}$ or $Fe^{IV}{=}O$.

Wang and Kao[36] found the autoxidation of bispyridine ferrous porphyrin complexes, $Fe(P)(py)_2$, in aqueous media and in benzene–ethanol mixtures to be first order in both Fe(II) and O_2.

$$\frac{-d[Fe(II)]}{dt} = [Fe(II)][O_2]$$

The effect of the dielectric constant of the medium was investigated by varying relative concentrations of ethanol and benzene. Fastest rates of autoxidation were observed in pure ethanol and slowest in pure benzene implying a direct correlation between rate and dielectric constant. To explain this solvent dependence, Wang proposed that oxidation proceeded at least partly through an intermediate having separation of charge or *via* outer sphere electron transfer (k_2) (Scheme III). However, a constant, large excess of pyridine

Scheme III

$$FeP(py)_2 + O_2 \overset{K}{\rightleftharpoons} py + PFeO_2$$

$$FeP(py)_2 \xrightarrow{k_2} Fe(III)\ \text{products} \qquad PFeO_2 \xrightarrow{k_1} Fe(III)\ \text{products}$$

was used in all studies, serving to suppress dissociation of the six-coordinate complex, $Fe(P)(py)_2$.

$$FeP(py)_2 \overset{K'}{\rightleftharpoons} FeP(py) + py$$

The polar products of dissociation, Fe(P)(py) and py, are probably best solvated in a medium of high dielectric constant suggesting that the concentration of the five-coordinate Fe(P)(py) is greatest in solvents such as ethanol. An alternate mechanistic path to that proposed by Wang is thus possible (Scheme IV). Formation of the dioxygen com-

Scheme IV

$$Fe^{II}P(py)_2 \rightleftharpoons Fe^{II}P(py) + py$$

$$Fe^{II}P(py) + O_2 \xrightarrow[\text{determining step}]{\text{rate}} FeP(py)O_2$$

$$FeP(py)O_2 + Fe^{II}P(py) \longrightarrow (py)PFe^{III}OOFe^{III}P(py)$$

or

$$2(py)PFe^{IV}{=}O$$

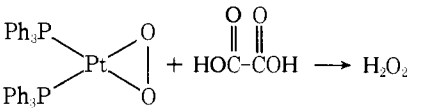
$$(py)PFe^{IV}{=}O + (py)PFe^{II} \longrightarrow PFeOFeP + 2py$$

plex as the rate limiting step still permits a subsequent bimolecular path of oxidation, as was suggested by Hammond[37] (Scheme II).

Consideration of this atom transfer redox mechanism suggests the role of the protein in promoting reversible oxygenation of the iron(II) porphyrin without irreversible oxidation to iron(III). By encapsulating the porphyrin the globin prohibits reaction between two iron centers. Furthermore in the deoxy form of Mb and Hb, the globin imposes five-coordination upon the iron by the agency of the proximal imidazole.[5] Solution equilibria involving free axial bases seem to favor the diamagnetic six-coordinate form[38] which does not appear to react with oxygen.[35] Another probable role of the protein which is simple to mimic is the hydrophobic nature of the oxygen binding environment and the shielding from acidic protons. Acids and other electrophiles are known[14] to react with the triangular

complexes forming peroxides (Scheme V). Such a reaction

Scheme V



with a ferrous dioxygen complex would probably initiate irreversible oxidation by forming iron(III) and hydroperoxyl (Scheme VI). Thus acids should catalyze the irreversible autoxidation of iron(II).

Scheme VI

$$Fe^{II}O_2 + H^+ \longrightarrow Fe^{III} + HO_2$$

There are other potential roles which the protein may play that are not well defined. A more distant imidazole (the "distal imidazole") from the histidine residue (E-7) projecting into the oxygen binding pocket is not close enough to coordinate to iron[7] but may somehow stabilize coordinated dioxygen (as first suggested by Pauling[11]) by hydrogen bonding.

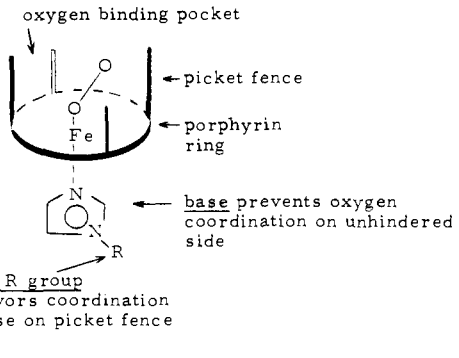


Figure 1. The "picket fence" concept.

In summary, kinetic stabilization of an iron dioxygen function would seem to require at the minimum a pocket to both shield coordinated dioxygen from reaction with another iron porphyrin and to provide a nonacidic environment. Additionally it would be desirable to enforce five-coordination on the deoxy form.

Results and Discussion

The concept of "picket fence porphyrins" (Figure 1) was developed in order to favor five-coordination and simultaneously inhibit bimolecular reactions.[39] Conceptually such a porphyrin should have great steric bulk on one side of the plane of the porphyrin yet leave the other side unencumbered. Employing a suitable bulky ligand such as an *N*-alkyl imidazole would allow coordination of the imidazole on the unhindered side of the porphyrin while restraining binding of the axial base on the hindered side, thus leaving a hydrophobic pocket for complexation of dioxygen. Moreover the "picket fence" would discourage bimolecular reactions involving two iron atoms and dioxygen.

By separating the four atropisomers of *meso*-tetra(*o*-hydroxyphenyl)porphyrin, $H_2T_{OH}PP$, Ullman first demonstrated[40] the concept of biphenyl-type atropisomerism in ortho-substituted *meso*-tetraphenylporphyrins. These porphyrins have the phenyl group oriented nearly normal to the porphine plane, projecting the ortho substituents above or below the porphine plane. In such cases the four atropisomers, depicted in Figure 2, can be interconverted, equilibrating to give the expected statistical ratios of abundance. The possibility of atropisomeric interconversion and the temperature required for rapid equilibration depend on the bulk of the ortho phenyl substituents. The $\alpha,\alpha,\alpha,\alpha$-atropisomer can be seen to represent the essence of a "picket fence porphyrin" provided that the substituent, X, is sufficiently bulky. The energy barrier to isomerism in Ullman's $H_2T_{OH}PP$ is sufficient to permit separation of the four atropisomers at ambient temperature[40] ($t_{1/2}$ = 30 min at 25°). However, preliminary attempts to synthesize a bulky "picket fence porphyrin" derived from $\alpha,\alpha,\alpha,\alpha$-$H_2T_{OH}PP$ were frustrated by the slow reactions of the sterically hindered phenolic groups.[41] For example, the formation of esters and ethers required reaction conditions leading to a mixture of atropisomeric products. Facile cleavage of esters and silyl ethers also proved troublesome.

Attempts to isolate the $\alpha,\alpha,\alpha,\alpha$-atropisomer of tetra(1-naphthyl)porphyrin by classical chromatography techniques were unsuccessful. *meso*-Tetra(2-methoxy-1-naphthyl)porphyrin readily yielded to such a separation, *via* silica gel chromatography, to give *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-2-methoxy-1-naphthyl)porphyrin. The ferrous complexes of this sterically hindered system did not appear to reversibly oxygenate in solution at 25°, but the rate of irreversible oxidation is significantly slower than that of Fe(II) complexes of tetraphenylporphyrin, Fe(TPP).[41]

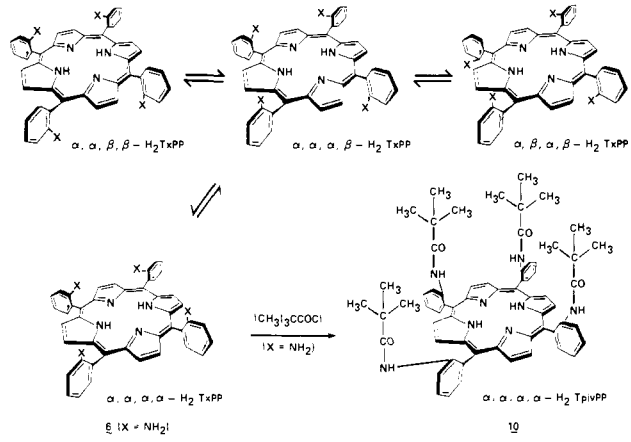
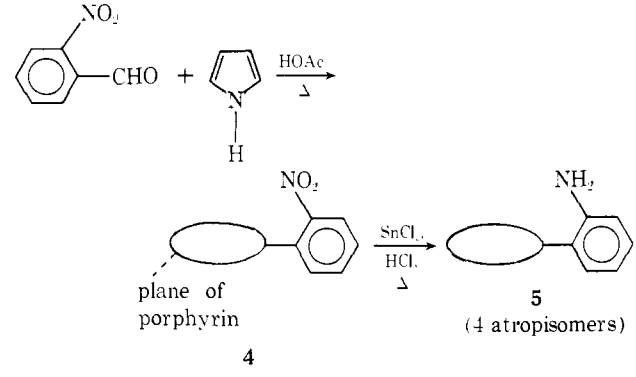


Figure 2. The four atropisomers of *meso*-tetra(ortho-substituted phenyl)porphyrin and "picket fence" formation with pivaloyl chloride.

Condensation of *o*-nitrobenzaldehyde and pyrrole followed by reduction of the product *meso*-tetra(*o*-nitrophenyl)porphyrin (**4**) led to a satisfactory yield[3a] of *meso*-tetra(*o*-aminophenyl)porphyrin, H_2TamPP (**5**) (Scheme VII). Thin-layer chromatography on silica gel gave excel-

Scheme VII



lent separation of four components which, in ratio 1:2:4:1, were presumed to be the four atropisomers in statistical abundance. With R_f values based on their expected polarity and considering the relative amounts of the individual atropisomers these are provisionally assigned as $\alpha,\beta,\alpha,\beta$-, $\alpha,\alpha,\beta\beta$-, $\alpha,\alpha,\alpha,\beta$-, and $\alpha,\alpha,\alpha,\alpha$-, with the most polar tetra-α-atropisomer, **6** (Figure 2), moving most slowly. Isolation of $\alpha,\alpha,\alpha,\alpha$-$H_2$TamPP by silica gel column chromatography afforded gram quantities of product. The mixture containing the remaining three atropisomers was reequilibrated in boiling toluene followed by chromatography to isolate more of the $\alpha,\alpha,\alpha,\alpha$-atropisomer. Repetition of these steps leads to ultimate conversion of nearly all of the H_2TamPP into the desired $\alpha,\alpha,\alpha,\alpha$-$H_2$TamPP, with some loss due to the repeated chromatographic separations.

Fortunately the four amino atropisomers are rather stable in solution at 25°, only partial isomerization being observed after 24 hr. The amino groups of H_2TamPP are also much more reactive than the H_2TOHPP phenolic groups. The $\alpha,\alpha,\alpha,\alpha$-atropisomer of H_2TamPP could be further modified and the configurational energy barrier raised through reaction with various acid chlorides forming amides. *p*-Toluenesulfonyl chloride gave a 75% yield of *meso*-tetra[$\alpha,\alpha,\alpha,\alpha$-*o*-(*p*-toluenesulfonamide)phenyl]porphyrin, $\alpha,\alpha,\alpha,\alpha$-$H_2T_{tos}PP$, which exhibited a single methyl resonance in its pmr spectrum (δ 2.45) consistent with the $\alpha,\alpha,\alpha,\alpha$-formulation. The iron complex could not be prepared from ferrous acetate or ferrous chloride in DMF, THF, or HOAc, possibly due in part to the increased steric hindrance of the porphyrin. Treatment with anhydrous

Table I. Mössbauer Data

Compound[a]	Center shift, δ (±0.01 mm/sec) Temp (°K) 4.2	77	195	Quadrupole splitting, ΔE_Q (±0.01 mm/sec) Temp (°K) 4.2	77	195	Spin state	Magnetic moment (BM) 300°
FeP(1-MeIm)O_2, **17**	0.29	0.28	0.25	2.10	2.00	1.34	$S = 0$	*e*
FeP(1-*n*-BuIm)O_2, **18**	0.27		0.24	2.10		1.33	$S = 0$	*e*
HbO_2[b]	0.24 (1.2°)	0.26	0.20	2.24 (1.2°)	2.19	1.89	$S = 0$	*e*
FeP(1-MeIm)$_2$, **12**	0.46	0.44	0.41	1.02	1.02	1.04	$S = 0$	*e*
FeP(1-MeIm)(CO), **19**	0.27			0.27			$S = 0$	*e*
FeP(THF)$_2$(O_2), **24**	0.33	0.33	0.29	2.64	2.58	2.14	$S = 1$	2.4
FeP(THF)$_2$, **23**	0.93	0.93	0.87	2.70	2.64	2.44	$S = 2$	4.9
Fe(TPP)(THF)$_2$[c]	0.97	0.95	0.89	2.76	2.66	2.41	$S = 2$	5.2
FeP(1-MeIm), **21**		0.88	0.84		2.32	2.01	$S = 2$	4.8
Fe(TPP)(2-MeIm)[c]	0.93	0.92	0.87	2.28	2.26	1.97	$S = 2$	5.3
Hb[d]	0.91		0.90	2.26	2.22		$S = 2$	5.4

[a] P = α,α,α,α-TpivPP. [b] Reference 48. [c] Reference 42, 44. [d] Reference 49. [e] Diamagnetic.

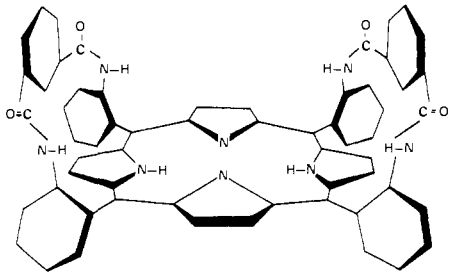


Figure 3. *meso*-Tetra(α,α,α,α-*o*-aminophenyl)porphyrin *N',N''*:*N''',N''''*-diisophthalamide, α,α,α,α-$H_2T_{phth}PP$ (**8**).

$FeBr_2$ in THF afforded a clean synthesis, without isomerization, of Fe(α,α,α,α-$T_{tos}PP$)Br, which was then reduced with $[Cr(acac)_2]_2$ in THF to give Fe(α,α,α,α-$T_{tos}PP$)(THF), **7**. Exposing dilute (5×10^{-5} *M*) benzene solutions of **7** containing excess 1-MeIm or 4-*t*-BuIm to oxygen at 25° led only to rapid irreversible oxidation despite the bulky nature of the porphyrin. *meso*-Tetra(α,α,α,α-*o*-aminophenyl)porphyrin *N',N''*:*N'''N''''*-diisophthalamide, α,α,α,α-$H_2T_{phth}PP$ (**8**), with isophthalamide bridging between adjacent amino substituents, Figure 3, was prepared in high yield by treatment of α,α,α,α-H_2TamPP with 1,3-phthaloyl dichloride. Molecular models show 1,3-phthaloyl dichloride capable of effectively bridging adjacent, cis amino substituents but unable to span the distance necessary for a trans bridge. In contrast models indicate 1,4-phthaloyl dichloride can bridge both cis and trans amino substituents, and indeed, that reaction gave rise to a number of products. As with **7**, ferrous complexes of **8**, Fe(α,α,α,α-TphthPP)(THF) (**9**), gave only irreversible oxidation when dilute (5×10^{-5} *M*) benzene solutions containing an excess of 1-MeIm or 4-*t*-BuIm were exposed to oxygen at 25°. We attribute rapid oxidation of **7** and **9** despite the supposed inhibition of bimolecular reaction of coordinated dioxygen by the "picket fence" to the acidic amide protons presumably directed into the cavity permitting protonation of coordinated dioxygen and consequent heme oxidation.

Treating α,α,α,α-TamPP (**6**) with pivaloyl chloride resulted in formation of the relatively soluble *meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrin, α,α,α,α-H_2TpivPP (**10**) (Figure 2), which has a single methyl resonance in its pmr spectrum (δ 0.05) shifted considerably upfield from that of the parent pivaloyl chloride (δ 1.40). In comparison the pmr spectrum of α,α,α,β-TpivPP has three methyl signals, centered at δ 0.05, with relative areas 2:1:1, respectively. The α,α,α,α-atropisomer, **10**, is much more stable to atropisomerization than the *o*-amino derivative. Heating **10** for 45 min at reflux in toluene gave less than 5% isomerization whereas boiling in xylene over the same period led to about 25% isomerization (as followed by pmr and tlc). Treatment of **10** with $FeBr_2$ in THF followed by reduction with $[Cr(acac)_2]_2$ (Scheme VIII) gave purple crystal-

Scheme VIII

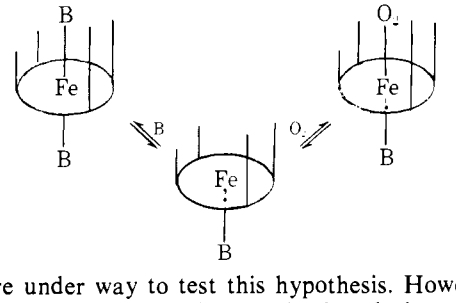
$$\alpha,\alpha,\alpha,\alpha\text{-}H_2TpivPP \xrightarrow[2.\,[Cr(acac)_2]_2]{1.\,FeBr_2/THF} Fe(\alpha,\alpha,\alpha,\alpha\text{-}TpivPP)$$

line Fe(α,α,α,α-TpivPP), **11**, which is highly air sensitive, irreversibly oxidizing in solution. This is not surprising as one side of the porphyrin ring is not sterically shielded.

The magnetic moment (μ = 5.0 BM, 25°) and Mössbauer spectrum (Table I) of the four-coordinate complex, **11**, indicate a spin state of $S = 2$, as expected for high spin Fe(II). This is in contrast to the assignment of the intermediate spin state $S = 1$ to the simpler iron(II) tetraphenylporphyrin complex FeTPP.[42,43]

The four-coordinate iron(II), **11**, reacts with strong-field ligands affording crystalline, diamagnetic complexes, Fe(α,α,α,α-TpivPP)L_2, **12–15** (L = 1-MeIm, 1-*n*-BuIm, 1-tritylIm, 4-*t*-BuIm) (Figure 4). Despite the isolation of six-coordinate complexes, it is probable that the binding constant of an imidazole on the "picket fence" side of the porphyrin is less than that on the "open" side, thus promoting five coordination (Scheme IX). Equilibrium measure-

Scheme IX. Schematic Representation of the Probable Equilibria Involved in the Oxygenation and Deoxygenation of Fe(α,α,α,α-TpivPP)B_2



ments are under way to test this hypothesis. However, regardless of the predominating species in solution, the least soluble complex may crystallize preferentially (provided the equilibria are fast). Recrystallization of **12** (L = 1-MeIm) from ethanol gave high spin Fe(α,α,α,α-TpivPP)(1-MeIm)(EtOH), **16** (μ = 4.8 BM), which is probably five-coordinate. It is thought that this "picket fence porphyrin" complex is similar to the crystallographically characterized,[42,44] high spin, five-coordinate, Fe(TPP)(2-MeIm)(EtOH) but with ethanol trapped as a solvate molecule in the pocket defined by the picket fence.

Table II. Visible Spectra of Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP) + B in C_6H_6 at 25° (in nm)

B	N_2				O_2		CO	
	α	β	Soret		α,β[a]	Soret	α,β[a]	Soret
None	565 (0.27)[b]	535 (1.17)	435 (9.32)	415 (9.66)	565 (1.15)	410 (9.78)		
1-MeIm	562 (0.38)	537 (2.10)		432 (22.8)	548 (1.47)	429 (15.9)	542 (2.30)	427 (31.3)
1-*n*-BuIm	561	536		432	549	426	542	426
1-tritylIm	560	538		435	548	426	542	426
4-t-BuIm	560	541		435	548	426	543	426
1,2-Me_2Im[c]	562	535		439	544	421	542	424
Pyridine		532		425	546	421	540	422
Piperidine	560	534		430	547	426	543	424
Tetrahydrothiophene	564			439, 430	560	427	561	426
THF[c]	590	545		429	540	423	534	417

[a] The α-band is usually not resolved but the peak observed is broad and somewhat asymmetric as in Figures 5, 8, and 10. [b] The figures in parentheses are extinction coefficients $\times 10^{-4}$. [c] THF as solvent.

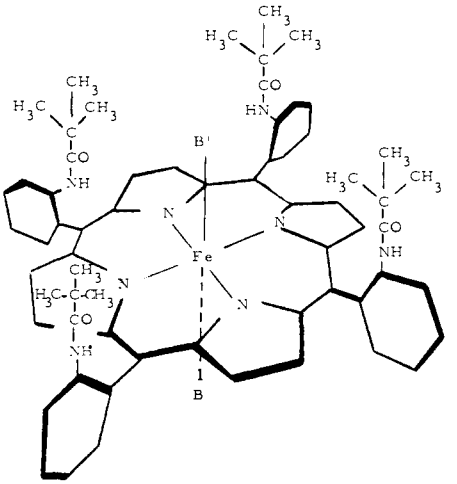


Figure 4. Iron(II) complexes of $\alpha,\alpha,\alpha,\alpha$-$H_2$TpivPP (B and B′, respectively, are given with the compound): **11**, none, none; **12**, 1-MeIm, 1-MeIm; **13**, 1-*n*-BuIm, 1-*n*-BuIm; **14**, 1-*n*-tritylIm, 1-*n*-tritylIm; **15**, 4-t-BuIm, 4-t-BuIm; **16**, 1-MeIm, none (ethanol "solvate"); **17**, 1-MeIm, O_2; **18**, 1-*n*-BuIm, O_2; **19**, 1-MeIm, CO; **20**, 1-*n*-BuIm, CO; **21**, 1-MeIm, none; **22**, 1-MeIm, CO (1-MeIm "solvate"); **23**, THF, none (THF "solvate"); **24**, THF, O_2 (THF "solvate"); **25**, THF, CO (THF "solvate").

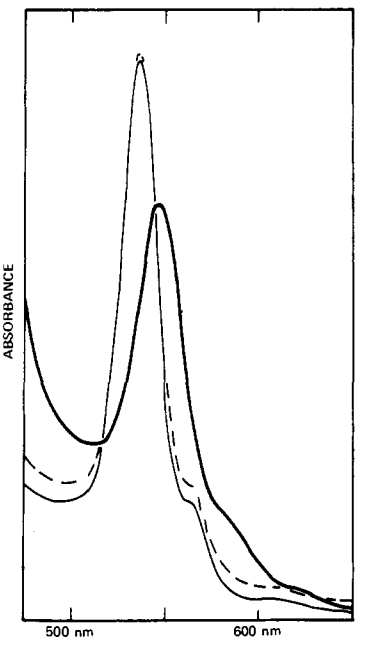


Figure 5. Visible spectrum (25°) of Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(1-MeIm)$_2$ (**12**) (3×10^{-5} *M*) with 1-MeIm (10^{-4} *M*) in benzene: (———) under nitrogen, (———) under oxygen (1 atm), (– – – –) under nitrogen after two oxygenation–deoxygenation cycles.

Benzene solutions of **11** (5×10^{-5} *M*) prepared under nitrogen and containing an excess of a given axial base (Im, 1-MeIm, 1-*n*-BuIm, 1-tritylIm, 4-*t*-BuIm, 1,2-Me_2Im, pyridine, piperidine, or tetrahydrothiophene) were treated with molecular oxygen (1 atm) at 25° resulting in the visible spectral changes shown in Figure 5 and Table II. Purging the solution with nitrogen restored the original spectrum. This reversible oxygenation was repeated several times without appreciable decomposition for some axial ligands (imidazoles, pyridine, piperidine) and with only a small amount of decomposition for the poorer ligand, tetrahydrothiophene. The optimum concentration of ligand for complete oxygenation yet minimal oxidation is dependent on the steric bulk of the ligand and its ability to coordinate, 3 or 4 equiv being ideal for 1-MeIm.[45]

Benzene solutions of the six-coordinate complex, Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(1-MeIm)$_2$ (**12**), prepared under nitrogen in the presence of a small excess of the axial base, then treated with oxygen (1 atm) followed by addition of heptane, gave the essentially diamagnetic dioxygen complex, Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(1-MeIm)($O_2$) (**17**). Similar benzene solutions not exposed to oxygen gave only the starting material, **12**. Recrystallization of the dioxygen complex, **17**, under nitrogen, from benzene containing excess 1-MeIm, afforded the crystalline six-coordinate complex **12** indicating complete reversibility. Elemental analysis and manometric oxygen evolution studies (when **17** was treated with pyridine) confirmed the formulation. Manometric oxygen uptake at 25° of 10^{-3} *M* benzene solutions of the bisimidazole complex, **12**, containing no excess axial ligand indicated 70% adduct formation (1 atm of O_2). Oxygenation is probably suppressed by formation of the six-coordinate complex **12** as depicted in Scheme IX. Use of 1-*n*-BuIm as an axial ligand gave identical results but a more soluble dioxygen complex, **18**. All attempts to isolate the dioxygen complex with 4-*t*-BuIm or 1-tritylIm led only to reisolation of the six-coordinate complexes **14** and **15**. This is seemingly related to solubility, the least soluble six-coordinate species being preferentially precipitated (Scheme IX).

Structural Data. The preliminary X-ray structural characterization[5] of this first oxymyoglobin model, **17**, L = 1-MeIm, shows oxygen to be within the picket fence with the 1-MeIm coordinated to iron(II) on the unhindered side of the porphyrin (Figures 6 and 7). Present structural resolution is limited due to disorder and twinning of crystals, but the semiquantitative features of the structure are clear. Dioxygen is coordinated "end-on," in an angular fashion, with an Fe–O–O bond angle of 136 (4)° and an O–O separation of 1.24 (8) Å. The 1-MeIm is twofold disordered, with respect to the orientation of the *N*-methyl group, and

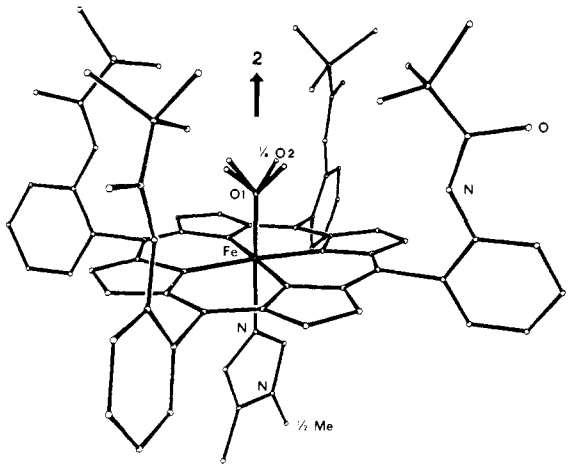


Figure 6. Perspective view of one molecule of the iron(II) dioxygen complex, **17**, showing the crystallographic twofold axis of symmetry and the four-way statistical disorder of the terminal O_2 oxygen atom of dioxygen.

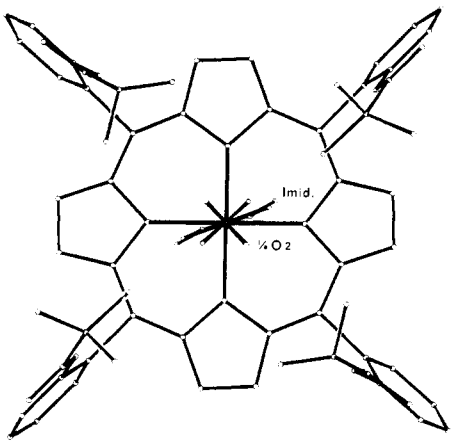


Figure 7. Projection of one molecule of the iron dioxygen complex down the O1-Fe-N axis, perpendicular to the porphinato skeleton.

the Fe-O-O plane four-way statistically disordered, bisecting the N-Fe-N right angles of the equatorial porphyrin plane. Thus there are two types of coordinated dioxygen, the Fe-O-O plane being either parallel or perpendicular to the trans axial imidazole plane. However, structural parameters for the two types of coordinated dioxygen are crystallographically indistinguishable at the present resolution (R = 0.15). The tertiary butyl and amide N-H groups of the picket fence are turned inward toward coordinated O_2, but the estimated distance between the N-H proton and the terminal O atom is too great for hydrogen bonding.[5] The Fe-O distance, 1.75 (2) Å, is about 0.1 Å shorter than both that expected from summation of covalent radii and that observed (1.86 Å) in angular dioxygen complexes of Co(II),[15-18] possibly indicating significant multiple bonding. Iron is in the porphine plane but the Fe(II)-imidazole nitrogen distance, 2.07 (2) Å, is longer than predicted[46] from covalent radii (1.98 Å) suggesting that dioxygen is asserting a mild trans effect on the trans axial imidazole.

Table I lists Mössbauer and magnetic data for the "picket fence porphyrin" complexes, HbO_2, and a few reference complexes.

The dioxygen complexes, **17** (L = 1-MeIm) and **18** (L = 1-*n*-BuIm), like HbO_2,[47] are essentially diamagnetic. The peculiar temperature dependence of the quadrupole splitting, ΔE_Q, observed[48,49] for HbO_2 is seen to be paralleled by that of the model complexes. That the terminal oxygen atom, O(2), is four-way statistically disordered may account for the temperature dependence of ΔE_Q if the disorder represents a rapid equilibrium between two energetically different coordination states and if the Mössbauer spectrum reflects an averaged electric field arising from the relative populations of these states. Presumably as the temperature is decreased, the relative populations of these two states, and hence the Mössbauer parameters, would change. The preparation of a ferrous dioxygen complex without this disorder which might not manifest a temperature dependent ΔE_Q is being explored. Oxygenated Fe(II) cytochrome P_{450} lacks such a temperature dependence in its quadrupole splitting[50] which may reflect greater symmetry in its axial ligands or the presence of a single O_2 orientation, the other orientations being blocked by the protein or the presence of a hydrocarbon substrate.

Detailed analysis of these Mössbauer spectra including their behavior in magnetic fields is forthcoming from the Pennsylvania laboratories.

At ambient temperature the diamagnetic dioxygen complexes, **17** (L = 1-MeIm) and **18** (L = 1-*n*-BuIm), do not exhibit ir or Raman absorptions attributable to coordinated dioxygen[3a] despite comparison with samples prepared from $^{18}O_2$. Angular bound dioxygen gives a strong ir absorption in acetylacetone complexes of Co(II), $Co(acac)_2(B)(O_2)$,[51] but only a weak absorption in the corresponding salicylaldehyde-ethylenediamine complexes, $Co(salen)(B)(O_2)$.[52] However, the low temperature (−175°) ir spectra[4] of the iron(II) dioxygen complexes, **17** and **18**, reveal a remarkably sharp band at 1385 cm^{-1}! The absorption, which we tentatively assign as ν_{O_2}, is not seen in solid samples of **17** deoxygenated *in vacuo* (as described below) but reappears upon admission of O_2. The $Fe-O_2$ complex, **17**, derived from $^{18}O_2$ (>90% ^{18}O) shows only a minor absorption at 1385 cm^{-1} with no new absorption observed, but harmonic oscillator calculations indicate $\nu_{^{18}O_2}$ may be masked by strong porphyrin bands (1306 cm^{-1}).

The remarkable temperature dependence of the observed ν_{O_2} absorption may be accounted for by a rapid thermal equilibrium of several different rotomeric states, each differing slightly in their O_2 stretching frequency. These may be related to structural features such as the two forms of coordinated dioxygen, bumping interactions with the *tert*-butyl methyl groups and thermal motion of the terminal oxygen (as indicated in the crystallographic analysis[5]). Retrospective examination of the 1385-cm^{-1} region in the ir spectrum of the dioxygen complexes, **17** and **18**, at ambient temperature reveals a small, broad peak which may have the same integrated intensity as the very sharp, low temperature absorption.

When comparing the observed ν_{O_2} for dioxygen coordinated in the model Fe(II) complexes, **17** and **18**, to other types of O_2 (Table III), the 1385-cm^{-1} absorption clearly implies a higher O-O bond order than is found in any other O_2 complexes. Since the observed ν_{O_2} is about 100 cm^{-1} below that of singlet oxygen,[53] a reasonable description of the nature of the dioxygen in these oxymyoglobin models would be coordinated singlet (Δ) oxygen, possibly experiencing modest $d\pi-p\pi$ back-bonding from iron to O_2. Caughey recently reported[56] ν_{O_2} for HbO_2 as 1107 cm^{-1}, but the discrepancy with the present work seems too large to be explained by hydrogen bonding from the distal imidazole. A low temperature ir analysis of HbO_2 is planned.

Stability of the Dioxygen Complexes. As outlined above, the remarkable stability of MbO_2 and HbO_2 has been partly attributed to the enveloping protein providing an environment of low dielectric constant[57] and acidity about the heme. Such a medium would presumably hinder paths of irreversible oxidation involving charge separation or protic acids (Scheme VI). The influence of the medium's dielec-

Table III. Comparison of Infrared Oxygen-Stretching Frequencies for Compounds with the O–O Moiety

	ν_{O_2} (cm^{-1})	Ref
O_2(R)	1556	54
$O_2(^1\Delta)$	1483.5	53
FeP(1-MeIm)O_2[a]	1385	Present work
FeP(1-*n*-BuIm)O_2	1385	Present work
KO_2	1145	54
Co(acacen)(B)O_2	1123–1140	51
Co(salen)(py)O_2	1140	52
$(NH_4)HO_2$	836	54
Na_2O_2	738	55

[a] P = $\alpha,\alpha,\alpha,\alpha$-TpivPP.

tric constant and acidity on the stability of the model dioxygen complexes, **17** and **18**, was investigated to help clarify the role of these factors in MbO_2 and HbO_2. Benzene, toluene, DMF, cyclohexene, anisole, DMSO, HMPA, EtOH, and 10% H_2O in DMF, DMSO, and HMPA as solvents all support clean, reversible oxygenation of **12** (5×10^{-5} *M*) (L = 1-MeIm), with no appreciable oxidation at 25°. In addition, DMF solutions containing 0.1 *M* Et_4NClO_4 support reversible oxygenation at 25° (Figure 8) with little oxidation even after 30 hr. Thus it appears that a medium of high dielectric constant does not significantly decrease the stability of heme coordinated dioxygen. Ibers, *et al.*, have shown that polar solvent systems favor oxygen binding to Co(II) porphyrins,[58] a fact not inconsistent with the present observations. Indeed, the amide substituents of the pivalamide picket fence could even serve to help stabilize oxygen coordination in the model Fe(II) complexes, **17** and **18**, though crystallographic analysis[5] precludes any possibility of hydrogen bonding in the solid state. However, the orientation of the amide groups and the possible existence of hydrogen bonding in the complexes in solution have not been determined.

In contrast, acids added to solutions of the model complexes, **17** or **18**, in DMF or THF lead to irreversible oxidation (as followed by visible spectra). Quantitative data have not been obtained but the rates of oxidation are generally proportional to the strength and concentration of acid employed. Ethanol can be used as a solvent to support reversible oxygenation with little oxidation but phenol (pK_a = 9.9) gave rapid oxidation (at 25°, $t_{1/2} \sim 10$ min when 50 equiv are added). The strongest acids used without changing the concentration of free imidazole available for coordination, *vis.*, 1-methylimidazolium tosylate and 1-*n*-butylimidazolium tosylate, also gave irreversible oxidation (at 25°, $t_{1/2} \sim 10$ min, 20 equiv of acid) (Figure 9). Oxidation was essentially instantaneous when acetic acid was employed. The stability of comparable solutions without added acids implies a dramatic antagonistic effect by protic acids. Thus earlier speculation[59] that tyrosine substitution for the distal histidine in hemoglobins Boston and Saskatoon leads to stabilization of Fe(III) might be misleading. The phenolic side chain of tyrosine could simply serve to catalyze irreversible oxidation of Fe(II).

Pauling has suggested[11] that "the positive charge of the distal imidazolium group (of Hb) probably serves, through its electrostatic interaction with the iron atom, to stabilize the bipositive state and assist in preventing oxidation of hemoglobin to ferrihemoglobin." However, in hemoglobin Zurich[59] reversible combination with oxygen occurs despite the replacement of the distal histidine by the larger and strongly basic arginine, which is thought to project outside of the O_2 binding cavity. The model complexes, **12** (L = 1-MeIm, 1-*n*-BuIm), obviously are quite stable in the absence of a "distal" imidazole but the present studies have not otherwise permitted any direct evaluation of the merits of Pauling's[11] suggestion.

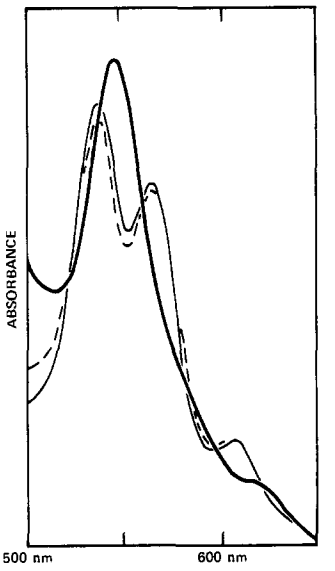


Figure 8. Visible spectrum (25°) of Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(1-MeIm)$_2$ (**12**) (3×10^{-5} *M*) with 1-MeIm (10^{-4} *M*) in DMF containing Et_4NClO_4 (0.1 *M*): (——) under nitrogen, (——) under oxygen (1 atm), (– – –) under nitrogen after two oxygenation-deoxygenation cycles.

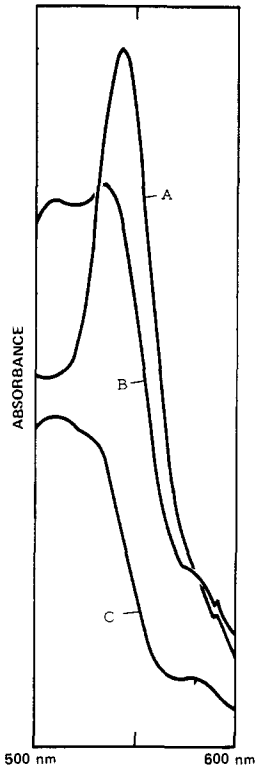


Figure 9. Visible spectrum (25°) of Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(1-*n*-BuIm)$_2$ (**13**) (3×10^{-5} *M*) with 1-*n*-BuIm (10^{-4} *M*) in THF under oxygen (1 atm), before (A) and after ((B) 5 min, (C) 90 min) the addition of 1-*n*-butylimidazolium tosylate (6×10^{-4} *M*).

Carbonyl Complexes and Solid–Gas Reactions. The diamagnetic monocarbonyl complexes Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(L)(CO), **19** (L = 1-MeIm) and **20** (L = 1-*n*-BuIm), were isolated by treating benzene solutions of **12** or **13** with CO. In contrast to the corresponding iron(II) tetraphenylporphyrin system,[60] the picket fence carbonyl complexes, **19** and **20**, are homogeneous, exhibiting a single ν_{CO} peak at 1965 cm^{-1} in close accord with that of HbCO (1970[61] or 1951 cm^{-1} [62]). Preliminary structural analysis[63] reveals the

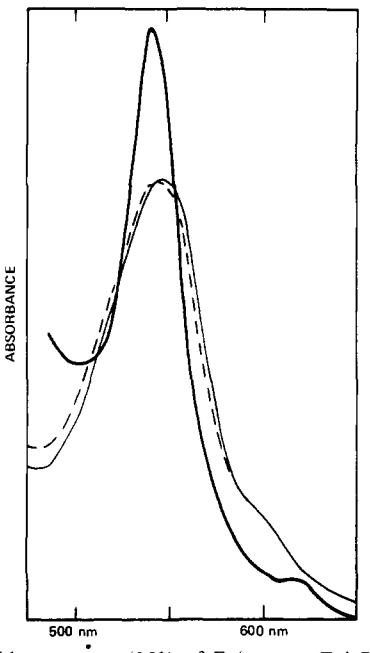
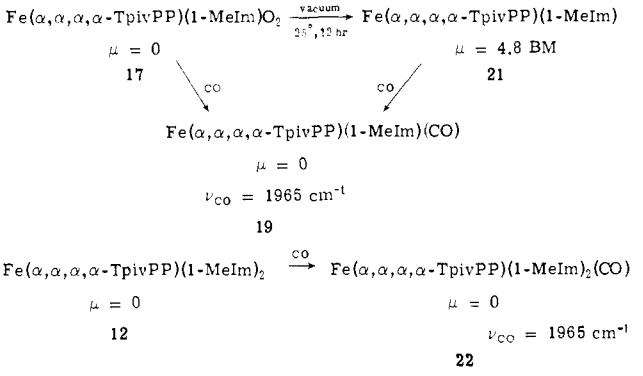


Figure 10. Visible spectrum (25°) of Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP) (**11**) ($5 \times 10^{-5}$ *M*) in THF: (———) under nitrogen, (———) under oxygen (1 atm). (– – – –) under nitrogen after two oxygenation-deoxygenation cycles.

Fe–C–O unit to be colinear, in sharp disagreement with the bent structure proposed[62] for HbCO.

Apparently the crystalline lattice of these "picket fence porphyrins" is highly porous[3b]—permitting rapid gas–solid reactions, as shown in Scheme X and outlined in detail in

Scheme X. Gas–Solid Reactions of Fe(II) Complexes of $\alpha,\alpha,\alpha,\alpha$-$H_2$TpivPP



the Experimental Section. For example the parent diamagnetic dioxygen complex, **17**, loses oxygen under vacuum affording a high spin deoxy compound, **21**, which upon exposure to air again becomes diamagnetic as dioxygen is coordinated. Exposure to carbon monoxide affords the carbonyl, **19**, identical with that prepared in solution. It is intriguing that crystals of the diamagnetic six-coordinate, bisimidazole complex, **12**, also react with CO forming a carbonyl derivative, **22**. Presumably the reaction involves motion of one of the axial 1-MeIm ligands to make room for the CO, a point which remains to be investigated by crystallographic analysis.

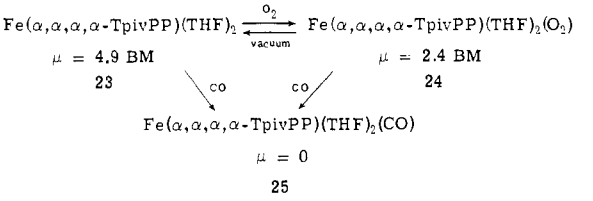
Paramagnetic Dioxygen Complex. Reduction of Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)Br in THF, or recrystallization of the four-coordinate Fe(II) complex, **11**, from THF, yields[3b] paramagnetic (μ = 4.9 BM) Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(THF)$_2$ (**23**).

The Mössbauer spectrum of **23** (Table I) is similar to that of the presumed[44b] five-coordinate Fe(TPP)(THF)$_2$, and solid **23** readily loses 1 equiv of THF while the second seems more firmly bound. These observations are consistent with formulation of **23** as a five-coordinate complex with one THF coordinated to iron(II), the other as a crystal solvate. In dilute (5×10^{-5} *M*) solution at 25°, THF can support reversible oxygenation of **11** with no other added bases (Figure 10), but attempts to isolate the dioxygen complex, from THF solution, led to the irreversibly oxidized [Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)]$_2$O.

The apparent concentration dependence of the rate of oxidation of **23** is consistent with the expected bimolecular nature of the oxidation reaction and emphasizes the difficulty in crystallizing such dioxygen complexes even when physical evidence can be obtained for reversible oxygenation in dilute solutions. The stability of all such iron(II)–dioxygen complexes is kinetic. The rate of irreversible oxidation is affected by temperature, concentrations of iron complex and axial base, and acidity of the medium. Thus in discussions of the "stability" of such complexes all of these factors and the time scale must be clearly noted.

Exposing crystals of the THF complex, **23**, to oxygen or air results in the formation of a new species which is presumed to be the *paramagnetic* dioxygen complex Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(THF)$_2$($O_2$) (**24**) ($\mu$ = 2.4 BM), Scheme XI. Coor-

Scheme XI. Gas–Solid Reactions of Fe(II) Complexes of $\alpha,\alpha,\alpha,\alpha$-$H_2$TpivPP



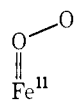
dinated dioxygen can be removed from solid **24** *in vacuo* and the reversible solid state oxygenation was followed through several cycles by monitoring changes in magnetic susceptibility. Addition of pyridine to **24** liberated 0.96 ± 0.05 equiv of oxygen gas. Possible irreversible oxidation affording an Fe(III) complex was ruled out by displacing coordinated dioxygen from **24** with dry CO producing the diamagnetic carbonyl complex Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(THF)$_2$(CO) (**25**). Furthermore, the Mössbauer spectrum of **24** indicated >95% conversion from the deoxy **23**. Thus the observed magnetic moment for **24** seems not to be an artifact from partial oxidation or incomplete oxygenation.

The magnetic moment of this paramagnetic oxygen complex, **24**, at ambient temperature, 2.4 BM, suggests two unpaired electrons, S = 1, and a description as Fe(III) complexed superoxide. Consideration has been given to the possibility of a low lying triplet state at ambient temperature converting to a diamagnetic singlet state at reduced temperatures. However, low temperature (−125°) magnetic susceptibility and Mössbauer (to liquid helium temperatures) studies give no indication of a spin change. Preliminary attempts to obtain an esr spectrum[64a] have not been successful. Low temperature ir spectra[4] of the paramagnetic dioxygen complex, **24**, also show ν_{O_2} at 1385 cm^{-1}, though somewhat reduced in intensity from that of the diamagnetic dioxygen complexes, **17** and **18**. It is remarkable that the diamagnetic dioxygen complexes **17** and **18** and the apparently paramagnetic complex **24** all show a low temperature 1385-cm^{-1} band provisionally assigned to ν_{O_2}. The 1385-cm^{-1} band in the THF complex **24** is much weaker than those in the imidazole dioxygen complexes **17** and **18**. There are several possible explanations of this observation. The paramagnetism of **24** may be an artifact although attempts to find other sources of paramagnetism (*e.g.*, from ferric or chromic impurities) have so far been unsuccessful. At low

temperatures where the ν_{O_2} band is observed some of **24** may be diamagnetic. Lack of suitable low temperature magnetic equipment and problems associated with the facile loss of O_2 from crystals of **24** under vacuum have so far frustrated measurement of μ over a wide temperature range. A superoxide ferric[12] and a dioxygen ferrous complex might coexist in a spin equilibrium involving structurally distinct species. Mössbauer studies of **24** in the presence of an external magnetic field are planned to clarify this point. Some of the oxygen binding sites could lack a coordinate THF and those dioxygen groups might account for this strange result. Structural X-ray diffraction studies of **24** in progress may resolve this point. Recently we have prepared a similar but *diamagnetic* dioxygen complex having tetrahydrothiophene as an axial base and found no detectable low temperature absorption at 1385 cm^{-1}.[64b] Such negative evidence suggests but does not establish the hypothesis that the trans axial base can shift the band we assign to ν_{O_2}.

Conclusion

At present the model systems reported here suggest that molecular oxygen coordinates in the hemoproteins, Hb and Mb, in an angular, end-on fashion, possibly with multiple bond character in the Fe–O bond, as first suggested by Pauling,[11] **26**. Possible H-bonding to dioxygen in the hem-



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oproteins, a full understanding of cooperativity in HbO_2, and satisfactory explanations for the peculiar Mössbauer spectra of HbO_2, are problems which await further resolution. In addition, the exact influence of the trans axial ligand on magnetic properties and on the reduction potential of the dioxygen complexes seems crucial to understanding the more complex oxygenase enzymes, such as cytochrome P_{450}. The latter are thought to have a mercaptan as the axial ligand and rely on a one-electron reduction of the dioxygen complex for enzymic activity.

Experimental Section

All experimental operations with Fe(II) complexes, including the reduction of Fe(III) to Fe(II) were performed in a Vacuum Atmospheres Co. nitrogen atmosphere chamber, unless otherwise noted. Solution spectra in the uv and visible were obtained on a Beckman DB-G or Cary 15 spectrometer in fused silica cells of 1-cm path length, sealed to air, when necessary, with tightly fitting serum caps. Infrared spectra at ambient temperature were obtained as KBr disks or Nujol mulls on a Perkin-Elmer 457 spectrometer. Varian A-60 or T-60 spectrometers were used for the pmr spectra. Elemental analyses were performed by the Stanford Microanalytical Laboratory.

Magnetic susceptibilities of 10–30-mg solid samples at 25° were measured on a Cahn Faraday magnetic susceptibility device, Model 7600, and corrected for the diamagnetic susceptibilities of all ligands using Paschal's constants[66] ($\alpha,\alpha,\alpha,\alpha$-$H_2$TpivPP = 6.08×10^{-4} cgsu/mol). A simple device for examining air-sensitive complexes, essentially a glass hanging tube with a gas inlet, permitted measurements in an argon atmosphere. Virtually all Fe(II) samples which were expected to be diamagnetic were found to exhibit some residual paramagnetism, after magnetic moments were corrected for diamagnetic susceptibilities of ligands. Contamination by Fe(III) or high spin Fe(II) could account for the slight paramagnetism. The present treatment considers all materials with a molar susceptibility of less than $\chi = 5 \times 10^{-5}$ cgs units (corresponding to a magnetic moment μ of 0.35 BM) as essentially diamagnetic. It is to be noted that the magnitude of this "correction" ($\chi = 5 \times 10^{-5}$) is significantly smaller than that of the diamagnetic correction ($\chi = 7 \times 10^{-4}$).

Reagents. All solvents were deaerated before bringing them into the nitrogen chamber by either bubbling prepurified nitrogen through the solvent for 15 min or by distilling the solvent in a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from CaH_2, benzene from Na/K alloy, DMF from 4A molecular sieves, and pyridine and pyrrole from KOH. All solvents were further deoxygenated in the nitrogen chamber by purging with the purified nitrogen (<1 ppm of O_2) in the chamber. Imidazoles, including 1-*n*-butylimidazole[67] (1-*n*-BuIm), 1-tritylimidazole,[67] and 4-*tert*-butylimidazole[68] (4-*t*-BuIm), and $[Cr(acac)_2]_2$[69] were prepared by published methods. Anhydrous $FeBr_2$ (Alfa), 1-methylimidazole (1-MeIm), and all other reagents were used as supplied unless otherwise noted.

Solvate Analyses. The picket fence porphyrins and complexes tend to form solvates or otherwise occlude molecules of solvent. All products were routinely analyzed for solvent by dissolving samples (10 mg) in pyridine (0.1 ml) containing octane as an internal standard followed by quantitative glc analysis of the solution.

Oxygen Analysis. A preweighed sample (50–100 mg) was added to oxygen saturated pyridine (5 ml) and the evolved gas measured *via* a constant pressure gas buret. A separate qualitative experiment utilized helium saturated pyridine to cause evolution of a gas into a helium atmosphere. The identity of the evolved gas as oxygen was confirmed by glc on a 5A molecular sieve column.[70]

meso-Tetra(-nitrophenyl)porphyrin, $H_2T_{NO_2}PP$ (4). *p*-Nitrobenzaldehyde (101 g, 0.67 mol) was dissolved in refluxing glacial acetic acid (2 l.). Pyrrole (46.5 ml, 0.67 mol) was then slowly added to the boiling solution, caution being taken to prevent excessive heating as the reaction is somewhat exothermic. The resulting dark solution was heated under reflux for 20 min, then $CHCl_3$ (250 ml) was added, while the solution was allowed to cool, preventing the separation of tarry by-products. The resulting mixture was cooled by an ice bath to 35° and the purple crystalline product was isolated by suction filtration and washed well with $CHCl_3$ until the washings were essentially colorless (three 100-ml portions). The crude product was dried at 100° for several hours, yield 17.5 g (13.2%). The free porphyrin, $H_2T_{NO_2}PP$, is insoluble in most organic solvents and hence not easily purified. The crude product was used as obtained in further reaction, though no acceptable elemental analysis was obtained: visible spectrum (DMF): 652, 594, 551, 518, 409 nm.

***meso*-Tetra(*o*-aminophenyl)porphyrin, $H_2T_{am}PP$ (5).** The nitroporphyrin, $H_2T_{NO_2}PP$ (12 g), was dissolved in concentrated hydrochloric acid (600 ml) at room temperature, in a 4-l. beaker, followed by the addition of excess $SnCl_2 \cdot 2H_2O$ (50 g). The resulting green mixture was quickly heated to 65–70° for 25 min, then cautiously neutralized with concentrated aqueous ammonia. Chloroform (1 l.) was added to the hot suspension and the mixture stirred for 1 hr. The $CHCl_3$ layer was separated, the aqueous layer extracted several times with $CHCl_3$, and all $CHCl_3$ extracts were combined and filtered. The $CHCl_3$ solution was reduced to a smaller volume (500 ml) on a rotary evaporator, washed first with dilute aqueous ammonia then twice with water and dried over anhydrous sodium sulfate. Ethanol (150 ml) and heptane (100 ml) were added, and the mixture was slowly reduced in volume on a rotary evaporator to produce a very dark purple crystalline product, which was isolated and washed well with methanol, yield 9.2 g (90%). The sample analyzed was recrystallized from $CHCl_3$–MeOH and dried in air. *Anal.* Calcd for $C_{44}H_{34}N_8$: C, 78.5; H, 5.05; N, 16.6. Found: C, 78.3; H, 5.29; N, 16.2. Pmr ($CDCl_3$) δ 3.6 (s, 8 H), 6.8–7.8 (m, 8 H), 9.0 (s, 8 H); visible spectrum ($CHCl_3$) 653, 591, 550, 516, 422 nm.

Separation of $\alpha,\alpha,\alpha,\alpha$-$H_2$TamPP (6). As obtained above, H_2TamPP is a mixture of the four atropisomers in statistical abundance. The most polar, $\alpha,\alpha,\alpha,\alpha$-atropisomer, can be easily separated from the other three atropisomers by tlc (silica gel, 1:1 benzene:ether) as indicated by relative retention factors (atropisomer, R_f: $\alpha,\beta,\alpha,\beta$, 0.77; $\alpha,\alpha,\beta,\beta$, 0.64; $\alpha,\alpha,\alpha,\beta$, 0.43; $\alpha,\alpha,\alpha,\alpha$, 0.04). The mixture of atropisomers was chromatographed twice successively on silica gel columns. The first column effected 90% enrichment of the $\alpha,\alpha,\alpha,\alpha$-atropisomer while the second, shorter column removed all traces of the other three atropisomers.

Column 1. The atropisomeric mixture of H_2TamPP (**5**) (9 g) in $CHCl_3$ was loaded onto a silica gel column (6–7 in. × 2 in., $CHCl_3$). Most of the unwanted three atropisomers passed through this column before it was fully loaded. The column was eluted with $CHCl_3$ until the eluant was light red in color followed by elution

with $CHCl_3$–Et_2O (1:1) until the eluant was very pale in color. Acetone–ether (1:1) was then used to remove the $\alpha,\alpha,\alpha,\alpha$-$H_2$TamPP. The solution containing the 4:0 isomer was brought to dryness on a rotary evaporator with the aid of a luke warm water bath. Care was exercised to prevent excessive heating which leads to isomerization of the $\alpha,\alpha,\alpha,\alpha$-atropisomer.

Column 2. The crude $\alpha,\alpha,\alpha,\alpha$-atropisomer from the first column, dissolved in $CHCl_3$, was loaded onto a silica gel column (5–6 in. × 2 in., $CHCl_3$) then eluted with C_6H_6–Et_2O (1:1) until the eluant was very pale. The pure $\alpha,\alpha,\alpha,\alpha$-$H_2$TamPP was removed by elution with acetone–ether (1:1) and used immediately, in solution, in derivatization, as in the formation of an amide by reaction with an acid chloride. Alternatively, crystalline product could be obtained by evaporating the acetone–ether solution to dryness on a rotary evaporator using a water bath at ambient temperature for heating and a receiving flask cooled in a Dry Ice–acetone bath. The resulting solid was redissolved in $CHCl_3$, methanol added, and the solution similarly carefully reduced in volume on a rotary evaporator to give crystalline product which was isolated, washed well with methanol, and dried in air, yield 0.8 g (9% of the original mixture). When stored in a refrigerator the crystalline material is apparently indefinitely stable to isomerization.

The mixture of the $\alpha,\beta,\alpha,\beta$-, $\alpha,\alpha,\beta,\beta$-, and $\alpha,\alpha,\alpha,\beta$-atropisomers obtained from the first column was reequilibrated to the statistical mixture of four atropisomers in the following way. The combined eluants were heated to a boil under nitrogen, toluene being added as the chloroform and ether evaporated. After the temperature had reached 100°, the mixture was boiled another 30 min then cooled under nitrogen. The resulting solution was used directly, as described above, in the isolation of the tetra-α-atropisomer. Through successive repetitions of this procedure the starting atropisomeric mixture of H_2TamPP was converted to a good overall yield of the desired tetra-α-atropisomer. However, uncharacterized impurities which appear green in solution or on a tlc plate accumulated in the atropisomeric mixture. These were collected during each run of the first column, while eluting with $CHCl_3$–Et_2O, and discarded.

***meso*-Tetra[$\alpha,\alpha,\alpha,\alpha$-*o*-(*p*-toluenesulfonamide)phenyl]porphyrin, $\alpha,\alpha,\alpha,\alpha$-$H_2$TtosPP.** Solid $\alpha,\alpha,\alpha,\alpha$-$H_2$TamPP (**6**) (1 g) was added to a precooled (−79°) solution of excess *p*-toluenesulfonyl chloride (25 g) and pyridine (12 ml) in CH_2Cl_2 (200 ml). The resulting solution was stirred and allowed to warm to the ambient temperature. After 90 min MeOH (10 ml) was cautiously added, with substantial evolution of heat, and the solution was stirred for several hours. Washing with H_2O (three 50-ml portions) gave a dark purple organic layer which was reduced in volume to about 50 ml on a rotary evaporator. Addition of MeOH (50 ml) followed by slow removal of solvent on a rotary evaporator at the ambient temperature produced crude product as fine red-purple crystals (1.6 g) which was recrystallized from CH_2Cl_2–MeOH (1.4 g, 75% overall yield). The porphyrin is very hygroscopic and satisfactory elemental analyses were not obtained: visible spectrum ($CHCl_3$) 650, 564, 510, 421 nm; pmr ($CDCl_3$) δ 2.45 (s, 12 H), 6.15 (s, 4 H), 7.0–8.5 (m, 42 H).

Bromo[*meso*-tetra[$\alpha,\alpha,\alpha,\alpha$-*o*-(*p*-toluenesulfonamide)phenyl]porphyrin]iron(III), Fe($\alpha,\alpha,\alpha,\alpha$-TtosPP)Br. Anhydrous $FeBr_2$ (1.7 g) and $\alpha,\alpha,\alpha,\alpha$-$H_2$TtosPP (1.7 g) were heated to reflux, under nitrogen, in dry THF (300 ml). The progress of the reaction was followed by examining the visible spectrum in the Soret region of aliquots of the solution, made acidic with dilute HBr (as described for the synthesis of Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)Br). After 2.25 hr the mixture was brought to dryness on a rotary evaporator, and the residue was extracted with $CHCl_3$. The $CHCl_3$ solution was treated with concentrated aqueous KOH (2 ml), the mixture stirred for 1 min, then dried over anhydrous Na_2SO_4. The solution was reduced to a small volume on a rotary evaporator and poured directly onto a small (3 in. × 1 in.) neutral alumina column. Elution with $CHCl_3$ gave one broad band which was collected and reduced to a small volume (20 ml) on a rotary evaporator. Addition of MeOH (10 ml) and concentrated HBr (3–4 drops) followed by slow removal of solvent, at ambient temperature, on a rotary evaporator produced very fine black-purple crystals (1.55 g, 82%). *Anal.* Calcd for $C_{72}H_{56}N_8S_4O_8FeBr$: C, 60.65; H, 3.95; N, 7.85; Fe, 3.9. Found: C, 60.3; H, 4.1; N, 7.9; Fe, 3.95. The compound is somewhat hygroscopic: visible spectrum ($CHCl_3$) 650, 564, 510, 421 nm.

Mono(tetrahydrofuran)-*meso*-tetra[$\alpha,\alpha,\alpha,\alpha$-*o*-(*p*-toluenesulfonamide)phenyl]porphyriniron(II), Fe($\alpha,\alpha,\alpha,\alpha$-TtosPP)(THF) (7). Solid $[Cr(acac)_2]_2$ (0.5 g) was added to a hot mixture of Fe($\alpha,\alpha,\alpha,\alpha$-TtosPP)Br (1 g) in THF (80 ml), the mixture boiled and stirred for several minutes then was filtered hot. After cooling to ambient temperature EtOH (100 ml) was added and the volume of the solution was reduced by about 10% *via* partial vacuum and gentle heating. After 12 hr fine dark purple crystals were isolated by suction filtration and washed with EtOH. A second crop of bright purple powder (0.5 g) was obtained by addition of heptane. *Anal.* Calcd for $C_{76}H_{64}N_8O_9S_4Fe$: C, 64.4; H, 4.55; N, 7.9. Found: C, 64.2; H, 4.7; N, 7.95. One equivalent of THF was confirmed by glc solvent analysis as described above: visible spectrum (C_6H_6) 613, 538, 440 nm.

Bis(4-*tert*-butylimidazole)-*meso*-tetra[$\alpha,\alpha,\alpha,\alpha$-*o*-(*p*-toluenesulfonamide)phenyl]porphyriniron(II), Fe($\alpha,\alpha,\alpha,\alpha$-TtosPP)(4-*t*-BuIm)$_2$. Solid Fe($\alpha,\alpha,\alpha,\alpha$-TtosPP)(THF) (0.1 g) in the minimum amount of C_6H_6 needed to effect solution was treated with 4-t-BuIm (30 mg). The solution was filtered and heptane was added to the mother liquor to precipitate the product. The resulting essentially diamagnetic dark purple powder was filtered off and washed with C_6H_6–heptane (1:4) and heptane, yield 70 mg (62%). *Anal.* Calcd for $C_{86}H_{80}N_{12}O_8S_4Fe$: C, 64.8; H, 5.05; N, 10.55. Found: C, 65.65; H, 5.41; N, 10.25.

Bis(1-methylimidazole)-*meso*-tetra[$\alpha,\alpha,\alpha,\alpha$-*o*-(*p*-toluenesulfonamide)phenyl]porphyriniron(II), Fe($\alpha,\alpha,\alpha,\alpha$-TtosPP)(1-MeIm)$_2$. This essentially diamagnetic complex was prepared as for the 4-t-BuIm complex above, yield 60 mg (57%). *Anal.* Calcd for $C_{80}H_{68}N_{12}O_8S_4Fe$: C, 63.65; H, 4.55; N, 11.15. Found: C, 63.1; H, 4.55; N, 11.10.

***meso*-Tetra($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl)porphyrin *N′,N″:N‴,N⁗*-Diisophthalamide, $\alpha,\alpha,\alpha,\alpha$-$H_2$TphthPP (8).** The reaction was carried out under rigorously dry conditions in the nitrogen atmosphere chamber using glassware which had been flamed, then cooled, under dry nitrogen. Isophthaloyl chloride (1.2 g) in THF (200 ml) was slowly added, with stirring, to a solution of $\alpha,\alpha,\alpha,\alpha$-$H_2$TamPP (**6**) (0.5 g) in THF (250 ml). After additional stirring at ambient temperature (30 min) the solution was removed from the nitrogen chamber, concentrated aqueous Na_2CO_3 was added until the green solution turned deep purple, and the resulting mixture was stripped to dryness. The residue was taken up in $CHCl_3$, washed with H_2O (three 100-ml portions), reduced to a small volume, and purified by chromatography on a silica gel column ($CHCl_3$), eluting with Et_2O–$CHCl_3$ (1:4). The single bright purple band which developed was collected and the product crystallized by evaporation of $CHCl_3$ and addition of MeOH, yield 0.44 g (57%) of bright purple powder. *Anal.* Calcd for $C_{60}H_{38}N_8O_4\cdot CHCl_3$: C, 69.5; H, 3.75; N, 10.65; Cl, 10.0. Found: C, 69.45; H, 4.0; N, 10.9; Cl, 9.6; $CHCl_3$ (by glc), 0.95 ± 0.1 equiv. Pmr ($CDCl_3$) δ 1.55 (s, 2 H), 7.0–8.2 (m, 24 H), 8.3–8.7 (m, 4 H), 8.9–9.3 (m, 8 H); visible spectrum ($CHCl_3$) 654, 600, 563, 525, 428 nm.

Bromo[*meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl)porphyrin *N′,N″:N‴,N⁗*-diisophthalamide]iron(III), Fe($\alpha,\alpha,\alpha,\alpha$-TphthPP)Br. Anhydrous $FeBr_2$ (0.1 g) and $\alpha,\alpha,\alpha,\alpha$-TphthPP (**8**) (0.1 g) were heated at reflux, under nitrogen, in a mixture of $CHCl_3$ (40 ml) and THF (120 ml) for 2 hr. Progress of the reaction was monitored by observation of the protonated porphyrin Soret band at 448 nm as described for Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)Br. The solvent was removed, the residue dissolved in $CHCl_3$ (100 ml), and the resulting solution treated with concentrated aqueous KOH (2 ml). After stirring for a few minutes, the mixture was dried over Na_2SO_4 and the solution reduced to a small volume and chromatographed on neutral alumina. Elution with $CHCl_3$ gave a single dark green-brown band which was collected and acidified with a few drops of concentrated HBr. Addition of MeOH and slow removal of solvent under vacuum gave a purple-black crystalline product, yield 78 mg (77%). *Anal.* Calcd for $C_{60}H_{38}N_8O_4FeBr\cdot 0.25CHCl_3$: C, 65.75; H, 3.50; N, 10.2. Found: C, 65.7; H, 3.55; N, 10.3; $CHCl_3$ (by glc), 0.23 ± 0.1 equiv. Visible spectrum ($CHCl_3$): 511, 427 nm.

Tetrahydrofuran[*meso*-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl)porphyrin *N′,N″:N‴,N⁗*-diisophthalamide]iron(II), Fe($\alpha,\alpha,\alpha,\alpha$-TphthPP)(THF) (9). Solid Fe($\alpha,\alpha,\alpha,\alpha$-TphthPP)Br (0.1 g) and $[Cr(acac)_2]_2$ (50 mg) were boiled gently in THF (50 ml) for several minutes. The solution was allowed to cool, heptane (40 ml) was added, and the mixture was stirred gently for 3 hr. The purple product (70 mg) was filtered off and washed well with heptane–THF (3:1). The complex is very air sensitive and a satisfactory elemental anal-

ysis could not be obtained.

All solution spectral studies utilized 5×10^{-5} *M* benzene solutions of this complex with excess of the added axial base.

***meso*-Tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrin, α,α,α,α-$H_2T_{piv}PP$ (10).** Pivaloyl chloride (5 ml) and pyridine (5 ml) were added to the acetone–ether solution of α,α,α,α-H_2TamPP (**6**) resulting from the second silica gel column, as described above. The mixture was stirred for 1 hr at ambient temperature, then brought to dryness on a rotary evaporator. The resulting solid was dissolved in $CHCl_3$ and the $CHCl_3$ solution was washed first with dilute aqueous ammonia then twice with water. After drying over anhydrous sodium sulfate and reducing the volume on a rotary evaporator, the product was purified by chromatography on a silica gel column (75 g, $CHCl_3$), eluting with 4:1 $CHCl_3$–Et_2O, followed by recrystallization from $CHCl_3$–EtOH–heptane, yield 1 g (84%). *Anal.* Calcd for $C_{64}H_{66}N_8O_4$: C, 76.2; H, 6.6; N, 11.2. Found: C, 75.7; H, 6.75; N, 11.15. Pmr ($CDCl_3$) δ 0.05 (s, 36 H), 7.1–8.1 (m, 18 H), 8.7 (s, 4 H), 8.9 (s, 8 H); visible spectrum ($CHCl_3$) 641, 587, 544, 512, 420 nm.

Bromo[*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrin]iron(III), Fe(α,α,α,α-TpivPP)Br. Solid α,α,α,α-TivPP (**10**) (3 g), pyridine (1 ml), and anhydrous $FeBr_2$ (3 g) in THF (200 ml) were heated to reflux under nitrogen. The progress of the reaction was conveniently followed by examining the visible spectrum in the Soret region of aliquots of the solution, made acidic with dilute HBr. The 445-nm absorption, attributed to α,α,α,α-$H_4TpivPP^{2+}$, decreased in intensity and the 418-nm absorption, due to Fe(α,α,α,α-TpivPP)Br, increased in intensity as the reaction proceeded. The reaction was finished after 1 hr when there was no sign of any remaining free porphyrin. The mixture was then brought to dryness on a rotary evaporator and extracted with $CHCl_3$ and the resulting solution was chromatographed on a column of basic alumina (250 g), eluting with $CHCl_3$. The first and second fractions coming off of the column, Fe(α,α,α,α-TpivPP)Br and [Fe(α,α,α,α-TpivPP)]$_2$O, respectively, were combined, treated with concentrated HBr (1 ml), dried over anhydrous sodium sulfate, filtered, and brought to dryness on a rotary evaporator. The purple solid was dissolved in CH_2Cl_2, MeOH was added and the solution was very slowly reduced in volume on a rotary evaporator to give microcrystalline product. A second crop was obtained by addition of heptane and further evaporation, yield 2.5 g (75%). *Anal.* Calcd for $C_{64}H_{64}N_8O_4FeBr \cdot 0.5CH_2Cl_2$: C, 65.3; H, 5.4; N, 9.45; Fe, 4.9; Br, 6.9. Found: C, 65.45; H, 5.7; N, 9.5; Fe, 4.55; Br, 7.0. μ = 5.9 BM at 25°; visible spectrum ($CHCl_3$) 675, 648, 578, 508, 418 nm.

μ-Oxo-bis[*meso*-tetra(α,α,α,α-*o*-pivamidophenyl)porphyriniron(III)], [Fe(α,α,α,α-TpivPP)]$_2$O. Solid Fe(α,α,α,α-TpivPP)Br (0.5 g) in a mixture of CH_2Cl_2 (25 ml) and MeOH (10 ml) was treated with dilute aqueous NaOH (1 ml). The solution was slowly reduced in volume on a rotary evaporator to produce very dark purple, nearly black, product which was isolated by suction filtration, washed with MeOH and heptane, and dried in air. *Anal.* Calcd for $C_{128}H_{128}N_{16}O_9Fe_2$: C, 71.5; H, 6.0; N, 10.45; Fe, 5.2. Found: C, 71.6; H, 6.0; N, 10.35; Fe, 5.1. Visible spectrum ($CHCl_3$) 575, 408 nm.

***meso*-Tetra(α,α,α,α-*o*-pivalamidophenyl)porphyriniron(II), Fe(α,α,α,α-TpivPP) (11).** Solid Fe(α,α,α,α-TpivPP)Br (1 g) in warm benzene (20 ml) was treated with [Cr(acac)$_2$]$_2$ (0.35 g) and the mixture was heated and stirred for a few minutes. The red solution was filtered hot, heptane (10 ml) was added, and the mixture was cooled slowly so as to allow crystallization. More heptane (40 ml) was added, in small increments, during the period of an hour. The product was isolated by suction filtration, washed with benzene–heptane (1:2) and heptane, and dried in the atmosphere of the inert atmosphere box, yield 0.8 g (86%). The product is highly air sensitive, both in solution and in the solid state and was stored in closed vials in the nitrogen chamber until needed. The great air sensitivity precluded elemental analysis but the mass spectrum did show a parent ion at 1065 amu: μ = 5.3 BM at 25°; visible spectrum (C_6H_6) 538, 440 nm.

Bis(tetrahydrofuran)-*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyriniron(II), Fe(α,α,α,α-TpivPP)(THF)$_2$ (23). Solid Fe(α,α,α,α-TpivPP)Br (1 g) and [Cr(acac)$_2$]$_2$ (0.35 g) were heated together in THF (35 ml) for a few minutes; the resulting red solution was filtered hot, heptane (10 ml) was added, and the mixture was cooled slowly with stirring to the ambient temperature. More heptane (60 ml) was added in small increments in the course of 1 hr before isolating the crystalline product by suction filtration and washing with THF–heptane (1:3), then heptane, yield 0.85 g (80%). The solid complex reacts with oxygen in air so only the derivative dioxygen complex, described below, was subjected to elemental analysis. However, glc solvent analysis confirmed the presence of 2.0 ± 0.2 equiv of THF: μ = 4.9 BM at 25°, under nitrogen: visible spectrum (THF) 590, 545, 422 nm (Figure 8).

Bis(substituted imidazole)-*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyriniron(II), Fe(α,α,α,α-TpivPP)B_2. All of these complexes were prepared in essentially the same manner. Fe(α,α,α,α-TpivPP), **11**, or Fe(α,α,α,α-TpivPP)(THF)$_2$ was dissolved in the appropriate solvent containing a fivefold excess of the requisite substituted imidazole. Excess heptane was then slowly added with stirring, usually over the course of 1 hr, to effect crystallization of the desired complex which was then isolated by suction filtration and washed with heptane. The crystalline complexes, all essentially diamagnetic, were stable to oxidation in air and were routinely analyzed for solvent of crystallization; visible spectra data are given in Table II.

Fe(α,α,α,α-TpivPP)(1-MeIm)$_2$ (12). Tetrahydrofuran was used as a solvent to give a 95% yield of complex containing no solvate. *Anal.* Calcd for $C_{72}H_{76}N_{12}O_4Fe$: C, 70.2; H, 6.35; N, 13.6; Fe, 4.55. Found: C, 70.0; H, 6.6; N, 13.65; Fe, 4.3.

Fe(α,α,α,α-TpivPP)(1-*n*-BuIm)$_2$ (13). This complex has a tendency to form oils but can be isolated by slowly cooling hot saturated THF–heptane solutions. *Anal.* Calcd for $C_{78}H_{88}N_{12}O_4Fe$: C, 71.3; H, 6.7; N, 12.8; Fe, 4.25. Found: C, 71.2; H, 6.7; N, 12.6; Fe, 4.1.

Fe(α,α,α,α-TpivPP)(*N*-tritylIm)$_2$ (14). This complex is very soluble and difficult to crystallize, having a high tendency to form oils. The complex was isolated from dimethoxyethane–heptane. *Anal.* Calcd for $C_{108}H_{100}N_{12}O_4Fe$: C, 76.9; H, 6.0; N, 10.0. Found: C, 76.2; H, 6.1; N, 9.9.

Fe(α,α,α,α-TpivPP)(4-*t*-BuIm)$_2$ (15). The complex was isolated from benzene–heptane solution. *Anal.* Calcd for $C_{78}H_{88}N_{12}O_4Fe \cdot 0.5\ C_6H_6$: C, 71.8; H, 6.9; N, 12.4. Found: C, 72.2; H, 7.05; N, 12.6; C_6H_6 (by glc), 0.5 ± 0.1 equiv.

Ethanol[mono(1-methylimidazole)-*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrin]iron(II), Fe(α,α,α,α-TpivPP)(1-MeIm)(EtOH) (16). Solid Fe(α,α,α,α-TpivPP)(1-MeIm)$_2$ (**12**) (0.2 g) was dissolved in hot EtOH (50 ml), the solution filtered while still hot and then cooled to the ambient temperature to produce minute purple crystalline crowns. The product was isolated, washed with ethanol, and dried under nitrogen; μ = 4.8 BM, 25°. *Anal.* Calcd for $C_{68}H_{70}N_{10}O_4Fe \cdot C_2H_6O$: C, 70.4; H, 6.4; N, 11.7; Fe, 4.8. Found: C, 69.9; H, 6.3; N, 11.8; Fe, 4.5; EtOH (by glc), 0.92 ± 0.1 equiv. Visible spectrum (EtOH–C_6H_6) 555, 540 nm.

Dioxygen[mono-1-methylimidazole-*meso*-tetra)α,α,α,α-*o*-pivalamidophenyl)porphyrin]iron(II). Fe(α,α,α,α-TpivPP)(1-MeIm(O$_2$) (17). Solid Fe(α,α,α,α-TpivPP)(1-MeIm)$_2$ (**12**) (0.4 g, 0.32 mmol) and excess 1-MeIm (0.5 drops, 0.32 mmol) were dissolved in benzene (80 ml), under nitrogen, gentle heating being used to effect complete solution. The deep red solution was cooled to ambient temperature and removed from the drybox. Oxygen was bubbled into the solution, crystallization ensuing after a few moments. Heptane (5 ml) was slowly added with stirring followed by more heptane (20 ml) 15 min later. The product was isolated by suction filtration, washed well with benzene–heptane (1:4) and heptane, and dried in air, yield 0.36 g (94%). *Anal.* Calcd for $C_{68}H_{70}N_{10}O_6Fe \cdot 0.75C_6H_6$: C, 70.2; H, 6.2; N, 11.3; Fe, 4.5. Found: C, 70.1; H, 6.3; N, 11.15; Fe, 4.5; C_6H_6 (by glc), 0.8 ± 0.1 equiv. Quantitative gas evolution indicated 0.96 ± 0.05 equiv oxygen, confirmed to be oxygen by glc.

The complex was also obtained from toluene and analyzed. *Anal.* Calcd for $C_{68}H_{70}N_{10}O_6Fe \cdot 0.5C_7H_8$: C, 70.1; H, 6.05; N, 11.45; Fe, 4.6. Found: C, 70.05; H, 6.2; N, 11.45; Fe, 4.4; C_7H_8 (by glc), 0.45 ± 0.1 equiv.

The complex isolated from THF also formed as a solvate. *Anal.* Calcd for $C_{68}H_{70}N_{10}O_6Fe \cdot THF$: C, 69.1; H, 6.2; N, 11.2; Fe, 4.5. Found: C, 68.8; H, 6.4; N, 11.35; Fe, 4.4; THF (by glc), 0.85 ± 0.1 equiv. The compound is essentially diamagnetic and apparently indefinitely stable in the solid state.

Dioxygen[mono-1-*n*-butylimidazole-*meso*-tetra)α,α,α,α-*o*-pivalamidophenyl)porphyrin]iron(II), Fe(α,α,α,α-TpivPP)(1-*n*-BuIm-(O$_2$) (18). This complex was prepared from THF in a fashion analogous to that of the 1-MeIm complex, **17**. However, it is more soluble and more difficult to crystallize than the 1-MeIm complex.

Anal. Calcd for $C_{71}H_{76}N_{10}O_6Fe$: C, 69.8; H, 6.25; N, 11.5; Fe, 4.6. Found: C, 69.9; H, 6.4; N, 11.4; Fe, 4.4. Quantitative analysis indicated 0.95 ± 0.05 equiv of oxygen, confirmed to be oxygen by glc.

Carbonyl[mono-1-methylimidazole-*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrin]iron(II), Fe(α,α,α,α-TpivPP)(1-MeIm)(CO) (19). Solid Fe(α,α,α,α-TpivPP)(1-MeIm)$_2$ (**12**) (0.35 g) and excess 1-MeIm (0.5 drop) were dissolved in THF (30 ml), and the solution was removed from the drybox under nitrogen. Carbon monoxide was bubbled into the solution resulting in immediate crystallization. Heptane (50 ml) was slowly added, with stirring, and 30 min later the purple product was isolated, washed with THF—heptane (1:4) and heptane and dried in air, yield 0.3 g (90%). The essentially diamagnetic complex has ν_{CO} = 1965 cm^{-1}. *Anal.* Calcd for $C_{69}H_{70}N_{10}O_5Fe$: C, 70.5; H, 6.2; N, 11.9; Fe, 4.8. Found: C, 70.6; H, 6.4; N, 12.1; Fe, 4.6.

Carbonyl[mono-1-*n*-butylimidazole-*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrin]iron(II), Fe(α,α,α,α)-TpivPP)(1-*n*-BuIm)(CO) (20). This complex is more soluble than the corresponding 1-MeIm complex but was prepared in an analogous fashion from benzene-heptane. *Anal.* Calcd for $C_{72}H_{76}N_{10}O_5Fe$: C, 71.0; H, 6.25, N, 11.5; Fe, 4.6. Found: C, 70.75; H, 6.35; N, 11.55; Fe, 4.5. ν_{CO} = 1965 cm^{-1}.

Mono-1-methylimidazole-*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyriniron(II), Fe(α,α,α,α-TpivPP)(1-MeIm) (21). The dioxygen complex, Fe(α,α,α,α-TpivPP)(1-MeIm)O_2 (**17**), was evacuated at 10^{-4} Torr for 12 hr. During evacuation the solid turned from bright burgundy to dark red in color, accompanied by a change in magnetic susceptibility from diamagnetic to high spin Fe(II) (4.8 BM).

Exposing the paramagnetic complex, **21**, to oxygen afforded the dioxygen complex, **17**, while carbon monoxide gave the carbonyl Fe(α,α,α,α-TpivPP)(1-MeIm)CO (**19**).

Carbonyl[bis(1-methylimidazole)-*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrin]iron(II), Fe(α,α,α,α-TpivPP)(1-MeIm)$_2$-(CO) (22). Solid Fe(α,α,α,α-TpivPP)(1-MeIm)$_2$ was exposed to 1 atm of CO for 12 hr. The reaction was monitored by the appearance of ν_{CO} = 1965 cm^{-1}. Elemental analysis confirmed the presence of 2 equiv of 1-MeIm in the essentially diamagnetic product. *Anal.* Calcd for $C_{73}H_{76}N_{12}O_5Fe$: C, 69.4; H, 6.2; N, 13.3; Fe, 4.45. Found: C, 69.3; H, 6.4; N, 13.3; Fe, 4.3.

Dioxygen[bis(tetrahydrofuran)-*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porpyrin]iron(II), Fe(α,α,α,α-TpivPP)(THF)$_2$(O$_2$) (24). This complex was formed in the solid state simply by exposing Fe(α,α,α,α-TpivPP)(THF)$_2$ to dry air or pure oxygen for at least 1 day. The reaction was monitored by a change in the observed magnetic moment from 4.9 BM for the starting Fe(α,α,α,α-TpivPP)(THF)$_2$ to 2.4 BM for the product dioxygen complex. *Anal.* Calcd for $C_{72}H_{80}N_8O_8Fe$: C, 69.7; H, 6.45; N, 9.0; Fe, 4.5. Found: C, 69.8; H, 6.45; N, 8.9; Fe, 4.4; THF (by glc), 1.8 ± 0.1 equiv. Quantitative gas evolution indicated 0.96 ± 0.05 equiv of oxygen confirmed to be oxygen by glc.

Carbonyl[bis(tetrahydrofuran)-*meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrin]iron(II), Fe(α,α,α,α-TpivPP)(THF)$_2$(CO) (25). Solid Fe(α,α,α,α-TpivPP)(THF)$_2$ (**23**) was exposed in the solid state to 1 atm of dry CO for 6–8 hr. The reaction was monitored by changes in the magnetic moment from the paramagnetism (μ = 4.9 BM) of the starting material to the diamagnetism of the product and by the appearance of a strong carbonyl stretch in the ir (ν_{CO} = 1955 cm^{-1}). *Anal.* Calcd for $C_{73}H_{80}N_8O_7Fe$: C, 70.9; H, 6.5; N, 9.05; Fe, 4.5. Found: C, 70.8; H, 6.5; N, 9.1; Fe, 4.2; THF (by glc) 1.85 ± 0.1 equiv. This product was also prepared by similar treatment of solid Fe(α,α,α,α-TpviPP)(THF)$_2$(O$_2$) (**24**) with CO (1 atm, 12 hr).

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(1) (a) Stanford University. (b) The Pennsylvania State University. (c) The University of Canterbury.
(2) Coordinated molecular oxygen is referred to as the dioxygen ligand. Abbreviations used in this paper include: α,α,α,α-H_2TpivPP, *meso*-tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrin; H_2TPP, *meso*-tetraphenylporphyrin; Mb, myoglobin; Hb, hemoglobin; Im, imidazole; py, pyridine; THF, tetrahydrofuran; DMF, *N,N*-dimethylformamide; EtOH, ethanol; Et_2O, diethyl ether; MeOH, methanol.
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Bis(η^5-cyclopentadienyl)vanadium Tetrahydroborate. A Covalent Organotransition Metal Borohydride with Unusual Spectroscopic and Dynamic Properties

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Abstract: The synthesis and spectroscopic (vibrational, nmr) characterization of $(\eta^5\text{-}C_5H_5)_2VBH_4$ are described. In comparison to $(\eta^5\text{-}C_5H_5)_2TiBH_4$, both $(C_5H_5)_2VBH_4$ and $(C_5H_5)_2NbBH_4$, which also have bidentate MH_2BH_2 ligation, appear to be more covalent and show considerable weakening of B–H bridging bonds and possibly some strengthening of M–H bonds in the vibrational spectra. In addition, the free energy barrier to bridge–terminal hydrogen interchange is surprisingly high for the vanadium compound ($\Delta G^{\ddagger} \approx 7.6 \pm 0.3$ kcal/mol) and the fluxional behavior can be slowed on the nmr time scale. The permutation process is too rapid to slow in the niobium compound, and the reasons for the difference in rate are discussed in terms of the proposed rearrangement mechanism and the size of the metal ion.

It has been recently noted[3] that the tetrahydroborate ligand, BH_4,[4] appears to be in some ways electronically analogous to multihapto organometallic ligands such as η^3-allyl. The degree to which this might be so, and the fact that the structural and dynamic features of metal–BH_4 coordination may shed light on hydrogen transfer processes involving transition metals, has prompted our further exploration of this area. We report here the synthesis and some unusual spectroscopic and dynamic characteristics of the new compound $(\eta^5\text{-}C_5H_5)_2VBH_4$. Vanadium(III) formally possesses a d^2 electronic configuration and this new compound provides an especially informative comparison to the closely related, and structurally well-characterized, titanium(III) (d^1) complex $(\eta^5\text{-}C_5H_5)_2TiBH_4$.[5] Contrast is also made with the recently noted[6] compound $(\eta^5\text{-}C_5H_5)_2NbBH_4$. The results we present here further elaborate the electronic versatility of the tetrahydroborate functionality as a ligand, demonstrate that vibrational spectra can yield important information on bonding trends in such complexes, and provide the first evidence that differences in metal–ligand bonding can have an appreciable influence on the molecular dynamics.

Experimental Section

The synthesis and manipulation of all organometallics was necessarily carried out in an atmosphere of prepurified nitrogen or argon, with rigorous exclusion of air and moisture. Samples were handled by Schlenk methodology or in a glove box. All solvents were thoroughly dried in a manner appropriate to each and were distilled under nitrogen immediately prior to use. Melting points were determined in sealed, nitrogen-filled capillaries and are uncorrected. The reagent $(C_5H_5)_2VCl_2$ was prepared by the general method of Wilkinson and Birmingham[7] or was purchased from Pressure Chemical Co., Pittsburgh Pa.

Bis(η^5-cyclopentadienyl)tetrahydroboratovanadium(III). To 2.30 g (9.13 mmol) of $(C_5H_5)_2VCl_2$ in 200 ml of dimethoxyethane at −10° was added 1.03 g (27.2 mmol) of $NaBH_4$. The reaction mixture was stirred for 12 hr at −10°, during which time the color changed from dark green to dark violet. The reaction mixture was then suction filtered under nitrogen and the solvent removed under high vacuum. The residue was transferred to a sublimer and subli-