

Mössbauer-Zeeman Spectra of Some Octaethylporphyrinato- and Tetraphenylporphyrinatoiron(III) Complexes

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Abstract: Mössbauer spectra at 4.2 K in zero field and in applied magnetic fields of up to 5.0 T are reported for three pairs of high-spin ($S = 5/2$) iron(III) complexes: Fe(P)Cl, Fe(P)OMe, and [Fe(P)]₂O (P = dianion of octaethylporphyrin or tetraphenylporphyrin). These spectra have been analyzed in the spin Hamiltonian formalism to provide estimates of the crystal field splittings, components of the magnetic hyperfine tensors, signs of the electric field gradients (efg), and magnitudes of the asymmetry parameters η . In each of the four monomeric complexes the internal hyperfine field is large (~ 50 T) and the efg is positive with effectively axial symmetry. However, the zero-field splitting parameters for the methoxides appear to be substantially smaller than those for the chlorides. In the μ -oxo dimers the two high-spin iron atoms are strongly coupled, via an antiferromagnetic exchange interaction, to produce a spin singlet (nonmagnetic) ground state. In both dimers the efg is negative, η is nonzero, and the principal magnetic and efg axes are parallel. Careful measurements of the temperature dependences (4.2–295 K) of the intensities, widths, and areas of the two zero-field Mössbauer lines of the dimeric complexes indicate slight relaxation broadening at high temperatures, but provide no evidence of any Gol'danskii-Karyagin asymmetry.

Introduction

Although a large number of pentacoordinate high-spin ($S = 5/2$) porphyrinatoiron(III) complexes have been studied by Mössbauer spectroscopy,^{1–7} measurements in the presence of applied magnetic fields (Mössbauer-Zeeman spectra) are sparse. Following Johnson's⁸ elegant work on haemin [protoporphyrin IX iron(III) chloride, Fe(PP)Cl⁹] and the spin-dilution experiments on this compound by Lang and co-workers,¹⁰ we reported preliminary Mössbauer-Zeeman data for octaethylhaemin [octaethylporphyrinatoiron(III) chloride, Fe(OEP)Cl^{4,9}]. The only other iron(III) porphyrins for which such measurements have been published are the three compounds Fe(PPD)X^{9,11} (X = SC₆H₄NO₂, OC₆H₄NO₂, OEt). Measurements of this type are particularly useful in that they enable one to deduce values of the zero-field splitting parameter D , the components of the magnetic hyperfine tensor \mathbf{A} , and the sign of the principal component of the electric field gradient (efg) tensor at the ⁵⁷Fe nucleus.¹²

The present work was undertaken to provide data of this type for several other iron(III) porphyrins and to attempt to clarify some apparent anomalies and inconsistencies in the published literature. Specifically, we addressed ourselves to the following points:

(1) Mössbauer quadrupole splitting data are available for nine ferric porphyrin chlorides.^{1–6} With the single exception of the *meso*-tetraphenylporphyrin complex Fe(TPP)Cl, for which $|\Delta E_q|$ was reported⁵ to be 0.46 mm s⁻¹, the splittings for the chlorides¹² span the narrow range $|\Delta E_q| = 0.88 \pm 0.15$ mm s⁻¹. It was of interest to see if Fe(TPP)Cl was indeed an exception or if the reported⁵ splitting was an error,¹³ and at the same time to compare the spin Hamiltonian parameters obtained by fitting its Mössbauer-Zeeman spectra with those deduced for Fe(PP)Cl⁸ and Fe(OEP)Cl.⁴

(2) A few methoxyiron(III) porphyrin complexes have been studied, but there is lack of agreement on magnetic susceptibility data and spin state assignments. For Fe(PP)OMe, effective magnetic moments of 2.02 μ_B in pyridine solution and 5.30 μ_B in chloroform have been quoted.^{15,16} Cohen¹⁷ gave a value of not less than 5.6 μ_B for Fe(TPP)OMe in the solid state, although the compound studied was only about 90% pure. The last two values are close to, but slightly less than, the spin-only moment expected for high-spin ($S = 5/2$) ferric derivatives. On the other hand, Kobayashi et al.¹⁴ have claimed that Fe(TPP)OMe is a low-spin ($S = 1/2$) complex.¹⁸ An x-ray

crystallographic structure determination¹⁵ of methoxyiron(III) mesoporphyrin IX dimethyl ester, Fe(MP)OMe, showed that the iron atom was 0.455 Å above the mean plane of the four porphyrinato nitrogens, with Fe-N and Fe-O distances of 2.073 and 1.842 Å, respectively. This structure was held¹⁵ to be consistent with either a high-spin ground state for the Fe³⁺ ion, or possibly an intermediate-spin ($S = 3/2$) state with the d_{z^2} orbital vacant. In view of these varying reports we thought it important to study compounds of this type via Mössbauer-Zeeman spectroscopy in order to establish the spin state of the Fe³⁺ ion unambiguously. In addition, a very recent paper by Tang et al.¹¹ asserts that the principal component of the electric field gradient (efg) tensor, V_{zz} , is negative in Fe(PPD)OEt,⁹ whereas it is positive^{4,8,11} in the other four porphyrinatoiron(III) complexes for which its sign is known. This provided further impetus for studying iron(III) porphyrin complexes in which the axial ligand was an alkoxide.

(3) Compounds originally thought to be ferric porphyrin hydroxides have been shown to be dimeric species in which an oxygen dianion bridges two pentacoordinate iron(III) complexes.^{17,22} Except for certain protein derivatives (e.g., methemoglobin and metmyoglobin) in which dimerization is sterically prevented, monomeric iron(III) hydroxo porphyrin complexes are apparently unknown.²³ In these μ -oxo dimers the two spin sextet Fe³⁺ ions are antiferromagnetically coupled through the oxygen bridge.^{17,24,25} For the similar dimeric *N,N'*-ethylenebis(salicylaldehyde) (Salen) complexes [Fe(Salen)]₂O and [Fe(Salen)Cl]₂, in which there is also antiferromagnetic coupling, Mössbauer measurements²⁶ have revealed a number of interesting features. In addition to magnetic broadening of the spectral lines at temperatures above 4.2 K,^{4,27,28} there is also Gol'danskii-Karyagin²⁹ asymmetry (i.e., anisotropy of the recoilless fraction). Moreover, the quadrupole coupling constants e^2qQ in these Salen complexes are of opposite sign.²⁶ Comparison of the Salen derivatives with the oxo-bridged iron(III) porphyrin dimers was therefore of considerable interest.³⁰ Mössbauer data for several of the latter complexes have been published,^{17,23,28b,31} but no applied field measurements were available.

Discussion

Octaethylhaemin, Fe(OEP)Cl, was prepared as described previously,^{21,32} and an analogous route was employed for the corresponding tetraphenylporphyrin complex Fe(TPP)Cl. The

Table I. Mössbauer Data for High-Spin Porphyrinatoiron(III) Complexes^a

Compd	δ , mm/s ^b	$ \Delta E_Q $, mm/s	Ref ^c
Fe(TPP)Cl	0.30 ± 0.02	0.48 ± 0.03	5
	0.41	0.46	
Fe(OEP)Cl	0.41 ± 0.01	0.93 ± 0.02	11
Fe(TPP)OMe	0.29 ± 0.03	0.56 ± 0.05	
Fe(OEP)OMe	0.41 ± 0.02	0.65 ± 0.03	
	0.34	? ^d	
Fe(PPD)OEt	0.32 ± 0.03	0.46 ± 0.05	11
[Fe(TPP)] ₂ O	0.28 ± 0.02	0.62 ± 0.03	23
	0.41	0.67	
[Fe(OEP)] ₂ O	0.39 ± 0.01	0.77 ± 0.02	
	0.30 ± 0.02 ^e	0.59 ± 0.03 ^e	

^a Values at 4.2 K unless otherwise stated. ^b Relative to metallic iron. ^c This work unless otherwise noted. ^d $|\Delta E_Q|$ data for this complex not reported in ref 11. ^e 295 K.

effective magnetic moments at room temperature of 5.95 and 5.87 μ_B , respectively, are clearly indicative of high-spin ground states for the Fe^{3+} ions.

The oxo-bridged dimers $[Fe(OEP)]_2O$ and $[Fe(TPP)]_2O$ were readily obtained by treating solutions of the appropriate chlorohaemin in dichloromethane with aqueous sodium hydroxide.³³ The room-temperature magnetic moments of 1.16 μ_B per iron atom for both these compounds obviously result from the strong antiferromagnetic exchange interactions.²² The moments are quite strongly temperature dependent, and $[Fe(TPP)]_2O$ is reported²⁴ to be diamagnetic below 20 K.

$Fe(OEP)OMe$ was conveniently prepared in pure form, by reacting $Fe(OEP)Cl$ with a solution of sodium in anhydrous methanol. The complex is unquestionably high spin (see Experimental Section), and its electronic spectrum was in agreement with a previous report.³⁴

On the other hand, we were not able to prepare analytically pure $Fe(TPP)OMe$ by a route similar to that used for $Fe(OEP)OMe$ (even with the added precaution of carrying out the reaction under a dinitrogen atmosphere), nor by the method of Buchler and Schneehage³⁴ for $Fe(OEP)OMe$. Cohen¹⁷ likewise was unable to prepare $Fe(TPP)OMe$ with better than 90% purity. The mass spectrum of our sample showed a base peak corresponding to the parent ion $Fe(TPP)OMe^+$ at m/e 699, and Mössbauer spectra in applied magnetic fields (vide infra) provide convincing evidence that the major iron-containing impurity is the $[Fe(TPP)]_2O$ dimer. This accounts for the fact that the magnetic moment we observed at 295 K was only 5.35 μ_B , rather than the value of $\sim 5.9 \mu_B$ expected for a $S = 5/2$ Fe^{3+} complex.

Zero-Field Mössbauer Measurements. ⁵⁷Fe Mössbauer spectra were obtained in zero applied magnetic field with both source and absorbers at 4.2 K, and data for the six complexes are presented in Table I. The isomer shift values are in the range typically observed¹⁻⁶ for high-spin Fe^{3+} derivatives and appear to be insensitive to the nature of the axial ligand. However, one notes that the δ values for the octaethylporphyrin complexes are slightly higher than those of the tetraphenylporphyrin ones. This could presumably reflect differences in σ and/or π bonding characteristics of the tetradentate ligands, geometrical differences (e.g., extent of nonplanarity of the FeN_4 cores), or some combination of both.

Our results confirm the very small $|\Delta E_Q|$ previously reported⁵ for $Fe(TPP)Cl$, but the explanation of the unusually small splitting in this case remains unclear. Although in both the other pairs of complexes given in Table I the TPP derivative shows a slightly smaller quadrupole interaction, the differences are not nearly as pronounced as they are for the chlorides. As we shall see below, this large difference in $|\Delta E_Q|$ does not

appear to result from substantially different crystal field splittings.

At 4.2 K the Mössbauer spectra of these complexes consist of two lines of nearly equal intensity, but at higher temperatures the spectra of the chloro and methoxy derivatives show pronounced relaxation broadening. For this reason reliable isomer shift and quadrupole splitting data were not obtainable at temperatures of 77 K and above. This type of behavior has been observed with other synthetic and natural hemochromes.^{1,4-6,28,35}

Blume²⁷ has interpreted these effects in terms of a temperature-dependent spin-spin relaxation rate. The sixfold spin degeneracy of the ⁶A ground state of the Fe^{3+} ion is lifted by spin-orbit coupling to crystal field split excited states according to the Hamiltonian

$$\mathcal{H}_{CF} = D \left[S_z^2 - \frac{1}{3} S(S+1) + \frac{E}{D} (S_x^2 - S_y^2) \right] \quad (1)$$

where D and E are the axial and rhombic field splitting parameters, respectively. In the case of axial symmetry ($E = 0$), this zero-field splitting results in three Kramers doublets with $S_z = \pm 1/2, \pm 3/2,$ and $\pm 5/2$, at energies of 0, $2D$, and $6D$, respectively. At 4.2 K, D is large compared to kT so that most of the spins are in the $|S_z = \pm 1/2\rangle$ state. Spin relaxation within this doublet is much faster than the Larmor precession frequency of the nuclear spin; the nucleus therefore sees a time-averaged magnetic field which is effectively zero, and a symmetric spectrum is observed. At higher temperatures the more slowly relaxing²⁷ $|S_z = \pm 3/2\rangle$ and $|S_z = \pm 5/2\rangle$ levels will be thermally populated and the nucleus will now experience nonzero fluctuating magnetic fields. Since the $|m_1 = \pm 1/2\rangle$ and $|m_1 = \pm 3/2\rangle$ excited nuclear spin states³⁶ have different Larmor frequencies, the Mössbauer lines arising from transitions to these states will be affected differently and the spectrum will broaden asymmetrically.

The question as to which line is the first to broaden depends upon the sign of V_{zz} ($= eq$), the principal component of the efg tensor, and the relative orientations of V_{zz} and the z axis of the internal hyperfine magnetic field. This can usually be resolved by a Mössbauer-Zeeman experiment and we shall return to this point below. However, we should note here that for both chlorohaemins studied (as well as $Fe(PP)Cl$)⁸ it is the higher energy line which broadens first as the temperature is raised, but this asymmetry is reversed in the two methoxy complexes.

The dimeric compounds contain two $S = 5/2$ Fe^{3+} ions which are antiferromagnetically coupled^{17,24,25} via the isotropic exchange coupling Hamiltonian^{36,37}

$$\mathcal{H}_{EC} = -JS_1 \cdot S_2 \quad (2)$$

and have states with total quantum numbers $S' = 0, 1, \dots, 5$ and eigenvalues given by

$$E(S') = \frac{1}{2} J [2S(S+1) - S'(S'+1)] \quad (3)$$

This leads to a series of multiplets spread over $15J$ in energy. If $|J|$ is much larger than the splitting of these multiplets by the crystal field, only the nondegenerate $S' = 0$ ground state will be populated at low temperature. Since a singlet state can exhibit no magnetic properties, the Mössbauer spectrum under these conditions is a symmetric doublet,^{26,38} as observed in the present cases at 4.2 K. At sufficiently high temperatures the higher S' states will be thermally populated, spin fluctuations producing randomly varying magnetic fields at the nucleus can then occur, and the spectrum should broaden asymmetrically in obvious analogy to the monomeric haemins. However, it appears²⁵ that $|J|$ is very large in these μ -oxo porphyrin dimers ($|J|/k \gtrsim 400$ K) so that even at room temperature most of the

Table II. Ratios of Widths, Intensities, and Areas of the Mössbauer Spectral Lines of the Oxo Dimers as Functions of Temperature^a

Compd	Temp, K	Γ_1 , mm/s	Γ_2 , mm/s	Γ_1/Γ_2	I_1/I_2	A_1/A_2
[Fe(OEP)] ₂ O	4.2	0.268	0.271	0.99	1.02	1.01
	82	0.264	0.272	0.97	0.99	0.96
	100	0.269	0.272	0.99	1.04	1.02
	130	0.256	0.261	0.98	1.03	1.01
	160	0.275	0.277	0.99	1.03	1.02
	190	0.275	0.275	1.00	1.02	1.02
	220	0.272	0.266	1.02	1.01	1.03
	245	0.275	0.274	1.00	1.02	1.02
	270	0.286	0.270	1.06	0.93	0.98
	295	0.303	0.259	1.17	0.87	1.02
[Fe(TPP)] ₂ O	4.2	0.271	0.276	0.98	0.99	0.97
	115	0.277	0.280	0.99	0.98	0.97
	170	0.264	0.265	1.00	1.02	1.02
	210	0.272	0.281	0.97	1.01	0.98
	250	0.290	0.276	1.05	0.94	0.99
	295	0.302	0.263	1.15	0.83	0.95

^a Subscript 1 denotes the line at lower energy.

ions are still in the $S' = 0$ state with only a modest population of the first excited multiplet; hence the spectra tend to remain more or less symmetrical.

Torréns et al.²³ have noticed some asymmetry in the Mössbauer spectra of several μ -O[Fe(porphin)]₂ complexes at room temperature, which they attributed to the Gol'danskii-Karyagin effect²⁹ rather than magnetic broadening.³⁹ The two effects can be distinguished since in the case of Gol'danskii-Karyagin asymmetry the relative areas (but not the widths) of the two lines vary with temperature, while the converse is true for magnetic broadening. Unfortunately, Torrén et al.²³ gave only intensity ratios of the two lines, rather than area and line width ratios, which precludes any choice between the two effects on the basis of their data.

For this reason we have made a careful study of the temperature dependence, between 4.2 and 295 K, of the widths, intensities, and areas of Mössbauer lines for [Fe(OEP)]₂O. The data are given in the form of ratios in Table II.

At 245 K and below the areas, widths, and intensities of the two spectral lines are equal within experimental error, and it is only at temperatures higher than this that any significant asymmetry is evident. At the two highest temperatures studied one sees that the lower energy line becomes broader, but also loses intensity relative to the higher energy line, so that the area ratio remains essentially unity. Thus the asymmetry observed at high temperature is clearly magnetic in origin and not due to an anisotropy of the recoil-free fraction. Less extensive data for [Fe(TPP)]₂O (Table II) also support this conclusion. The fairly small degree of magnetic broadening observed is consistent with the very large $|J|$ values found in such complexes. NMR measurements²⁵ of the Knight shifts of the pyrrolic protons in [Fe(TPP)]₂O and [Fe(PMEPP)]₂O⁹ have yielded J values of -309 and -335 cm⁻¹, respectively. Presumably $|J|$ is of a similar magnitude in [Fe(OEP)]₂O.

The absence of a measurable Gol'danskii-Karyagin asymmetry in these complexes is interesting, since the presence of such an effect (in addition to magnetic broadening) appears to be necessary to explain the Mössbauer spectra of [Fe(Salen)]₂O.²⁶ Moreover, the anisotropic nature of the bonding^{15,40} in iron porphyrins might be expected to produce an anisotropic recoilless fraction, although this is apparently not so here. It should be noted that the Gol'danskii-Karyagin effect is also absent in the Mössbauer spectra of Fe(OEP)ClO₄ and Fe(OEP)ClO₄·2EtOH,^{33,41} where the axial bonding is very weak, and in the square planar porphyrinatoiron(II) complexes Fe(TPP),²⁰ Fe(OEP),²¹ and Fe(OMTBP),^{9,42} where no axial ligands are present.^{43,46}

Mössbauer-Zeeman Measurements. Mössbauer spectra of

paramagnetic iron complexes in the presence of an applied magnetic field are often quite complicated, but nonetheless contain a great deal of information about the electronic structure of the iron ion. When such spectra are analyzed in terms of suitable spin Hamiltonian^{4,8,48,49} much of this information can be extracted. We now outline briefly the procedures used to analyze the Mössbauer-Zeeman spectra obtained in the present work.

A. Theory. The spin Hamiltonian employed here includes terms which describe (1) the zero-field splitting of the spin sextet ground state of the Fe³⁺ ion, (2) the Zeeman interaction between the applied magnetic field \mathbf{H} and the electronic spin \mathbf{S} via the \mathbf{g} tensor, (3) the coupling of the electronic spin and nuclear spin \mathbf{I} by the magnetic hyperfine tensor \mathbf{A} , (4) the direct nuclear Zeeman interaction due to the applied field, and (5) the interaction of the nuclear quadrupole moment Q of the $|I = 3/2\rangle$ excited state with the efg. Thus

$$\mathcal{H} = D \left[S_z^2 - \frac{1}{3} S(S+1) + \frac{E}{D} (S_x^2 - S_y^2) \right] + \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} - g_n \beta_n \mathbf{I} \cdot \mathbf{H} + \frac{e^2 q Q}{4} \left[I_z^2 - \frac{5}{4} + \frac{\eta}{3} (I_x^2 - I_y^2) \right] \quad (4)$$

where the terms have been written in the order given above.

We shall assume that the \mathbf{g} , \mathbf{A} , and efg tensors all have the same principal axes,⁵⁰ and since we operate with a real spin ($S = 5/2$) Hamiltonian, the \mathbf{g} tensor is taken to be isotropic with $g_x = g_y = g_z = 2.00$. Moreover, EPR spectra of the present (nondimeric) complexes^{4,11} reveal no splitting of the resonance at $g \simeq 6$ (relative to a $S = 1/2$ spin Hamiltonian), indicating negligible rhombicity, and we have accordingly set E and η to zero in computing most of the spectra discussed below.⁵¹

The nucleus produces a magnetic field at the electrons of only $\sim 10^{-3}$ T. Thus, when the applied field is 0.1 T or more the quantization axis of the electron spins will be fixed by the electronic system, and the small perturbation by the nucleus can be ignored. One can then use the first two terms of eq 4 to calculate the expectation value $\langle S \rangle$ of the electronic spin, determined by the crystal field and applied field, and replace the spin operator \mathbf{S} in the third term of eq 4 by $\langle S \rangle$. This allows one to rewrite the spin Hamiltonian in a form which depends only on nuclear variables:

$$\mathcal{H}_n = \mathbf{I} \cdot \mathbf{A} \cdot \langle S \rangle - g_n \beta_n \mathbf{I} \cdot \mathbf{H} + \frac{e^2 q Q}{4} \left[I_z^2 - \frac{5}{4} + \frac{\eta}{3} (I_x^2 - I_y^2) \right] = -g_n \beta_n (\mathbf{H}_{\text{int}} + \mathbf{H}) \cdot \mathbf{I} + \mathcal{H}_Q \quad (5)$$

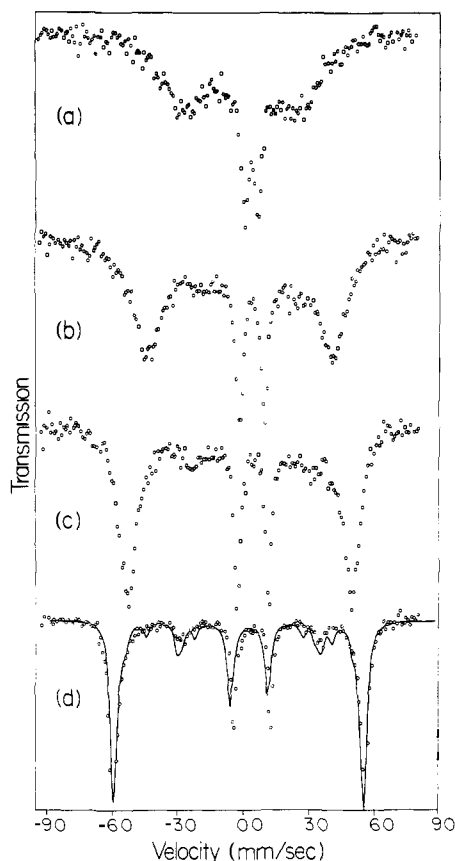


Figure 1. Mössbauer-Zeeman spectra of Fe(OEP)Cl at 4.2 K in applied longitudinal magnetic fields of (a) 1.0, (b) 2.0, (c) 3.0, and (d) 5.0 T. The solid line in (d) is a theoretical spectrum calculated from the spin Hamiltonian in the slow relaxation limit, using parameters listed in Table III.

where \mathcal{H}_Q has been written for the nuclear quadrupole coupling Hamiltonian and

$$\mathbf{H}_{\text{int}} = -\mathbf{A} \cdot \langle \mathbf{S} \rangle / g_n \beta_n \quad (6)$$

is the internal hyperfine magnetic field. The nucleus thus senses an effective magnetic field which is the vector sum

$$\mathbf{H}_{\text{eff}} = \mathbf{H}_{\text{int}} + \mathbf{H} \quad (7)$$

For a given Mössbauer-Zeeman spectrum at 4.2 K, \mathbf{H} is known and $|e^2qQ|$ and Γ can be obtained from the zero-field spectrum at this temperature.⁵² If we assume axial symmetry there are then only three parameters which can be adjusted to fit the observed spectrum: the zero-field splitting parameter D , and the magnetic hyperfine tensor components A_{\perp} ($= A_x = A_y$) and A_{\parallel} (A_z).

We have computed Mössbauer spectra for the complexes studied here in both slow and fast spin relaxation limits. For both limits one begins by calculating, from the first two terms of eq 4, the effective spin $\langle S_i \rangle$ ($i = 1, \dots, 6$) for each of the six levels of the ground multiplet in the presence of the crystal field D , when the external magnetic field \mathbf{H} makes angles θ_H , ϕ_H to the z axis. In the slow relaxation limit the effective magnetic field at the nucleus produced by each level is then given by

$$\mathbf{H}_{\text{eff}}^{(i)} = \mathbf{H} - \mathbf{A} \cdot \langle S_i \rangle / g_n \beta_n \quad (8)$$

and Mössbauer spectra are computed separately for each level using these $\mathbf{H}_{\text{eff}}^{(i)}$ values in the Hamiltonian (eq 5). These spectra are weighted by the appropriate Boltzmann factors and added to give the thermally averaged composite spectrum for a given direction of \mathbf{H} relative to the z axis of the efg. One then interates over all orientations θ_H , ϕ_H of \mathbf{H} to obtain the powder

averaged spectrum.^{53,54} In the fast relaxation limit the $\langle S_i \rangle$ values are used to compute the thermally averaged spin $\langle S \rangle_{\text{av}}$ of the ground multiplet, and $\mathbf{H}_{\text{eff}}^{(\text{av})}$ is calculated from eq 8 using this $\langle S \rangle_{\text{av}}$. The Mössbauer spectrum for a particular orientation of \mathbf{H} is computed from eq 5, and the powder averaged spectrum obtained as before.

Although spin relaxation in the nondimeric complexes studied here is fast in zero field, an applied magnetic field splits the Kramers doublets and affects the transition probabilities between the states. Thus, as the magnitude of the external field increases the spin relaxation rate decreases, and for the maximum fields of 5.0 T employed here the slow relaxation limit produces significantly better fits of the observed spectra than does the fast relaxation limit.⁵⁴ Therefore the calculated spectra displayed in the figures below have all been computed in the slow spin relaxation limit.

B. Porphyrinatoiron(III) Chlorides. Mössbauer spectra of Fe(OEP)Cl at 4.2 K in longitudinal applied magnetic fields of 1.0, 2.0, 3.0, and 5.0 T are presented in Figure 1. For a field of 1.0 T one observes broad, ill-defined absorptions in addition to a sharp central doublet. The outer lines gradually sharpen as the magnetic flux density increases, but it is only for $H > 3.0$ T that one sees a clearly resolved hyperfine pattern with narrow lines. These results are indicative of a field-dependent spin relaxation time, as discussed above. The spectra for $H \leq 3.0$ T are typical of cases where the electronic spin relaxation rate is comparable to the Larmor precession frequency of the ^{57}Fe nuclear spin.⁵⁵

The solid curve in Figure 1d is the theoretical spectrum calculated from the spin Hamiltonian of eq 5 in the slow relaxation limit, using values for the quadrupole splitting ΔE_Q , line width Γ , zero-field splitting D , and hyperfine tensor components A_{\perp} and A_{\parallel} listed in Table III. Very similar D and A values were obtained from fitting the spectrum of Fe(TPP)Cl measured at 4.2 K and $H = 5.0$ T via eq 5 (Table III). In both cases the theoretical spectra do not accurately match the observed intensities of the two innermost lines (see Figure 1d). We think that the reason for this is that an applied field of 5.0 T is not quite sufficient to slow the spin relaxation to the point where the slow relaxation limit employed to compute the theoretical spectra is strictly valid.⁵⁶ Spectra of similar complexes measured in applied fields of 8.0 T¹¹ show a diminished intensity of these innermost lines relative to the outermost ones.

The zero-field splittings D deduced here by fitting the Mössbauer-Zeeman spectra of Fe(OEP)Cl and Ge(TPP)Cl are consistent with values obtained directly from far-infrared spectra of several porphyrinatoiron(III) chlorides,⁵⁷⁻⁶⁰ which range from 6.5 cm^{-1} for Fe(TPP)Cl⁵⁸ to 8.9 cm^{-1} for Fe(DP)Cl.^{9,59} We find that the computed Mössbauer spectra are only moderately sensitive to the value of D employed (at least for this range of D values). Fits almost equally as good could be obtained with D either 1.0 cm^{-1} greater or smaller than the values tabulated, if we made concomitant shifts of $\sim \pm 0.05 \text{ mm s}^{-1}$ for A_{\perp} . That is, a smaller assumed D value requires a slightly smaller A_{\perp} to match the overall width of the spectrum.

For a given value of D the goodness of fit is very sensitive to A_{\perp} , a change of $\pm 0.01 \text{ mm s}^{-1}$ in the latter parameter having a significant effect. However, this is not true for A_{\parallel} , where we find that a variation in the value of this parameter of $\sim \pm 30\%$ (keeping D and A_{\perp} fixed) has almost no observable effect on the computed spectrum. This gross insensitivity of the theoretical spectra to A_{\parallel} is the only justification for our use of isotropic \mathbf{A} tensors for these two complexes. Presumably \mathbf{A} is not isotropic,^{28c,61} but we are unable to determine its anisotropy. The reason for this is that the separation of the two lowest Kramers doublets is sufficiently large compared to the thermal energy at 4.2 K ($\sim 2.9 \text{ cm}^{-1}$) that even with an applied mag-

Table III. Spin Hamiltonian Parameters Deduced from Fitting Mössbauer–Zeeman Spectra of the Complexes at 4.2 K^a

Compd	V_{zz} ^b	η	Γ , mm/s	A_{\perp} , mm/s	A_{\parallel} , mm/s	D , cm ⁻¹	H_{int} , T
Fe(TPP)Cl	>0	0	0.30	1.35 ± 0.02	1.35 ± 0.4	7.0 ± 1.0	49.0 ± 0.7
Fe(OEP)Cl	>0	0	0.30	1.37 ± 0.02	1.37 ± 0.4	8.0 ± 1.0	49.7 ± 0.7
Fe(TPP)OMe	>0	0	0.38	1.36 ± 0.03	1.42 ± 0.03	3.0 ± 0.6	50.0 ± 1.0
Fe(OEP)OMe	>0	0	0.38	1.35 ± 0.02	1.50 ± 0.02	3.3 ± 0.5	51.1 ± 0.6
[Fe(TPP)] ₂ O	<0	0.5	0.27				0 ± 0.2
[Fe(OEP)] ₂ O	0.3	0.27				0 ± 0.2	

^a For the monomeric complexes the electronic g tensor was taken to be isotropic, with $g_{\perp} = g_{\parallel} = 2.00$. The dimers are diamagnetic at 4.2 K. ^b Values of δ and $|\Delta E_Q|$ were taken from Table I; signs of V_{zz} were deduced from the applied field spectra.

netic field of 5.0 T the overwhelming majority of the electronic spins are in the $|S_z = -1/2\rangle$ and $|S_z = +1/2\rangle$ states. Thus the applied field tends to align the spins in the xy plane⁶² and the Mössbauer spectrum senses only the component of the hyperfine field perpendicular to the z axis. Strictly speaking, then, the values quoted in Table III for the internal hyperfine fields in these complexes refer to fields in the perpendicular direction.

The positive signs of V_{zz} found for both chlorohaemins identify the lines which broaden first in zero field upon raising the temperature (i.e., the higher energy lines) as arising from the $|m_I = +1/2\rangle \rightarrow |m_I = \pm 3/2\rangle$ nuclear spin transitions. In the presence of a magnetic field⁶³ the Mössbauer line from this transition is split (or broadened) by an amount $3\alpha \cos \theta$, where θ is the angle between the z axes of the magnetic field and the efg , and $\alpha = g_c \beta_n H$, g_c being the gyromagnetic ratio of the $I = 3/2$ excited state of ⁵⁷Fe and β_n the nuclear magneton. On the other hand, the Mössbauer line which arises from the $|m_I = \pm 1/2\rangle \rightarrow |m_I = \pm 1/2\rangle$ transitions splits by an amount $\alpha(4 - 3 \cos^2 \theta)^{1/2}$. Thus, if the major axis of the hyperfine field is parallel to V_{zz} ($\theta = 0$) the $|m_I = \pm 1/2\rangle \rightarrow |m_I = \pm 3/2\rangle$ line will be the first to broaden as H_{int} increases from zero, while if the magnetic and efg axes are perpendicular ($\theta = \pi/2$) the $|m_I = \pm 1/2\rangle \rightarrow |m_I = \pm 1/2\rangle$ line will broaden first. Our results confirm that H_z and V_{zz} are parallel in these complexes, and as Johnson⁸ has shown for Fe(PP)Cl, both principal axes are normal to the haeme plane.

C. Porphyrinatoiron(III) Methoxides. As we noted in the introductory section, Tang et al.¹¹ have reported that V_{zz} is negative in Fe(PPD)OEt. Thus the sign of V_{zz} in the two methoxide complexes studied here is of considerable interest. The Mössbauer spectrum of Fe(OEP)OMe at 4.2 K and $H = 5.0$ T is shown in Figure 2. The positions of the weak $\Delta m_I = 0$ lines, lines 2 and 5 reading from low to high velocity, relative to the outermost lines (1 and 5) can be used to deduce the sign of V_{zz} . In the spectrum shown in Figure 2 the difference in the separations of lines 1,2 (Δ_{12}) and lines 5,6 (Δ_{56}) defines a quadrupole interaction which is negative (i.e., $\Delta_{12} > \Delta_{56}$) and of approximately half the magnitude of ΔE_Q observed in zero field at the same temperature. For an axially symmetric field gradient, the only component of the efg which is sensed by the zero-field spectrum is V_{zz} , i.e., $|\Delta E_Q| = 1/2 eq |V_{zz}|$. Since the apparent splitting observed in an applied field is half the magnitude observed in the absence of a field, and since $V_{xx} = V_{yy} = -1/2 V_{zz}$, this means that the applied-field spectrum is sensing only the perpendicular component of the efg . Hence V_{zz} is *positive* in Fe(OEP)OMe, as it is in the chlorohaemins. Entirely similar considerations apply to Fe(TPP)OMe, where we also find $V_{zz} > 0$.

Although these arguments in no way depend upon detailed computer fitting of the spectra, we should also stress that no satisfactory fits via the spin Hamiltonian of eq 5 are possible on the assumption that $V_{zz} < 0$. On the other hand, as evident in Figure 2, the calculated spectrum based on a positive V_{zz} fits the observed line positions very satisfactorily.

The assignment of a negative V_{zz} in Fe(PPD)OEt¹¹ was

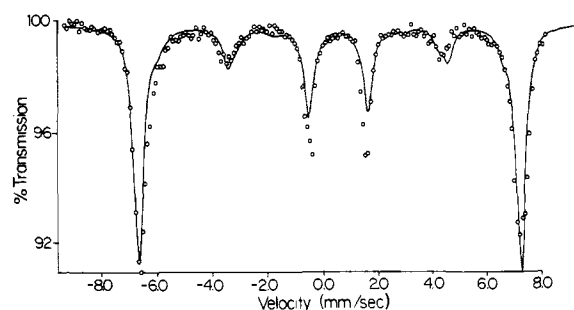


Figure 2. Mössbauer spectrum of Fe(OEP)OMe at 4.2 K and $H_{\parallel} = 5.0$ T. The solid curve was computed from the spin Hamiltonian with parameter values given in Table III.

based on the following considerations: (1) the fact that in an applied magnetic field of 8.0 T at 4.2 K, $\Delta_{12} < \Delta_{56}$, thus defining a positive quadrupole interaction; (2) the fact that at 77 K in zero field it is the low-energy line which is magnetically broadened; (3) the assumption that V_{zz} is perpendicular to the haeme plane while the induced spin $\langle S \rangle$ lies in this plane. The only other possibility to explain the experimental facts (1) and (2) is to make the contrary assumption to (3), namely, that V_{zz} and the induced magnetic field are parallel, in which case V_{zz} is positive.⁶⁴ A spin Hamiltonian fit of the Mössbauer–Zeeman spectrum of the complex should help resolve this ambiguity.

For the two methoxides studied here we have the experimental facts that $V_{zz} > 0$ at 4.2 K and that the low-energy lines of the zero-field doublets are broadened at 80 K. This certainly suggests that at 80 K V_{zz} is perpendicular to H_z in these complexes, although why the relative orientation of axes should be different from that in the chlorohaemins is not clear.

For pentacoordinate high-spin iron(III) porphyrins, Sharma and Moutsos^{65,66} have employed linear combinations of polarized atomic orbitals to calculate, for fixed in-plane bonding, the effect of varying the polarizability of the axial ligand. These calculations suggest that as the polarizability of the axial ligand increases, V_{zz} should decrease and eventually become negative. Tang et al.¹¹ used these arguments to rationalize the apparently negative V_{zz} in Fe(PPD)OEt, by assuming a high polarizability for the OEt⁻ ion. We think it unlikely that any difference in polarizability between OEt⁻ and OMe⁻ would be sufficient to account for sign change in V_{zz} .⁶⁷ Moreover, the calculations of Sharma and Moutsos^{65,66} appear to disagree with the recently observed⁴⁴ experimental fact that in the series Fe(P-MEPP)X⁹ ($X = \text{Cl}^-, \text{Br}^-, \text{I}^-$), V_{zz} is positive throughout and increases rather than decreases in magnitude with increasing polarizability of X. Further detailed studies of alkoxyiron(III) porphyrins are clearly needed to unravel these apparent inconsistencies.

The spin Hamiltonian parameters deduced from fitting the Mössbauer–Zeeman spectra of Fe(OEP)OMe and Fe(TTP)OMe (Table III) differ in some important ways from the corresponding values for the chlorohaemins. Firstly, it appears that D is substantially smaller in the methoxides, values in the

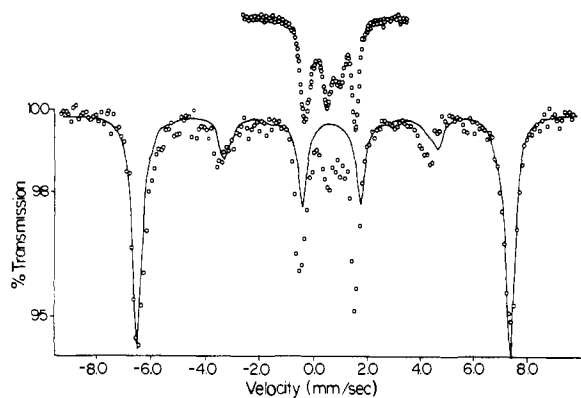


Figure 3. Mössbauer spectrum of Fe(TPP)OMe at 4.2 K and $H_{\parallel} = 5.0$ T. The lack of agreement between experimental and theoretical spectra in the region near zero velocity is due mainly to the presence in the sample of some $[\text{Fe}(\text{TPP})]_2\text{O}$, whose spectrum under the same experimental conditions is shown at the top of the figure.

range $D \approx 3 \text{ cm}^{-1}$ providing much better agreement between calculated and experimental spectra than values of $D \geq 5 \text{ cm}^{-1}$. Other porphyrinatoiron(III) alkoxides also appear to have smaller D values than the corresponding chloride complexes. For example, the far-IR measurements of Richards et al.⁵⁷ give $D = 4.6 \text{ cm}^{-1}$ for Fe(DP)OMe, compared with $D = 8.9 \text{ cm}^{-1}$ for Fe(DP)Cl, and a value $D = 5.3 \text{ cm}^{-1}$ has been obtained¹¹ for Fe(PPD)OEt from low-temperature magnetization measurements.

Secondly, the Mössbauer spectra calculated in this range of smaller zero-field splittings are more sensitive to the precise value of D employed, and for Fe(OEP)OMe we estimate a conservative error limit for D of $\pm 0.5 \text{ cm}^{-1}$. Finally, the fact that the Kramers doublets are much more closely spaced in the methoxides also increases the sensitivity of the computed spectra to A_{\parallel} , and better fits could be obtained by using anisotropic A tensors with A_{\parallel} slightly greater than A_{\perp} .

Owing to the fact that we were unable to obtain an analytically pure sample of Fe(TPP)OMe (vide supra), the spin Hamiltonian parameter values estimated for this complex are less accurate than those for the other three derivatives. Figure 3 shows the Mössbauer spectrum observed at 4.2 K and $H = 5.0$ T, together with the spectrum calculated via eq 5 using the parameters given in Table III. Although the fit to the outermost lines is satisfactory, the mismatch in the region near zero Doppler velocity is very apparent. To show that this mismatch is caused mainly by contamination of the sample with the oxo-bridged dimer, we have included in Figure 3 the spectrum of $[\text{Fe}(\text{TPP})]_2\text{O}$ measured under the same conditions of temperature and applied field.

D. μ -Oxo-bis[porphyrinatoiron(III)] Complexes. We mentioned above that at high temperatures both dimeric complexes show a slight degree of relaxation broadening in their Mössbauer spectra, and that in both cases it is the low-energy line which broadens. Application of 5.0 T magnetic fields at 4.2 K reveals that V_{zz} is negative in both complexes⁶⁸ (see Figure 4). Thus the lines which broaden at high temperature arise from the $|m_1 = \pm 1/2\rangle \rightarrow |m_1 = \pm 3/2\rangle$ nuclear spin transitions. As we have seen, this line will broaden first if the major axis of the internal hyperfine field is parallel to V_{zz} , whereas if the magnetic and efg axes are orthogonal the $|m_1 = \pm 1/2\rangle \rightarrow |m_1 = \pm 1/2\rangle$ line is the first to broaden. We see therefore that H_z and V_{zz} are parallel in $[\text{Fe}(\text{OEP})]_2\text{O}$ and $[\text{Fe}(\text{TPP})]_2\text{O}$. This is also the case for the similar pentacoordinate antiferromagnetically coupled complex $[\text{Fe}(\text{Salen})]_2\text{O}$, although the magnetic and efg axes are perpendicular in $[\text{Fe}(\text{Salen})\text{Cl}]_2$, where the iron atom is hexacoordinate.^{26,69}

Detailed computer fitting of the applied field spectra of the

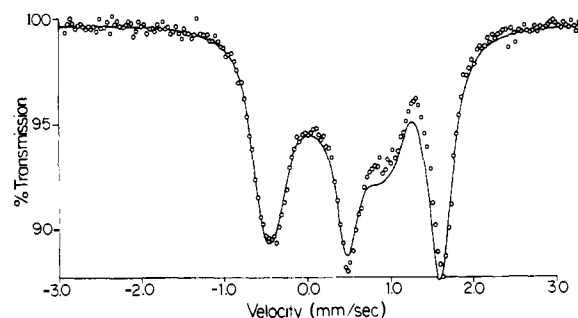


Figure 4. Mössbauer spectrum of $[\text{Fe}(\text{OEP})]_2\text{O}$ in a longitudinal magnetic field of 5.0 T at 4.2 K. The theoretical spectrum is based on the following parameter values: $\delta = 0.39 \text{ mm/s}$, $\Gamma = 0.27 \text{ mm/s}$, $\Delta E_Q = -0.77 \text{ mm/s}$, $\eta = 0.3$, and $H_{\text{eff}} = 5.0 \text{ T}$.

porphyrin dimers indicates nonzero asymmetry parameters for both complexes (Table III); nonzero η values have also been reported²⁶ for the two Salen dimers. Although geometrical factors such as the nonlinear Fe-O-Fe linkage²² may be partly responsible for the fact that $\eta \neq 0$, they seem unlikely to be the major cause since to first order the point group symmetry at iron is not affected.⁷⁰ We think that the principal effect may well be that the p_{π} orbital on oxygen can interact primarily with only one of the two available π orbitals on iron (d_{xz} or d_{yz}), making these two orbitals inequivalent and breaking the axial symmetry.

The negative V_{zz} 's and nonzero η 's found here for the porphyrin dimers are particularly interesting in view of the results for the Salen derivatives, where it is found^{26,30} that $V_{zz} < 0$ and η small for $[\text{Fe}(\text{Salen})\text{Cl}]_2$ but $V_{zz} > 0$ and $\eta \approx 0.8$ for $[\text{Fe}(\text{Salen})]_2\text{O}$. The factors controlling the sign of V_{zz} and magnitude of η in such bridged antiferromagnetic complexes are not at all well understood, and at present we are unable to offer a satisfactory explanation for the sign difference between the porphyrin compounds and $[\text{Fe}(\text{Salen})]_2\text{O}$. We should also note that although one is able to deduce the relative orientations of the principal efg and magnetic axes, the available data give no information concerning the relation of either of these axes systems to the symmetry axes of the molecules.

An important feature of the Mössbauer-Zeeman spectra of $[\text{Fe}(\text{TPP})]_2\text{O}$ and $[\text{Fe}(\text{OEP})]_2\text{O}$ at 4.2 K is that within experimental error $H_{\text{eff}} = H$, and there is no indication of a measurably large internal hyperfine field at the iron nucleus. In the absence of strong antiferromagnetic coupling one would expect to observe a large hyperfine field, and the absence of such a field provides definitive evidence for a nonmagnetic $S' = 0$ ground state and a large exchange integral J .

Experimental Section

Physical Measurements. Microanalyses were carried out either by Mr. P. Borda of this department or by Drs. F. and E. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany. Electronic spectra (dichloromethane solutions) were recorded on a Carey Model 14 spectrophotometer. Wavelengths of maximum absorption are quoted in nanometers with molar extinction coefficients in parentheses. Mass spectra were determined with an AEI MS-9 spectrometer, and magnetic susceptibilities were measured by the Gouy method at room temperature.⁵⁷ ^{57}Fe Mössbauer spectra were obtained with a 25-mCi $^{57}\text{Co}(\text{Cu})$ source and carefully powdered absorbers in transmission geometry, using spectrometers and cryostats described previously.⁷¹ For spectra recorded at 4.2 K source and absorber were both maintained at liquid helium temperature; in all other cases the source was at room temperature. A metallic iron foil absorber was used to calibrate the Doppler velocity scale, and isomer shifts are given relative to the centroid of the iron foil spectrum. Spectra measured in the absence of an applied field were fitted to Lorentzian line shapes using unconstrained least-squares techniques.

Preparations. All chemicals were of reagent grade and were used

without further purification. Fe(OEP)Cl was prepared as described previously.^{21,30} An exactly analogous route was employed to obtain Fe(TPP)Cl, and the product gave satisfactory elemental analyses.⁷²

Octaethylporphyrinatoiron(III) Methoxide, Fe(OEP)OMe. Fe(OEP)Cl (0.65 g) was dissolved in chloroform (50 mL) and a solution of sodium (0.5 g) in anhydrous methanol (200 mL) was added. The mixture was refluxed for 5 min and filtered while hot, and the filtrate was reduced in volume to 150 mL and left to stand overnight. The solid which had deposited was collected by filtration and dissolved in dichloromethane (100 mL). After the solution was filtered and its volume reduced to 30 mL, anhydrous methanol was added to precipitate the product. The precipitate was washed with methanol and dried in vacuo to yield 0.6 g of Fe(OEP)OMe. Anal. Calcd for C₃₇H₄₇N₄OFe: C, 71.73; H, 7.59; N, 9.05. Found: C, 71.07; H, 7.82; N, 9.18. λ (nm) 352 (5.5×10^4), 396 (1.05×10^5), 479 (1.1×10^4), 590 (8.5×10^3). μ_{eff} (295 K) = 5.97 μ_{B} . Mass spectrum m/e (rel intensity) 619 (0.3), 588 (1.0).

Tetraphenylporphyrinatoiron(III) Methoxide, Fe(TPP)OMe. The above route, whether carried out in air or under a dry nitrogen atmosphere, as well as the procedure of Buchler and Schneehage,³⁴ failed to yield pure products when applied to the preparation of Fe(TPP)OMe. The data given here pertain to the sample for which Mössbauer data are reported herein. Anal. Calcd for C₄₅H₃₁N₄OFe: C, 77.25; H, 4.43; N, 8.01. Found: C, 74.68; H, 4.53; N, 7.54. μ_{eff} (295 K) = 5.35 μ_{B} .

μ -Oxo-bis[octaethylporphyrinatoiron(III)], [Fe(OEP)]₂O. Fe(OEP)Cl (1 g) was dissolved in dichloromethane (300 mL) and gently shaken with 2 M aqueous NaOH (300 mL) in a separatory funnel for ca. 10 min. The aqueous layer was discarded and the process repeated twice more. The organic layer was then washed with several aliquots of water to remove excess alkali, and dried over anhydrous potassium carbonate. The solution was left to stand overnight and filtered. The filtrate was reduced in volume to about 30 mL, whereupon addition of hexane produced a blue precipitate. The product was collected by filtration, washed with hexane, and dried in vacuo to give 0.9 g of [Fe(OEP)]₂O. Anal. Calcd for C₇₂H₈₈N₈OFe₂: C, 72.48; H, 7.43; N, 9.39. Found: C, 72.29; H, 7.26; N, 9.51. μ_{eff} (295 K) = 2.34 μ_{B} .

μ -Oxo-bis[tetraphenylporphyrinatoiron(III)], [Fe(TPP)]₂O. The procedure was analogous to that used to prepare the corresponding octaethylporphyrin complex. Anal. Calcd for C₈₈H₅₆N₈OFe₂: C, 78.13; H, 4.14, N, 8.29. Found: C, 78.52; H, 4.23; N, 8.32. μ_{eff} (295 K) = 2.30 μ_{B} .

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References and Notes

- T. H. Moss, A. J. Bearden, and W. S. Caughey, *J. Chem. Phys.*, **51**, 2624 (1969).
- A. Amusa, P. Debrunner, E. Münck, and H. Frauenfelder, *Philos. Mag., Ser. 8*, **29**, 915 (1974).
- N. Sadasivan, H. I. Eberspaecher, W. H. Fuchsman, and W. S. Caughey, *Biochemistry*, **8**, 534 (1969).
- B. W. Fitzsimmons, J. R. Sams, and T. B. Tsin, *Chem. Phys. Lett.*, **38**, 588 (1976).
- C. Maricondi, D. K. Straub, and L. M. Epstein, *J. Am. Chem. Soc.*, **94**, 4157 (1972).
- M. A. Torr ns, D. K. Straub, and L. M. Epstein, *J. Am. Chem. Soc.*, **94**, 4162 (1972).
- L. Bullard, R. M. Panayappan, A. N. Thorpe, and P. Hambright, *Bioinorg. Chem.*, **3**, 161 (1974).
- C. E. Johnson, *Phys. Lett.*, **21**, 491 (1966).
- Abbreviations used in this paper: PP, protoporphyrin IX dianion; PPD, protoporphyrin IX dimethyl ester dianion; MP, mesoporphyrin IX dimethyl ester dianion; OEP, octaethylporphyrin dianion; TPP, tetraphenylporphyrine dianion; PMEPP, tetrakis(*p*-methoxyphenyl)porphyrine dianion; OMTBP, octamethyltetrabenzporphyrin dianion; DP, deuteroporphyrin IX dimethyl ester dianion; Me, methyl; Et, ethyl; Salen, *N,N*-ethylenebis(salicylaldehyde) dianion; THF, tetrahydrofuran.
- G. Lang, T. Asakura, and T. Yonetani, *Phys. Rev. Lett.*, **24**, 981 (1970).
- S. C. Tang, S. Koch, G. C. Papaefthymiou, S. Foner, R. B. Frankel, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.*, **98**, 2414 (1976).
- For reviews of the applications of M ssbauer spectroscopy to natural and synthetic haemins, and discussions of the hyperfine parameters, see (a) G. Lang, *Q. Rev. Biophys.*, **3**, 1 (1970); (b) J. R. Sams and T. B. Tsin in "The Porphyrins", Vol. 4, D. H. Dolphin, Ed., Academic Press, New York, N.Y., in press, Chapter 10.
- Kobayashi et al.¹⁴ failed to notice the presence of magnetic broadening in their M ssbauer spectra of Fe(TPP)Cl recorded at temperatures of 77 K and above, and incorrectly reported zero quadrupole splitting for this compound.
- H. Kobayashi, Y. Maeda, and Y. Yanagawa, *Bull. Chem. Soc. Jpn.*, **43**, 2342 (1970).
- J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Am. Chem. Soc.*, **87**, 2312 (1965).
- In pyridine (py) solution the magnetic moment of Fe(PP)OMe gradually drifts down to $\sim 2 \mu_{\text{B}}$, and it seems very likely that in this solvent the low-spin ($S = 1/2$) Fe(PP)(py)₂OMe adduct is formed.
- I. H. Cohen, *J. Am. Chem. Soc.*, **91**, 1980 (1969).
- This claim was apparently based on magnetic susceptibility measurements, but no supporting data were given in ref. 14. We might also note that the assignments^{14,19} of $S = 2$ and $S = 1$ spin states to the iron(II) complexes Fe(TPP) and Fe(TPP)(THF)₂, respectively, were subsequently shown^{20,21} to be spurious.
- H. Kobayashi and Y. Yanagawa, *Bull. Chem. Soc. Jpn.*, **45**, 450 (1972).
- (a) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975); (b) J. P. Collman, J. L. Hoard, N. Kim, G. Lang, and C. A. Reed, *ibid.*, **97**, 2676 (1975).
- D. H. Dolphin, J. R. Sams, T. B. Tsin, and K. L. Wong, *J. Am. Chem. Soc.*, **98**, 6970 (1976), and unpublished data.
- E. B. Fleischer and T. S. Srivastava, *J. Am. Chem. Soc.*, **91**, 2403 (1969).
- M. A. Torr ns, D. K. Straub, and L. M. Epstein, *J. Am. Chem. Soc.*, **94**, 4160 (1972).
- C. Maricondi, W. Swift, and D. K. Straub, *J. Am. Chem. Soc.*, **91**, 5205 (1969).
- P. D. W. Boyd and T. D. Smith, *Inorg. Chem.*, **10**, 2041 (1971).
- A. N. Buckley, I. R. Herbert, B. D. Rumbold, G. V. H. Wilson, and K. S. Murray, *J. Phys. Chem. Solids*, **31**, 1423 (1970).
- M. Blume, *Phys. Rev. Lett.*, **18**, 305 (1967).
- (a) R. G. Shulman and G. K. Wertheim, *Rev. Mod. Phys.*, **36**, 459 (1964); (b) U. Gonser and R. W. Grant, *Biochem. J.*, **5**, 823 (1965); (c) A. J. Bearden, T. H. Moss, W. S. Caughey, and C. A. Beaudreau, *Proc. Natl. Acad. Sci. U.S.A.*, **53**, 1246 (1965).
- V. I. Gol'danskii, E. F. Makarov, and V. V. Khrapov, *J. Exp. Theor. Phys. Acad. Sci. USSR*, **44**, 752 (1963).
- The dimeric iron(III) Schiff base complexes appear to be useful model compounds for certain biologically important systems such as the non-haeme iron protein hemerythrin, which is responsible for oxygen transport in certain invertebrates: M. Y. Okamura, I. M. Klotz, C. E. Johnson, M. R. C. Winter, and R. J. P. Williams, *Biochemistry*, **8**, 1951 (1969).
- W. Karger, *Z. Naturforsch.*, **17b**, 137 (1962).
- The only change in procedure from that described in ref. 21 is that the complexes were dried in vacuo rather than in air.
- D. H. Dolphin, J. R. Sams, and T. B. Tsin, *Inorg. Chem.*, **16**, 711 (1977).
- J. W. Buchler and H. H. Schneehage, *Z. Naturforsch. B*, **28**, 433 (1973).
- T. H. Moss, A. J. Bearden, R. G. Bartsch, and M. A. Cusanovich, *Biochemistry*, **7**, 1583 (1968).
- M. Gerlach, J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. A*, 112 (1968).
- W. M. Reiff, G. J. Long, and W. A. Baker, *J. Am. Chem. Soc.*, **90**, 6347 (1968).
- A. N. Buckley, G. V. H. Wilson, and K. S. Murray, *Solid State Commun.*, **7**, 471 (1969).
- The possibility of magnetic broadening of the M ssbauer lines in these dimeric complexes does not appear to have been considered in ref. 23.
- (a) D. M. Koenig, *Acta Crystallogr.*, **18**, 663 (1965); (b) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.*, **89**, 1992 (1967); (c) A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *ibid.*, **94**, 3620 (1972).
- In these complexes the iron(III) ion is in the unusual intermediate-spin ($S = 3/2$) state.
- J. R. Sams and T. B. Tsin, *Chem. Phys. Lett.*, **25**, 599 (1974).
- These three compounds all contain intermediate-spin ($S = 1$) iron(II).^{20,21,44} The closely related phthalocyaninatoiron(II) also fails to show Gol'danskii-Karyagin asymmetry.⁴⁵
- J. R. Sams and T. B. Tsin, unpublished data.
- B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, *J. Chem. Phys.*, **49**, 3445 (1968).
- Spin-lattice relaxation in these non-Kramers ions (i.e., the complexes containing iron(II)) is much faster than the Larmor frequency of the ⁵⁷Fe nucleus, and no magnetic broadening is seen at either high or low temperatures. Indeed, the M ssbauer spectrum of Fe(OMTBP) remains a symmetric quadrupole doublet down to 32 mK.⁴⁷
- B. Triplett, personal communication.
- A. Abragam and M. H. L. Pryce, *Proc. R. Soc. London, Ser. A*, **205**, 135 (1951).
- M. H. L. Pryce, *Nature (London)*, **164**, 116 (1949); B. Bleaney, *Philos. Mag.*, **42**, 441 (1951).
- This assumption is justified here since the three tensors will lie in the same frame as long as the symmetry at the iron site is not lower than rhombic.
- The calculated M ssbauer-Zeeman spectra are quite insensitive to small values of E and η in any case.
- The sign of e^2qQ can usually be obtained by inspection of a magnetically perturbed M ssbauer spectrum.
- G. Lang, *J. Chem. Soc. A*, 3245 (1971).
- J. R. Sams and T. B. Tsin, *Chem. Phys.*, **15**, 209 (1976).
- See, e.g., H. H. Wickman and G. K. Wertheim in "Chemical Applications of M ssbauer Spectroscopy", V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N.Y., 1968.
- The spectra of Figures 1a-d show that the relative intensities of the in-

- nermost and outermost pairs of lines are strongly dependent on the magnitude of the applied field.
- (57) P. L. Richards, W. S. Caughey, H. Eberspaecher, G. Feher, and M. Malley, *J. Chem. Phys.*, **47**, 1187 (1967).
- (58) H. Uenoyama, *Biochim. Biophys. Acta*, **230**, 479 (1971).
- (59) H. Uenoyama and K. Sakai, *Spectrochim. Acta, Part A*, **31**, 1517 (1975).
- (60) The far-IR spectra measure the separation of the $|S_z = \pm 1/2\rangle$ and $|S_z = \pm 3/2\rangle$ Kramers doublets, i.e., $2D$, with error limits for the chlorides usually reported as about $\pm 2.0 \text{ cm}^{-1}$.
- (61) (a) M. Weissbluth, *Struct. Bonding (Berlin)*, **2**, 1 (1967); (b) G. M. Harris, *J. Chem. Phys.*, **48**, 2191 (1968); (c) G. Lang, *Q. Rev. Biophys.*, **3**, 1 (1970).
- (62) Since the probability that the magnetic field makes an angle θ to the z axis is proportional to $\sin \theta$, geometrical factors also strongly favor the case where the magnetic field lies in the xy plane.
- (63) The magnetic field may be of either internal or external origin. In this paragraph we are specifically concerned with an internal magnetic field arising from slow spin fluctuations.
- (64) The magnitude of the quadrupole interaction given by $\Delta_{12} - \Delta_{56}$, relative to that observed in the zero-field spectrum, is not stated in ref 11, nor can an accurate estimate be made from the published spectrum of Fe(PPD)OEt in an applied field of 8.0 T.
- (65) R. R. Sharma and P. Moutsos, *J. Phys., Colloque C6*, **35**, 359 (1974).
- (66) R. R. Sharma and P. Moutsos, *Phys. Rev. Sect. B*, **11**, 1840 (1975).
- (67) Nor is it likely, in view of the present results, that slight differences in the nature of the β -pyrrole substituents could change the sign of the efg.
- (68) Because only the $S' = 0$ state is occupied at 4.2 K, the applied field spectra are exactly like those of diamagnetic complexes, and determination of the sign of V_{zz} is not complicated by induced spin polarization.
- (69) In $[\text{Fe}(\text{SalenCl})_2]$ bridging occurs through oxygen atoms of the Salen ligands, and not through the chlorine atoms.
- (70) In the diamagnetic complex 1,2-bis(diphenylphosphino)ethaneoctacarbonyliron(0) the two $\text{Fe}(\text{CO})_4$ moieties are nonlinearly bridged, but η is effectively zero: M. G. Clark, W. R. Cullen, R. E. B. Garrod, A. G. Maddock, and J. R. Sams, *Inorg. Chem.*, **12**, 1045 (1973).
- (71) (a) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **8**, 95 (1969); (b) J. R. Sams and T. B. Tslin, *ibid.*, **14**, 1573 (1975); (c) J. N. R. Ruddick and J. R. Sams, *J. Chem. Soc., Dalton Trans.*, **470** (1974); (d) J. R. Sams and J. C. Scott, *ibid.*, 2265 (1974).
- (72) Anal. Calcd for $\text{C}_{44}\text{H}_{28}\text{N}_4\text{ClFe}$: C, 75.06; H, 4.01; N, 7.96; Cl, 5.05. Found: C, 74.55; H, 4.20; N, 8.09; Cl, 4.90.

The Effect of Energy Gaps on Multiple Emissions in Heterotriscelated Rhodium(III) Complexes

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Abstract: Three groups of complexes have been prepared and studied by emission spectroscopy: (A) $[\text{Rh}(\text{bpy})_n(\text{phen})_{3-n}]^{3+}$; (B) $[\text{Rh}(\text{bpy})_n(5,6\text{-Mephen})_{3-n}]^{3+}$; (C) $[\text{Rh}(\text{phen})_n(5,6\text{-Mephen})_{3-n}]^{3+}$. The nonexponential luminescence decays of the group A complexes ($n = 1, 2$) have been time resolved by boxcar averaging techniques. The group B and C complexes are characterized by exponential luminescence decays. The results are correlated with the energy gaps between the $^3\pi\pi^*$ states of the coordinated ligands. These are found to be $\sim 100 \text{ cm}^{-1}$ for group A and $\sim 1600 \text{ cm}^{-1}$ for groups B and C.

I. Introduction

The occurrence of multiple emissions from polyatomic molecules containing only light atoms is commonplace as evidenced by simultaneous fluorescence and phosphorescence exhibited by numerous organic species. The effect of heavy central metal ions with a variety of electronic configurations on the emissions of organic ligands has been the subject of many studies. For example, systematic studies of metalloporphyrins² have shown that central metal ions with closed shells (groups 2A, 2B, 3A, 4A) form metalloporphyrins which show both fluorescence and phosphorescence;^{2a,e} modification of this behavior by the presence of metal ions with open shells but closed subshells $[\text{Rh}(\text{III})]$, $[\text{Ru}(\text{II})]$, $[\text{Pd}(\text{IV})]$, $[\text{Pt}(\text{II})]$, $[\text{Pd}(\text{II})]$ is manifested in enhancement of phosphorescence, although weak fluorescence is still observed.^{2d,e,g} Several cases of multiple fluorescence emissions ($S_2 \rightarrow S_0$, $S_1 \rightarrow S_0$) from metalloporphyrins have also been reported.^{2f,h}

Studies of the emissions of complexes of Rh(III) with the bidentate ligands 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) indicate that the homotriscelated complexes $[\text{Rh}(\text{bpy})_3]^{3+}$ and $[\text{Rh}(\text{phen})_3]^{3+}$ phosphoresce from one thermally equilibrated manifold of ligand localized $\pi\pi^*$ states at 77 K.^{3,4} At lower temperatures (7–9 K), spin-lattice relaxation processes are slowed sufficiently to cause nonexponential decay from the thermally nonequilibrated triplet sublevels.^{4c} The heterotriscelated complexes, $[\text{Rh}(\text{bpy})_2(\text{phen})]^{3+}$ and $[\text{Rh}(\text{bpy})(\text{phen})_2]^{3+}$, display multiple phos-

phorescence emissions at 77 K from $\pi\pi^*$ states localized on phen and on bpy.^{3b,4b} Furthermore, several heterotriscelated complexes of Ir(III) show multiple emissions from $d\pi^*$ and $\pi\pi^*$ states at low temperatures⁵ (77 K) and the homobiscelated complex, $[\text{IrCl}_2(\text{phen})_2]^{1+}$, emits from both $d\pi^*$ and dd states at intermediate temperatures ($\sim 230 \text{ K}$).⁶ Recent reports indicate that the *fac*- $\text{ClRe}(\text{CO})_3\text{L}_2$ ($\text{L} = 4\text{-phenylpyridine}$) complex emits from a $\pi\pi^*$ state at 77 K and from a CT state at 298 K,^{7a} suggesting that dual $\pi\pi^*$ and CT emissions are likely at intermediate temperatures, and simultaneous emissions from thermally nonequilibrated $n\pi^*$ and charge-transfer levels in *fac*- $\text{XRe}(\text{CO})_3(3\text{-benzoylpyridine})_2$ at 77 K have been observed.^{7b} Hence, there is mounting evidence that radiationless transitions between excited states of metal complexes are not always efficient.

The factors relevant to radiationless relaxation between electronic excited states have been widely discussed. Intramolecular features which influence spin-orbit coupling, energy gaps between electronic states, and vibrational frequencies are particularly important. Perturbations introduced by viscosity and temperature changes in the environment also make significant contributions to radiationless decay rates.⁸ In order to study the influence of these various factors, it is desirable to vary only one while keeping the others constant. In this paper, we report the effects of varying the energy gap between the lowest two $\pi\pi^*$ triplets of several heterotriscelated complexes of Rh(III). To a good approximation, other factors