

Synthesis and Mossbauer Spectra of Octaethylporphyrin Ferrous Complexes

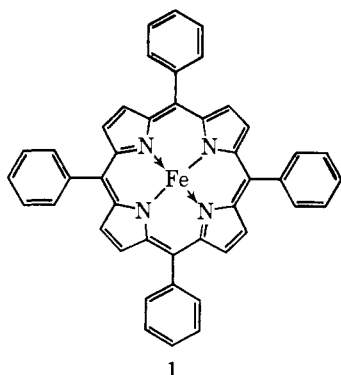
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Abstract: The preparation of the square planar complex octaethylporphyriniron(II), Fe(OEP), is reported. As in tetraphenylporphyriniron(II) and phthalocyanineiron(II), the ferrous ion in Fe(OEP) appears to be in the intermediate spin ($S = 1$) state. The hexacoordinate adducts of Fe(OEP) with pyridine, ammonia, 3- and 4-picoline are all diamagnetic. Mossbauer spectra have been measured between 4.2 and 300 K, and in applied magnetic fields of up to 50 kG. In every case the quadrupole coupling constant is positive and the electric field gradient at iron is axially symmetric. The nearly temperature-independent quadrupole splitting in Fe(OEP) suggests there are no low-lying excited orbital states in this complex. Comparisons of the Mossbauer parameters reported here with data for related ferrous porphyrin and phthalocyanine complexes provide insight into the σ and π bonding characteristics of the tetradentate ligands.

Synthetic iron porphyrins of unusual coordination or oxidation state are of interest both from the preparative point of view and as regards the detailed electronic structure of the central metal ion and their relationship to biological function. Since in most cases electron spin resonance cannot be observed in ferrous complexes, Mossbauer spectroscopy offers the only direct method of obtaining such structural details of the iron atom in ferrous porphyrins.

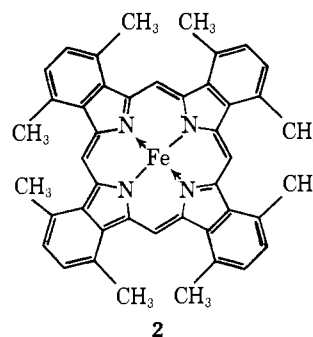
Owing to the difficulty in isolating ferrous porphyrins in the solid state, few applications of Mossbauer spectroscopy to such systems have been reported to date. Epstein et al.¹ studied some hexacoordinate adducts of the type FeLX₂, where L was either protoporphyrin IX (PP) or *meso*-tetraphenylporphine (TPP), and X = pyridine (py), piperidine (pip), and imidazole (im). Only Fe(TPP)(pip)₂ was isolated and characterized, the her complexes being studied as frozen solutions. Fe(TPP), **1**, was



the first example of a ferrous porphyrin to be isolated in the solid state without additional ligands in the axial coordination sites, and its preparation was reported independently by two groups.^{2,3} Kobayashi et al.⁴ have studied Fe(TPP) and its bis adducts with tetrahydrofuran (THF) and pyridine in the solid state, using Mossbauer and susceptibility measurements. These authors⁴ and Husain and Jones⁵ reported a magnetic moment of about 4.7 μ_B for Fe(TPP), and have assumed that the ferrous ion has a high-spin ($s = 2$) ground state. These results are not in agreement with the recent work of Collman et al.,⁶ who found the moment to be 4.4 μ_B . On the basis of Mossbauer and x-ray crystallographic data the latter authors⁶ have shown that the ferrous ion in Fe(TPP) is in the rare intermediate-spin ($S = 1$) state. The Mossbauer isomer shift at room temperature is 0.42 mm/s (relative to metallic iron), and the quadrupole splitting is 1.52 mm/s and independent of temperature. The x-ray data indicate that the iron(II) and the four porphyrinato nitrogen atoms are coplanar.

Kobayashi et al.⁴ have assigned an intermediate-spin ground state to iron in Fe(TPP)(THF)₂, but there is considerable doubt that this was the actual compound studied by them. In addition to the poor analytical data given in ref 4, the quoted room temperature magnetic moment (2.75 μ_B) is very different from that reported for this complex by Collman and Reed³ (5.1 μ_B). Moreover, in view of the facile oxidation of Fe(TPP) derivatives and recent Mossbauer data for several oxo-bridged ferric porphine dimers,⁷ we suspect that the compound studied⁴ was in fact μ -O[Fe(TPP)]₂. However, there is agreement²⁻⁴ that Fe(TPP)(py)₂ contains low-spin ($S = 0$) iron(II), as does⁶ Fe(TPP)(pip)₂.

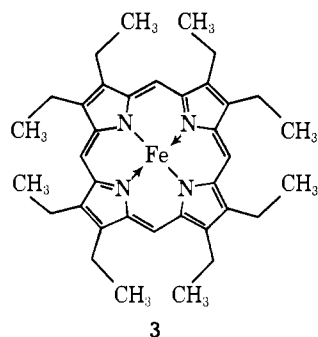
Only two tetracoordinate ferrous porphyrin complexes other than Fe(TPP) have been reported: the so-called "picket-fence" porphyrin tetra($\alpha, \alpha, \alpha, \alpha$ -orthopivalamide)phenylporphineiron(II)⁸⁻¹⁰ and octamethyltetraethylporphyriniron(II)¹¹ (Fe(OTBP), **2**). The former complex contains⁶ high-spin



iron(II) and has Mossbauer parameters¹² typical of this spin state. Similar results have been obtained for the pentacoordinate (2-MeIm)Fe(TPP)·C₂H₅OH (2-MeIm = 2-methylimidazole)⁶ and the hexacoordinate Fe(OTBP)(THF)₂,¹¹ where the magnetic moments of 5.2 and 5.4 μ_B , respectively, are typical of $S = 2$ ferrous ions. On the other hand Fe(OTBP)¹¹ shows behavior which is very different from that of either the "picket-fence" porphyrin or Fe(TPP). The magnetic moment of Fe(OTBP) is 5.9 μ_B , which suggests a high-spin ground state. However, the quadrupole splitting is only 0.6 mm/s and virtually independent of temperature between 4.2 and 295 K, and the isomer shift lies about half way between those for Fe(TPP) and the "picket-fence" porphyrin.

The fact that our results for Fe(OTBP) and its derivatives¹¹ are very different from those reported^{4,6,8-10} for other ferrous porphyrin complexes, and from results for the structurally related ferrous phthalocyanine derivatives,^{13,14} suggests that the detailed electronic environment of the ferrous ion in these systems is sensitive to changes in the structure of the tetra-

dentate ligand, even when such changes are relatively remote (e.g., three bonds removed) from the central metal. In order to investigate this sensitivity in more detail we have now prepared and characterized octaethylporphyriniron(II) (Fe(OEP), **3**) and several of its adducts with amine bases. The



present results, together with data previously published, help clarify the influence of various structural features of the ligands on the electronic environment of the iron(II) atom in these complexes.

Discussion

Bis(pyridine)octaethylporphyriniron(II), Fe(OEP)(py)₂, was prepared by reduction of octaethylhaemin with hydrazine hydrate in pyridine solution as described by Bonnett and Dimsdale.¹⁶ When the reduction was carried out using either 3- or 4-picoline as solvent the corresponding Fe(OEP)(3-pic)₂ and Fe(OEP)(4-pic)₂ complexes were obtained. However, in 2-picoline solution the reaction led to the formation of the diammine derivative Fe(OEP)(NH₃)₂, rather than the expected 2-picoline adduct. The inability to obtain Fe(OEP)(2-pic)₂ was presumably due to steric hindrance by the α -methyl group, and the more weakly coordinating ammonia, formed from hydrazine, coordinates instead.

The electronic and ¹H NMR spectra (pyridine solution) of Fe(OEP)(py)₂ are in agreement with those reported previously.¹⁶ The mass spectrum of this complex showed no parent peak, the base peak at *m/e* 588 corresponded to Fe(OEP)⁺. This was followed by peaks indicating the stepwise loss of eight methyl groups, with no other prominent peaks other than the doubly charged Fe(OEP)²⁺ species at *m/e* 294.

The dark brown square planar octaethylhaem Fe(OEP) was obtained by pyrolysis of the Fe(OEP)L₂ complexes in vacuo at 110–150 °C. It was also prepared directly by reduction of Fe(OEP)Cl with sodium borohydride in THF solution. We have been unable to obtain a THF adduct of Fe(OEP) by this or other routes, although both Fe(TPP)(THF)₂³ and Fe(OTBP)(THF)₂¹¹ have been reported, nor could the bisquo complex Fe(OEP)(H₂O)₂ be isolated.

Our route to Fe(OEP) and that of Collman and co-workers^{3,6} to Fe(TPP) is similar in that both involve reduction of an air-stable porphyrin ferric chloride complex under anaerobic conditions. However, Collman et al.^{3,6} use bis(acetylacetonato)chromium(II) as reducing agent in a noncoordinating solvent (benzene), whereas we employ hydrazine hydrate or sodium borohydride as reductant in a coordinating solvent to obtain first a hexacoordinate adduct (except in the case of THF, which appeared not to coordinate to Fe(OEP)). The adduct is then pyrolyzed to yield the tetracoordinate iron(II) porphyrin. Both routes are versatile, and we have also prepared Fe(TPP) by the present method.¹⁵

Spin State of Iron(II) in Fe(OEP). The room temperature susceptibility of Fe(OEP) indicates an effective magnetic moment of 4.7 μ_B . This lies between the spin-only values of 2.8 and 4.9 μ_B expected for *S* = 1 and *S* = 2 states, respectively, and close to the value 4.4 μ_B found⁶ for Fe(TPP). Ferrous complexes which can definitely be assigned to the intermedi-

ate-spin state^{6,13,17–19} have always been found to have moments $\geq 3.7 \mu_B$, well above the spin-only value, so that a moment of 4.7 μ_B is not inconsistent with an intermediate-spin iron(II) atom in Fe(OEP). Mossbauer spectra measured in the presence of large applied magnetic fields are potentially capable of distinguishing between *S* = 1 and *S* = 2 spin states of the iron(II) atom. As we discuss in more detail below, the spectra of Fe(OEP) at 4.2 K in applied fields up to 50 kG are unfortunately dominated by electronic spin relaxation effects. These effects produce broad and rather featureless spectra which have thus far prevented an unequivocal determination of the spin state. However, the zero-field Mossbauer parameters and crystallographic data for other tetracoordinate metalloporphyrins support the assignment of an intermediate-spin state to iron(II) in Fe(OEP).

It has been predicted on both experimental²⁰ and theoretical²¹ grounds that in tetracoordinate iron(II) porphyrins the *S* = 1 and *S* = 2 spin states should correspond to different coordination geometries. From stereochemical data Hoard et al.²⁰ concluded that an intermediate spin ferrous ion should be precisely centered among the four porphyrinato nitrogen atoms, whereas a high-spin ferrous ion should lie substantially out of the plane of these atoms. Similar conclusions have been reached by Gouterman and co-workers²¹ on the basis of extended Huckel MO calculations on ferrous porphine. These calculations predict an *S* = 1 ground state if the FeN₄ core is planar, and an *S* = 2 ground state if the iron(II) ion is 0.495 Å out of the porphine plane.

In both Fe(TPP)⁶ and Ni(OEP)²² the M^{II} atoms are constrained to effectively square planar coordinations. One should note particularly that the d⁸ nickel(II) atom in the latter complex adopts a fully spin-paired configuration (*S* = 0). Thus the 3d_{x²-y²} orbital is empty, a condition which also obtains for the *S* = 1 state of a d⁶ iron(II) atom, as in Fe(TPP).⁶ On the other hand the iron(II) atom in the "picket-fence" porphyrin is in the high-spin (*S* = 2) configuration⁶ and it seems likely that the iron atom is pulled out-of-plane by intramolecular interactions with amide oxygen atoms on the "pickets".⁶ In the absence of such specific interactions it seems entirely reasonable to assume that Fe(OEP) will adopt a square planar conformation and *S* = 1 spin state, particularly since the stereochemistries of the porphyrinato cores in Fe(TPP)⁶ and Ni(OEP)²² are very similar.

Further support for the *S* = 1 intermediate-spin state assignment derives from the zero-field Mossbauer parameters of Fe(OEP) discussed below. These parameters are similar to those reported⁶ for Fe(TPP) and unlike those of the high-spin complexes Fe(OTBP)(THF)₂,¹¹ (2-MeIm)Fe(TPP)·C₂H₅OH,⁶ and the "picket-fence" porphyrin derivatives.¹²

Mossbauer Data. ⁵⁷Fe Mossbauer parameters are given in Table I for the iron(II) OEP complexes together with relevant data for related compounds. Since both the Mossbauer data and magnetic properties of Fe(OTBP) are unlike those of Fe(TPP) and Fe(OEP), results for this complex will be discussed in detail elsewhere.²³ However, results for the low-spin Fe(OTBP)(py)₂ and high-spin Fe(OTBP)(THF)₂ derivatives are pertinent to the present discussion, and it is appropriate to consider them here. A few general comments on the data in Table I should be made.

Firstly, for the three square planar complexes Fe(OEP), Fe(TPP), and Fe(Pc), the two porphyrin derivatives have similar isomer shift (δ) and quadrupole splitting ($|\Delta E_Q|$) parameters, while $|\Delta E_Q|$ is much larger for Fe(Pc). Similar behavior is found for the bispyridine adducts with the exception of Fe(OTBP)(py)₂, which gives a much smaller splitting than do the other porphyrin complexes. We shall relate these differences to the σ and π bonding strengths of the tetradentate ligands.

Secondly, the isomer shifts for (2-MeIm)Fe(TPP) and

Table I. ^{57}Fe Mossbauer Parameters for the Ferrous Porphyrin Complexes^a

	T, K	δ , mm s ⁻¹	ΔE_Q , mm s ⁻¹	Γ_1 , mm s ⁻¹	Γ_2 , mm s ⁻¹	η	Ref ^b
Fe(TPP)	300	0.42	1.52				6
	195	0.47	1.52				
	77	0.50	1.51				
Fe(OEP)	4.2	0.52	+1.51			~0	
	295	0.54	1.49	0.25	0.20		
	115	0.61	+1.60	0.31	0.26	~0	
Fe(Pc)	4.2	0.59	1.60	0.28	0.27		13
	293	0.39	2.62				
	77	0.50	2.69				
Fe(OTBP)(py) ₂	4.2	0.48	+2.70			~0	
	295	0.42	0.73	0.25	0.26		
	115	0.46	0.70	0.28	0.31		
Fe(TPP)(py) ₂	84	0.50	0.68	0.28	0.31		4
	4.2	0.50	+0.67	0.28	0.32	~0	
	300	0.35	1.22				
Fe(PP)(py) ₂	77	0.40	1.15				1
	77	0.45	1.21				
	295	0.38	1.21	0.27	0.26		
Fe(OEP)(py) ₂	115	0.45	1.17	0.31	0.30		
	85	0.46	1.14	0.31	0.30		
	4.2	0.46	+1.13	0.36	0.36	~0	
Fe(Pc)(py) ₂	293	0.25	2.02				14
	77	0.32	1.97				
	4.2	0.31	+1.96			~0	
Fe(OEP)(3-pic) ₂	295	0.40	1.24	0.31	0.29		
	115	0.46	1.23	0.28	0.27		
	4.2	0.45	+1.24	0.30	0.28	~0	
Fe(OEP)(4-pic) ₂	295	0.38	1.18	0.26	0.26		
	115	0.45	1.12	0.27	0.28		
	4.2	0.44	+1.12	0.32	0.31	~0	
Fe(OEP)(NH ₃) ₂	295	0.41	1.18	0.23	0.28		
	115	0.51	1.10	0.30	0.30		
	4.2	0.49	+1.11	0.31	0.32	~0	
Fe(TPP)(pip) ₂	300	0.42	1.52				6
	195	0.47	1.49				
	77	0.50	1.44				
Fe(OTBP)(THF) ₂	4.2	0.51	+1.44				
	295	0.91	2.21	0.34	0.29		
	83	1.02	+2.67	0.24	0.23	~0	
Fe(TPP)(2-MeIm)	4.2	1.03	2.74	0.25	0.22		6
	300	0.82	1.74				
	195	0.87	1.97				
	77	0.92	2.26				
	4.2	0.93	2.28				

^a Isomer shifts are relative to metallic iron. Error limits for the Mossbauer parameters are estimated to be ± 0.01 mm/s for this work. ^b This work unless otherwise noted.

Fe(OTBP)(THF)₂ are fairly typical of high-spin ferrous systems, whereas all the other complexes have δ values close to 0.5 mm/s, a value often considered to be the empirical dividing line between paramagnetic and diamagnetic iron(II) derivatives. Moreover, in going from a square planar intermediate-spin compound to an octahedral low-spin one only a modest change in δ is observed.

Thirdly, the $|\Delta E_Q|$ values vary widely, ranging from about 0.7 mm/s for Fe(OTBP)(py)₂ to 2.7 mm/s for Fe(Pc) and Fe(OTBP)(THF)₂. The two high-spin complexes show the temperature dependence of $|\Delta E_Q|$ typical of octahedral $S = 2$ iron(II) compounds, but for the remaining derivatives $|\Delta E_Q|$ is nearly independent of temperature.

Finally, magnetic perturbation Mossbauer measurements show that for all the complexes listed in Table I where such results are available V_{zz} , the principal component of the electric field gradient (efg) tensor, is positive and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ is indistinguishable from zero. The sign of V_{zz} has not been reported for Fe(TPP)(py)₂ or Fe(PP)(py)₂, but it seems safe to assume positive signs in these cases as well.

Before discussing the Mossbauer parameters in relation to the bonding in these complexes, it is important to consider in general the structural characteristics of the tetradentate ligands and the differences expected in their σ and π bonding properties.

The three porphyrins OEP, TPP, and PP are all expected to have similar ring sizes, and in the iron(II) complexes the Fe-N bond distances should be nearly identical. Thus, no significant differences in N \rightarrow Fe σ -donor strength is expected among these porphyrins. Because of the fused benzene rings in OTBP, there should be little or no S₄ ruffling of the porphyrinato core and we anticipate a planar conformation in this case. This should lead to a slightly greater Fe-N distance than in the S₄-ruffled porphyrins so that OTBP is probably a weaker σ donor than OEP, TPP, or PP. On the other hand, phthalocyanine has a substantially smaller ring size²⁴⁻²⁹ since the pyrrole units are connected by nitrogen bridges rather than methine bridges, and the Fe-N distance should be appreciably shorter in Fe(Pc) than in the ferrous porphyrins. Thus, phthalocyanine should be the strongest σ donor of the ligands considered here.

The nitrogen bridging atoms in phthalocyanine are also expected to influence its π -donor strength. Simple Huckel π electron calculations³⁰ on these ring systems have shown that the total electronic charge at the bridge atoms is lower than at the other ring atoms. That is, the formation of an aromatic π electron system favors the removal of electron density from the bridge atoms. Since nitrogen is more electronegative than carbon, the π system with a methine bridge will be inherently stronger than with a nitrogen bridge. However, the fused benzene rings in phthalocyanine should contribute additional resonance energy which will probably more than compensate for any weakening of the π system induced by the bridging nitrogens. It therefore seems reasonable to suggest that OTBP will have the greatest π -donor strength of the ligands under discussion, followed by phthalocyanine.

Of the remaining porphyrins, TPP should have the next highest π bonding strength because of the electron releasing phenyl groups in the four meso positions. However, these phenyl groups are oriented nearly perpendicular to the plane of the porphyrin^{6,29} so that the phenyl π system will not contribute directly to the π system of the porphine ring. PP is expected to be the weakest π bonding ligand because of the electron-withdrawing vinyl and acidic side chains on the pyrrole rings. Thus, the suggested order of π donor strengths is OTBP > Pc > TPP > OEP > PP. This order is at least partially verified by NMR data for Fe(OEP)(py)₂ and Fe(OTBP)(py)₂, since the position of the methine proton resonance is a good indication of the strength of the π electron system. This resonance occurs at 11.8 ppm in Fe(OTBP)(py)₂,²³ 1.8 ppm further downfield than in Fe(OEP)(py)₂, indicating a stronger deshielding of the methine protons in the former complex.

With these qualitative considerations in mind we turn to a more detailed examination of the Mossbauer data. Of the three square planar complexes, Fe(TPP) and Fe(OEP) have much smaller quadrupole splittings than that of Fe(Pc), although all three have similar isomer shifts. As Collman et al.⁶ have pointed out, the fact that the isomer shifts for the tetracoordinate iron(II) porphyrins are essentially the same as those for the corresponding hexacoordinate low-spin complexes with amine bases is consistent with the absence of an electron in the iron $3d_{x^2-y^2}$ orbital in both types of compound. Although ΔE_Q for Fe(TPP) is completely independent of temperature within experimental error, the splittings for both Fe(OEP) and Fe(Pc) increase by approximately 0.1 mm/s in going from room temperature to 4.2 K. This temperature dependence is much smaller than that usually observed for $S = 2$ ferrous complexes. For the latter it is generally found that there is at least one low-lying excited orbital state which can be thermally populated at room temperature, and the ΔE_Q value observed is a thermal average of the values for the ground and excited states. A decrease in temperature depletes the excited state(s) and produces the usual temperature-dependent ΔE_Q . The lack of any appreciable temperature dependence for these $S = 1$ compounds implies that they have no low-lying excited orbital states.

At 4.2 K in zero applied magnetic field Fe(Pc),¹³ Fe(TPP),^{6,15} and Fe(OEP) all show simple quadrupole-doublet spectra with no indication of asymmetric line broadening. (Line widths were not reported in ref 6, but we have recorded the spectrum¹⁵ of Fe(TPP) under these conditions and it was a symmetric doublet with narrow lines.) This indicates that the spin relaxation rates in these compounds are sufficiently fast compared to the nuclear precession frequency that no magnetic hyperfine structure can be seen in the absence of an external field.

In applied magnetic fields, however, each of the three compounds behaves differently. For Fe(Pc) at 4.2 K in an applied field of 30 kG, the spectrum¹³ is a clearly defined

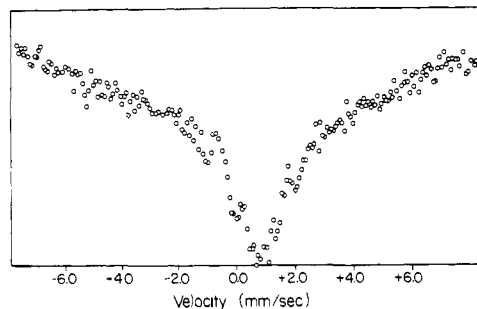


Figure 1. Mossbauer spectrum of Fe(OEP) at 4.2 K in a longitudinal applied magnetic field of 28 kG.

triplet-doublet pattern of the type normally associated with a diamagnetic compound.³¹ The effective magnetic field at the nucleus, H_{eff} , was estimated¹³ to be 53.5 kG. Fe(TPP) also gives a spectrum with sharp, well-resolved lines at 4.2 K in an applied field,¹⁵ and for $H_{\text{app}} = 32$ kG Collman et al.⁶ reported that H_{eff} was about 48 kG at this temperature. The effective field is related to the applied field by³²

$$H_{\text{eff}} = H_{\text{app}} + \langle S \rangle / S H_{\text{int}}$$

where H_{int} is the internal hyperfine field and $\langle S \rangle / S$ is the magnetization of the electron spins expressed as a fraction of the saturation value. The above results indicate that either H_{int} or $\langle S \rangle$ is slightly different in Fe(Pc) and Fe(TPP), or both. In any case, however, since the hyperfine field is expected to be large (it has been estimated¹³ to be 270 kG in Fe(Pc)), it is clear that $\langle S \rangle / S$ must be small for both complexes, and hence the electron spin relaxation rates are fast.

For Fe(OEP) on the other hand, at 115 K with $H_{\text{app}} = 50$ kG we estimate $H_{\text{eff}} \approx 67$ kG from the observed Zeeman splitting, so that there is a small augmentation from the internal field even at this temperature. At 4.2 K the behavior of this complex in applied fields was much more complicated. The spectra were diffuse and ill-defined (see Figure 1), and the detailed spectral shape depended strongly on the magnitude of H_{app} . In connection with other work³³ we have recently computed a large number of simulated applied field Mossbauer spectra for various spin states of iron(II) and iron(III) systems in both slow and fast relaxation limits. From these results it appears likely that Fe(OEP) represents an example of intermediate relaxation, where in the presence of an applied field the spin relaxation rate and the nuclear Larmor frequency have comparable time scales. Theoretical interpretation of our low-temperature applied-field spectra of Fe(OEP) will therefore be difficult and has not yet been attempted.

Turning now to the diamagnetic hexacoordinate bispyridine adducts, one sees from Table I that Fe(Pc)(py)₂ has the largest $|\Delta E_Q|$, Fe(OTBP)(py)₂ the smallest, and that the other three porphyrin complexes have intermediate and nearly identical values. The Mossbauer spectrum of Fe(OEP)(py)₂ at 4.2 K in a longitudinal magnetic field of 50 kG is shown in Figure 2, and V_{zz} is clearly positive with η effectively zero.

The only possible ground state for an octahedral low-spin ferrous system is $^1A_{1g}$, and in the "pure" crystal field limit this state has zero quadrupole splitting. However, differences in bonding interactions can produce a nonzero efg. Gouterman and co-workers²¹ have performed extended Huckel MO calculations for the ferrous porphine bisaqueo adduct. Using their calculated d orbital populations the predicted ΔE_Q value is +1.10 mm/s, remarkably close to the values found for the bispyridine adducts of Fe(OEP), Fe(TPP), and Fe(PP). It appears²¹ that the major contribution to V_{zz} in these diamagnetic complexes comes from the imbalance in electron densities in the iron $d_{x^2-y^2}$ and d_{z^2} orbitals, and the positive

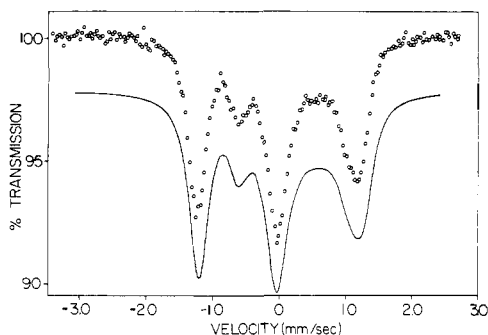


Figure 2. Mossbauer spectrum of $\text{Fe}(\text{OEP})(\text{py})_2$ at 4.2 K in a longitudinal magnetic field of 50 kG. The solid curve is the theoretical spectrum calculated with the parameters $\delta = 0.73 \text{ mm s}^{-1}$, $\Delta E_Q = +1.13 \text{ mm s}^{-1}$, $\Gamma = 0.36 \text{ mm s}^{-1}$, $H_{\parallel} = 50 \text{ kG}$, and $\eta = 0$.

signs observed show that the covalent bonding to the planar porphyrin is stronger than that to the axial pyridine ligands.

The fact that $\text{Fe}(\text{Pc})(\text{py})_2$ has the largest ΔE_Q of the pyridine adducts considered here presumably reflects very strong σ donation into the iron $d_{x^2-y^2}$ orbital in this case ($4p_x$ and $4p_y$ may also contribute). Since the porphyrins should be poorer σ donors than phthalocyanine there will be smaller imbalances in $d_{x^2-y^2}$ and d_{z^2} charge densities, and smaller ΔE_Q values. The very small splitting for the OTBP complex probably results both from the slightly poorer σ -donor ability of this porphyrin relative to the others, and to its very strong forward π -bonding capacity which would preclude any appreciable back-donation from the iron d_{xz} , d_{yz} orbitals into the e_g π orbitals of the porphyrin. For the other three porphyrins the rather modest differences in their overall σ and π bonding characteristics appear to be effectively masked by the presence of the axial pyridine ligands.

The isomer shift data for the bispyridine adducts appear to reflect primarily σ bonding differences among the tetradentate ligands. At ca. 80 K $\text{Fe}(\text{Pc})(\text{py})_2$ has the smallest δ value, $\text{Fe}(\text{OTBP})(\text{py})_2$ the largest, and the other three porphyrin complexes have intermediate values. Since a decrease in δ corresponds to an increase in the effective s electron density at the ^{57}Fe nucleus, a smaller δ value indicates either a larger $4s$ orbital occupancy, a smaller $3d$ occupancy, or both. In view of the quadrupole splitting data, the δ value for $\text{Fe}(\text{Pc})(\text{py})_2$ suggests substantial σ donation from the phthalocyanine ligand into the iron $4s$ orbital. Conversely, the high δ value for $\text{Fe}(\text{OTBP})(\text{py})_2$ is consistent with its being the weakest σ donor (and weakest π acceptor) of the tetradentate ligands considered here. $\text{Fe}(\text{PP})(\text{py})_2$ and $\text{Fe}(\text{OEP})(\text{py})_2$ have essentially identical isomer shifts, but the smaller δ for $\text{Fe}(\text{TPP})(\text{py})_2$ is unexpected since these three porphyrins should have very similar σ donor properties. Moreover, TPP is expected to be a slightly poorer π acceptor than either PP or OEP, and if anything this should raise the isomer shift.

The Mossbauer parameters for all four of the diamagnetic $\text{Fe}(\text{OEP})\text{L}_2$ complexes are similar, and in every case we find $V_{zz} > 0$ and $\eta \approx 0$. On the other hand, $\text{Fe}(\text{TPP})(\text{pip})_2$ has a significantly larger ΔE_Q than $\text{Fe}(\text{TPP})(\text{py})_2$, consistent with piperidine being a weaker Lewis base than pyridine.

Experimental Section

Materials. All chemicals were of reagent grade and were obtained from either Fisher Scientific Co. or Aldrich Chemical Co. Tetrahydrofuran and 2-, 3-, and 4-picoline were freshly distilled over calcium hydride prior to use.

Physical Measurements. Microanalyses were performed either by Mr. P. Borda of this department or by Drs. F. and E. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany. The percentage weight loss upon vacuum pyrolysis was determined for each of the $\text{Fe}(\text{OEP})\text{L}_2$ complexes. These data are given below together with the

conditions employed and the calculated weight loss for the process $\text{Fe}(\text{OEP})\text{L}_2 \rightarrow \text{Fe}(\text{OEP})$. Electronic spectra (pyridine solution) were recorded on a Carey Model 14 spectrophotometer. Wavelengths of maximum absorption are given in nanometers with molar extinction coefficients in parentheses. Magnetic susceptibilities were measured at room temperature by the Gouy method. ^1H NMR spectra were obtained on a Varian T-60 spectrometer. Chemical shifts are reported in parts per million downfield from internal Me_4Si , with integrations and multiplicities indicated in parentheses. Mass spectra were measured with an AEI MS-9 spectrometer. The Mossbauer spectrometers and the cryostats employed for variable temperature and magnetic perturbation measurements have been described.^{33b,34} All spectra were obtained in transmission geometry using a 25 mCi $^{57}\text{Co}(\text{Cu})$ source and carefully powdered absorbers. For spectra recorded at 4.2 K and/or in applied magnetic fields both source and absorber were at the same temperature; in all other cases the source was maintained at room temperature. The Doppler velocity scale was calibrated with a metallic iron foil absorber, the isomer shifts are quoted relative to the centroid of the iron foil spectrum. Spectra obtained in zero applied magnetic field were fitted to Lorentzian components by least-squares techniques, using unconstrained fitting parameters.

Preparations. Except for the preparation of octaethylhaemin, all procedures described below were carried out in a dry nitrogen (or argon) atmosphere. The ferrous complexes of octaethylporphyrin are all air sensitive ($\text{Fe}(\text{OEP})$ extremely so), and strict precautions must be taken to avoid oxidation.

Octaethylhaemin, $\text{Fe}(\text{OEP})\text{Cl}$. Octaethylporphyrin (H_2OEP) (1 g) was dissolved in refluxing DMF (150 ml) and $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2 g) was added in one portion. The solution was boiled for 15 min, cooled to room temperature, and added to 500 ml of saturated aqueous NaCl. The mixture was then left to stand in air overnight. The colloidal precipitate which formed was collected on an F grade sintered filter and washed with hot water to remove inorganic salts. The residue was dissolved in 100 ml of CHCl_3 and the solution washed with several 50-ml portions of 5 M HCl in a separatory funnel. The chloroform layer was then washed with water, dried with anhydrous CaCl_2 , and filtered. The volume of the filtrate was reduced to 100 ml on a hot plate, and then kept constant by addition of ethanolic HCl (100:1) while the solution was boiled. The $\text{Fe}(\text{OEP})\text{Cl}$ which precipitated was washed with ethanol and dried in air. Anal. Calcd for $\text{C}_{36}\text{H}_{44}\text{N}_4\text{ClFe}$: C, 69.28; H, 7.05; N, 8.98. Found: C, 69.18; H, 6.98; N, 8.93.

Bis(pyridine)octaethylporphyriniron(II), $\text{Fe}(\text{OEP})(\text{py})_2$. $\text{Fe}(\text{OEP})\text{Cl}$ (1 g) was dissolved in pyridine (170 ml) in a 500-ml flask equipped with condenser and dropping funnel. The solution was heated to 50 $^\circ\text{C}$ under a nitrogen atmosphere, and 3.3 ml of hydrazine hydrate added through the dropping funnel. The solution immediately turned from brown to red. The temperature was maintained at 50 $^\circ\text{C}$ for 15 min and the solution, under nitrogen, was cooled in an ice bath. Deoxygenated acetic acid (7 ml) was added, and after a few minutes deoxygenated water was added to precipitate the product. The precipitate was washed with deoxygenated ice cold water and dried in vacuo to give the diamagnetic orange $\text{Fe}(\text{OEP})(\text{py})_2$. Anal. Calcd for $\text{C}_{46}\text{H}_{54}\text{N}_6\text{Fe}$: C, 73.70; H, 7.19; N, 11.19. Found: C, 74.00; H, 7.24; N, 11.25. λ (nm) 409 (1.2×10^5), 520 (1.5×10^4), 549 (2.5×10^4); δ (ppm) 1.9 (24 H, t), 4.0 (16 H, q), 10.0 (4 H, s). Weight loss (2.5 h, 150 $^\circ\text{C}$): 21.3% (calcd 21.2%).

Bis(4-picoline)octaethylporphyriniron(II), $\text{Fe}(\text{OEP})(4\text{-pic})_2$. The complex was prepared from $\text{Fe}(\text{OEP})\text{Cl}$ dissolved in 4-picoline by the same route described for the bispyridine adduct. The orange-brown complex is diamagnetic. Anal. Calcd for $\text{C}_{48}\text{H}_{58}\text{N}_6\text{Fe}$: C, 74.43; H, 7.49; N, 10.85. Found: C, 74.33; H, 7.70; N, 10.86. Weight loss (1 h, 140 $^\circ\text{C}$): 24.7% (calcd 24.0%).

Bis(3-picoline)octaethylporphyriniron(II), $\text{Fe}(\text{OEP})(3\text{-pic})_2$. The procedure was identical with that used for the bispyridine complex, except that 3-picoline was used as solvent. The orange-brown complex is diamagnetic. Anal. Calcd for $\text{C}_{48}\text{H}_{58}\text{N}_6\text{Fe}$: C, 74.43; H, 7.49; N, 10.85. Found: C, 74.20; H, 7.46; N, 10.86. Weight loss (4 h, 110 $^\circ\text{C}$): 25.1% (calcd 24.0%).

Diammineoctaethylporphyriniron(II), $\text{Fe}(\text{OEP})(\text{NH}_3)_2$. The diamagnetic brown complex was obtained when $\text{Fe}(\text{OEP})\text{Cl}$ dissolved in 2-picoline was treated with hydrazine hydrate as described above for the bispyridine complex. Anal. Calcd for $\text{C}_{36}\text{H}_{50}\text{N}_6\text{Fe}$: C, 69.25; H, 8.01; N, 13.46. Found: C, 69.38; H, 7.60; N, 13.50. Weight loss (2 h, 150 $^\circ\text{C}$): 6.40% (Calcd. 6.45%).

Octaethylporphyriniron(II), $\text{Fe}(\text{OEP})$. A sample of $\text{Fe}(\text{OEP})(\text{py})_2$ was heated in vacuo at 150 $^\circ\text{C}$ for 2.5 h to afford the pure dark brown

ferrous porphyrin. Anal. Calcd for $C_{36}H_{44}N_4Fe$: C, 73.46; H, 7.49; N, 9.53. Found: C, 73.58; H, 7.59; N, 9.44. μ_{eff} (295 K) = 4.7 μ_B .

Attempted Preparation of Bis(tetrahydrofuran)octaethylporphyriniron(II), Fe(OEP)(THF)₂. (i) Fe(OEP) (0.5 g) was dissolved in deoxygenated THF and the solution was evaporated to dryness in vacuo at room temperature. This procedure afforded only Fe(OEP), identified by microanalysis, magnetic moment, and Mossbauer spectrum. (ii) Fe(OEP)Cl (0.2 g, 0.32 mmol) and NaBH₄ (0.15 g, 0.39 mmol) were suspended in 40 ml of THF and stirred under an Ar atmosphere for 15 h at room temperature. The reaction mixture was filtered to give a reddish purple solution. Upon removal of THF a brown precipitate was obtained, which was collected by filtration and dried in vacuo. Chemical analysis indicated the product to be Fe(OEP), and this was confirmed by Mossbauer spectroscopy.

Attempted Preparation of Bis(aquo)octaethylporphyriniron(II), Fe(OEP)(H₂O)₂. Fe(OEP) (0.1 g) was reacted with rigorously degassed H₂O (5 ml) at room temperature for 2 h. The water was removed in vacuo and Fe(OEP) was recovered unchanged.

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High Pressure Studies. 21. Volume Changes for Base-Catalyzed Hydrolysis of *p*-Nitrophenyl Esters^{1,2}

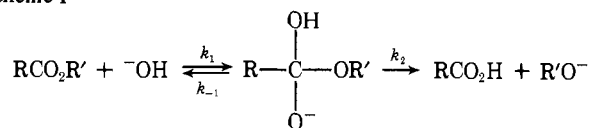
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Abstract: Effects of pressure on the hydroxide ion catalyzed hydrolysis of *p*-nitrophenyl acetate, propionate, dimethylacetate, and trimethylacetate have been determined in 0.005 M Tris buffer (24.5 °C). The activation volumes for hydrolysis are -3, -4, -4, and -10 cm³/mol, respectively. Data are presented indicating that contributions from Tris catalysis and that of other nucleophiles is unimportant under these conditions so that it is likely that these values of ΔV^*_{obsd} correspond to those for hydroxide attack. Since reversion of tetrahedral intermediates to starting esters is unlikely with these systems, the activation volumes are interpreted as directly reflecting the volume change on formation of the transition state leading to the tetrahedral intermediate. The variation in the values of ΔV^*_{obsd} with ester structure may reflect steric effects associated with solvation. The data are contrasted with available pressure results for base-catalyzed hydrolysis of some simple alkyl acetates.

Base-catalyzed hydrolysis of esters of aliphatic carboxylic acids is generally accepted to occur via the reversible formation of a tetrahedral intermediate (Scheme I) so that the rate

Scheme I



constant (k_{obsd}) measured for disappearance of the ester ($\text{RCO}_2\text{R}'$) is given by the combination of rate constants shown in the following equation:⁴

$$k_{obsd} = k_1[k_2/(k_{-1} + k_2)] \quad (1)$$

The extent of reversibility depends on the structure of R'. For example, k_{-1}/k_2 is much smaller when R'O⁻ is a phenoxide anion than when it is an alkoxide anion, and when R'O⁻ is the very stable *p*-nitrophenoxide anion, k_{-1}/k_2 is essentially zero.⁵

In connection with studies^{1a,6,7} of pressure effects on enzyme-catalyzed hydrolyses of a series of aliphatic *p*-nitrophenyl esters (1), where R is Me, MeCH₂, Me₂CH, and Me₃C, we have determined the effects of pressure on their nonenzymic alkaline hydrolysis rates. Since k_{obsd} equals k_1 for these esters,⁸ the pressure dependence of k_{obsd} directly gives the activation