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ELECTRONIC STRUCTURE OF METALLOPORPHYRINS*

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The article reviews electronic structure of iron(III), iron(II) and manganese-(III) porphyrin complexes in the light of their physical properties, and discusses its relevance with reference to heme proteins.

Key Words : Metalloporphyrins; Heme Proteins; Electronic Structure of Hemes; Magnetic and Spectroscopic Properties of Hemes

INTRODUCTION

HEME proteins are a class of biologically important macromolecules which perform various distinctive functions. They act as reversible oxygen transport and storage proteins in hemoglobin and myoglobin, as reversible electron transfer agents in cytochromes, and are involved in irreversible covalent transformations of substrates in peroxidases. Inspite of these diverse functions, all heme proteins have the unifying feature of a common active site or prosthetic group composed of an iron-porphyrin complex (Fig. 1). It is this metal porphyrin chromophore which is the centre of all the diverse functions of heme proteins.

It is now known that while remainder of the protein plays a significant role in modulating their biological activity, the biological function of the heme proteins is determined largely by the conformational and electronic properties of the heme group.[1-4] There exists an enticing relationship between the electronic and conformational structure, physical properties, and function, and a well-defined link between the properties of the active site and the function of the protein.[5,6] It is for this reason that there is considerable interest in the electronic structure of the metal ion in the heme chromophore.

In this article physical properties and electronic structure of iron-porphyrin (and briefly manganese porphyrin) complexes will be discussed in relation to their biological functions. As shown in Table I, different substituents on the porphyrin ring constitute different porphyrins. Protoporphyrin IX is the most important among naturally occurring ones and occurs in heme proteins. Among the synthetic porphyrins, tetraphenyl- and octaethyl-porphyrins are the most common ones.

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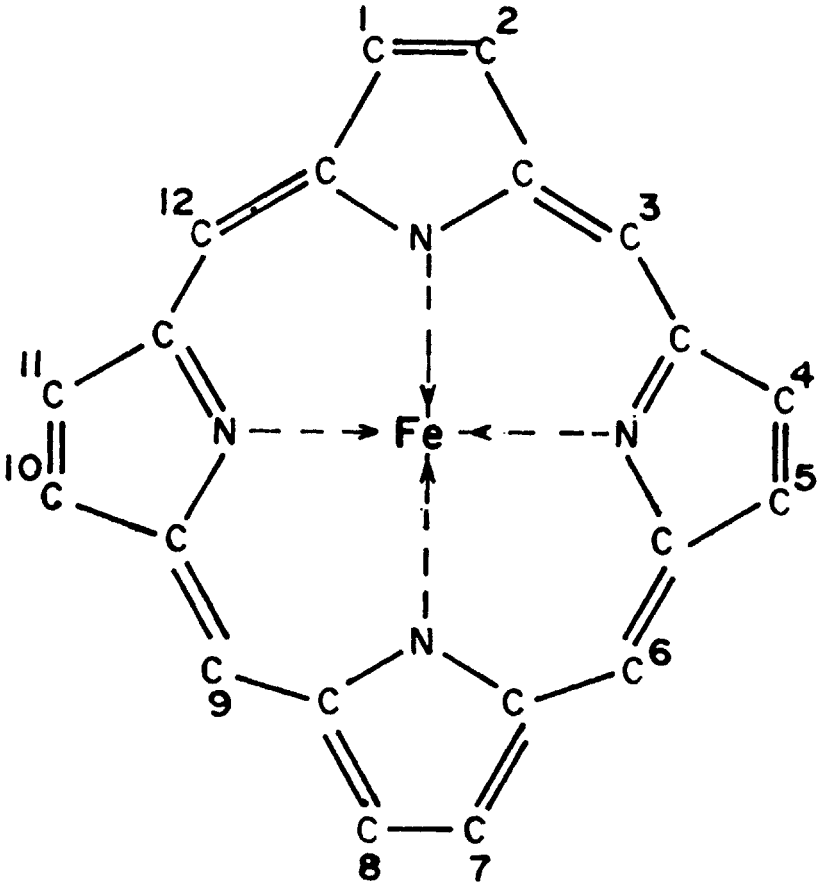

FIG 1 Structure of iron porphyrin complex. The code for the numbers representing various substitutions is given in Table I.

TABLE I

Porphyrin ring substituents in different porphyrin compounds
(Position numbering refers to Fig. 1)

Position	TPP	OEP	Proto	DPDME	Meso
1	H	CH_2CH_3	CH_3	CH_3	CH_3
2	H	CH_2CH_3	$CH = CH_2$	H	CH_2CH_3
3	C_6H_5	H	H	H	H
4	H	CH_2CH_3	CH_3	CH_3	CH_3
5	H	CH_2CH_3	$CH = CH_2$	H	CH_2CH_3
6	C_6H_5	H	H	H	H
7	H	CH_2CH_3	CH_3	CH_3	CH_3
8	H	CH_2CH_3	CH_2CH_2COOH	$CH_2CH_2COOCH_3$	CH_2CH_2COOH
9	C_6H_5	H	H	H	H
10	H	CH_2CH_3	CH_2CH_2COOH	$CH_2CH_2COOCH_3$	CH_2CH_2COOH
11	H	CH_2CH_3	CH_3	CH_3	CH_3
12	C_6C_5	H	H	H	H

Iron(III) Porphyrins

Though +3 oxidation state of iron is biologically not the most important one for oxygen-carrying heme proteins, this oxidation state plays a significant role in cytochromes. More significantly, huge amount of structural and physical studies have been done on heme proteins with trivalent iron, and many important information about iron(II) heme proteins have been derived from studies on iron(III) hemes. Iron(III) porphyrin complexes are generally stable and suitable for detailed examination by various physical techniques.

Iron(III) porphyrins with d^5 electron configuration can have ground state of high ($S = 5/2$), low ($S = 1/2$) or intermediate ($S = 3/2$) spin state.[7] Of these the first two situations are the most common for iron(III) hemes. Examples of intermediate-spin state are very rare. There is also a possibility that the ground state of the ferric ion may not be a pure spin state but 'spin-mixed' because of quantum mechanical spin state mixing with some other spin state.[8,9] In special circumstances the ferric ion in the hemes may be in the 'spin-crossover' region and show thermal spin-equilibrium between two spin states.[10-12] All these possibilities have actually been observed in heme proteins adding considerable significance to their studies in the model complexes.[7] Physical properties of the model ferric porphyrin complexes showing these various spin situations are utilised here to deduce their distinctive electronic structure.

High-Spin Iron(III) Porphyrins

Among the high-spin iron(III) porphyrins, tetraphenylporphinato iron(III) halides Fe(TPP)X (X = Cl, Br, I, NCS) provide the best characterised series for discussion.[7] The iron in these synthetic hemes is five-coordinated[13,14] with Fe-N_4X chromophore as shown in Fig. 2. Some representative physical properties of these complexes together with those of a few others are listed in Table II. The data are consistent with their high-spin behaviour. However, the interesting features of their ground electronic state are revealed in the temperature-dependent studies of their powder and single-crystal magnetic studies.[15-20] Figs. 3 and 4 show typical

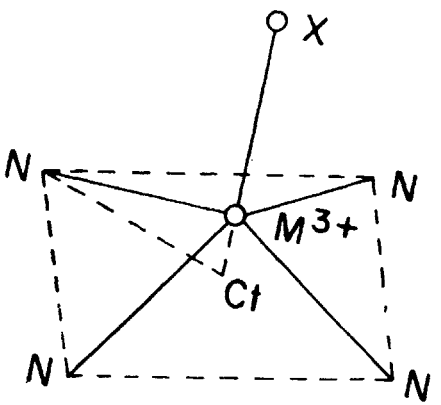

FIG 2 The Fe-N_4X chromophore for the high-spin iron(III) porphyrins.

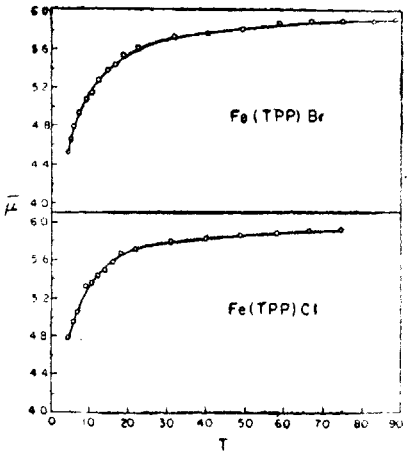

FIG 3 The temperature-dependence of average magnetic moment (μ) for Fe(TPP) Cl and Fe(TPP) Br.[7]

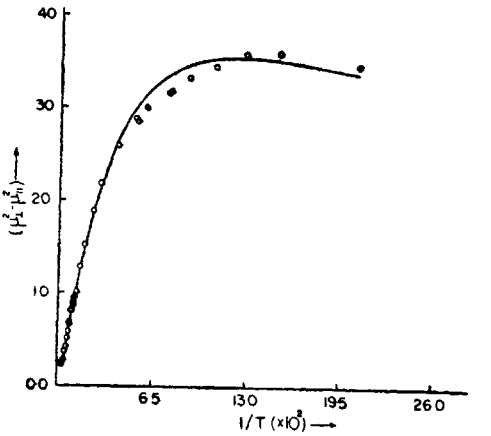

FIG 4 The temperature-dependence of $(\mu_{\perp}^2 - \mu_{11}^2)$ for the single crystal of Fe(TPP) Cl. Here $\mu_{||}$ $\mu_{\perp}$ are the principal moments parallel and perpendicular to the symmetry axis of the molecule, respectively. The solid line is the theoretical one calculated for $D = 6.0\text{cm}^{-1}$.[7,16]

TABLE II

Structural and physical properties of high-spin iron(III) porphyrins and heme proteins

	Fe–Ct (Å)	Fe–N_{pyr} (Å)	ΔE (mm/sec)	δ* (mm/sec)	D (cm^{-1})
Fe(TPP) (NCS)	0.49	2.065	0.49	0.39	5.0
Fe(TPP) Cl	0.39	2.060	0.46	0.40	6.0
Fe(TPP) Br	0.49	2.069	0.72	0.45	12.5
Fe(TPP) II	0.46	2.066	0.75	0.45	13.5
Hemin Chloride	0.48	2.062	1.02	0.36	7.0
Fe(DPDME) Cl	—	—	0.78	0.35	8.95
MbF	—	—	1.3	—	6.5
HbF	—	—	0.7	0.3	7.5

*w.r.t. metallic iron

results for Fe(TPP) Cl. Here μ is referred to average magnetic moment; $\mu_{||}$ and $\mu_{\perp}$ are the principal magnetic moments measured along parallel and perpendicular directions to the symmetry axis of the molecule respectively. μ shows a sharp decrease below 40 K and $(\mu_{\perp}^2 - \mu_{||}^2)$ shows that this quantity remains significantly large at all temperatures. The ESR measurements carried out at 5 K on Fe(TPP) Cl give g-values close to 2.0 and 6.0. All these features are characteristic of an important property of their electronic ground state $^6A_1$ which is split into three spin doublets through spin-orbit interaction (Fig. 5). This splitting, called zero-field

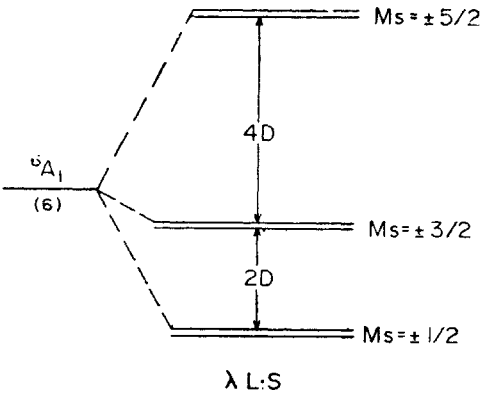

FIG 5 The zero-field splitting diagram for high-spin iron(III) ion. D is the zero-field splitting parameter.

splitting (ZFS, D), is the most dominant feature of the electronic structure of heme proteins and is highly sensitive to their physical properties.[7,21] The sign and magnitude of the ZFS is delicately related to the symmetry and nature of the chemical bonding in the heme chromophore. Experimental results as in Figs. 3 and 4 are therefore generally used to determine this parameter which is listed in Table II for the TPP and other complexes. Many features of the ZFS in the heme complexes deserves mention. First, in all the the synthetic hemes, D is positive and large and is similar to that in myoglobin etc. The positive sign of D implies that $Ms = \pm 1/2$ lies lowest (*see* Fig. 5). The magnitude of D lies between 5 and 15cm^{-1}. The significance of this value becomes evident when we recall that the D values for most high spin ferric inorganic complexes lie between 0.01 and 0.5cm^{-1}. It is thus obvious that the large value of D in the hemes is a consequence of the nature of the iron-porphyrin chemical bonding. We next find that in the Fe(TPP) X series the ZFS varies as $D_{NCS} < D_{Cl} < D_{Br} < D_I$, which is same as the spectrochemical series for the halides.[18] The ZFS seem to vary significantly with the substitution on the porphyrin ring. For example, D varies from 6cm^{-1} for the Fe(TPP) Cl to 9cm^{-1} for the Fe(DPDME) Cl, though a trend in D with the basicity of the porphyrin ring may be difficult to ascertain in view of the limited data available at this stage.

Since the ZFS in the hemes is sensitive to the chemical bonding between the metal and the porphyrin ligand or to the axial ligation, such data can be used to understand details of the electronic structure of the metal ion. The ZFS in an ion of d^5 electron configuration arises from many factors, but in the heme complexes the most dominant contribution is the spin-orbit interaction with the excited states.[8,21] It is thus possible to determine the nature and position of the excited states using the ZFS or the experimental data such as in Figs. 3 and 4, and in Table II. This is conveniently accomplished through crystal field calculations. One such calculation uses three variable parameters :[25] Δ, C' and μ', where Δ is the total crystal field; C' and μ' relate to differences between the axial and in-plane

interactions. Using values of these parameters which give good fit to the experimental results, the position and nature of the excited states may be calculated. The result for one member of the Fe(TPP) *X* series is included in Table III. It may be seen that the three components of the $^6A_1$ state exhibit the separation as demanded in Fig. 5. The first closest excited state is $^4A_2$, with ^2E (and not ^4E) being the next closest state. The $^4A_2$ shows a large ZFS as well, with $^4A_2$ ($\pm 3/2$) lying about 100cm^{-1} below the $^4A_2(\pm 1/2)$. The ^4E and other doublets lie much higher in energy. The ground state of the ferric ion remains here nearly pure $^6A_1$ with largest mixing of $^4A_2$ being less than 4 per cent in Fe(TPP) I; in other compounds this mixing is still less.

TABLE III

Eigenfunctions and eigenvalues of lowest-lying states in the high-spin Fe(TPP) I[25]

States	Main component	Energy (cm^{-1})	$^6A_1$ ($\pm 1/2$)	$^6A_1$ ($\pm 3/2$)	$^6A_1$ ($\pm 5/2$)	$^6A_2$ ($\pm 3/2$)	$^6A_2$ ($\pm 1/2$)
Ground	$^6A_1$ ($\pm 1/2$)	—118.1	0.9738	0.0000	0.0000	0.0000	0.2248
1st excited	$^6A_1$ ($\pm 3/2$)	—90.9	0.0000	0.9804	—0.0011	0.1917	0.0000
2nd excited	$^6A_1$ ($\pm 5/2$)	—27.9	0.0000	0.0011	0.9989	0.0002	0.0000
3rd excited	$^4A_2$ ($\pm 3/2$)	1887.8	0.0000	—0.1933	0.0002	0.9630	0.0000
4th excited	$^4A_2$ ($\pm 1/2$)	1989.4	—0.2250	0.0000	0.0000	0.0000	0.9694
5th excited	^2E	4592	—	—	—	—	—

Note : All other states lie much higher in energy.

Using the above theoretical model, a parameter space diagram can be generated[25] for various possible spin situations. Fig. 6 defines such a diagram and delineates regions of different ground states. The crystal field parameters for the Fe(TPP) *X* series are observed to lie in the crossover region between high- and low-spin states. This would make these synthetic hemes very susceptible to change in the spin state by even minor changes in axial ligation etc. This easeness of the change in the spin state of the ferric ion in the heme protein holds key to many biochemical functions of the ferric heme proteins.

Intermediate-Spin and Spin-Mixed Iron(III) Porphyrins

Fig. 6 shows that for $\Delta > 36000\text{cm}^{-1}$ and $C' > 10000\text{cm}^{-1}$, a small parameter-space region exists to stabilise intermediate-spin ground state. There is also a significant region in the diagram between $36000 > \Delta > 32000\text{cm}^{-1}$ in which the ground state in spin-mixed between $S = 5/2$ and $S = 3/2$. In both the possibilities, the electronic structure of the ferric ion is expected to be very novel to allow for these rare situations to occur. Experimental examples conforming to the above theoretical predictions are not many and only a few hemes have so far been well characterised. The most celebrated among them are the perchlorato iron(III) porphyrins.

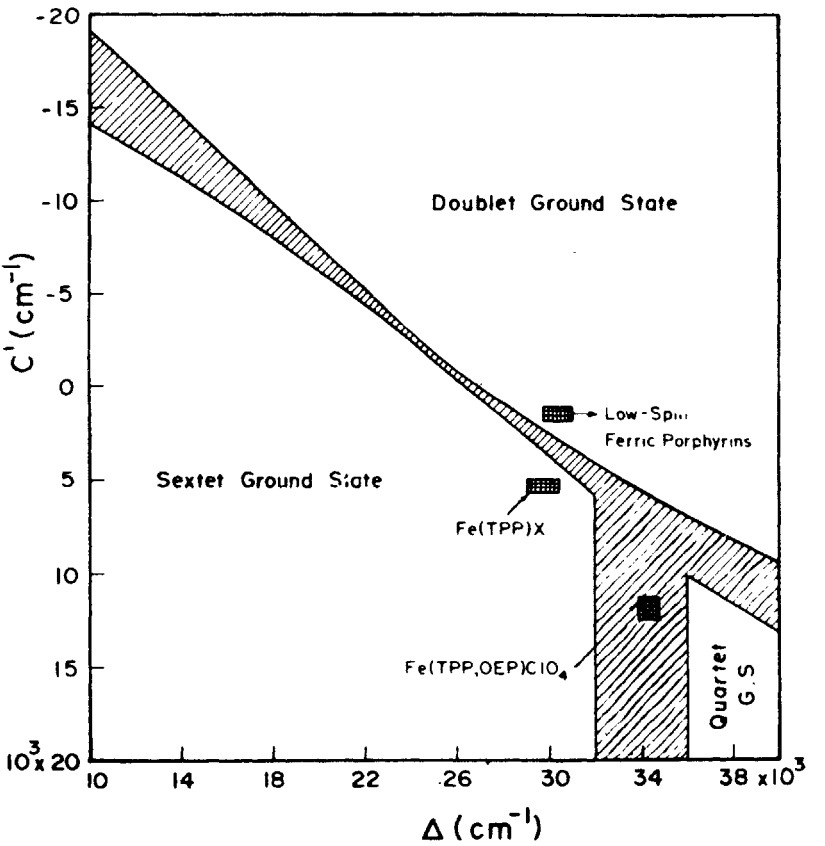

FIG 6 Parameter-space diagram for iron(III) porphyrins. The significance of the parameters C' and Δ is discussed in the text.

Perchlorato iron(III) porphyrins are five-coordinated iron(III) complexes where the perchlorate occupies the apical fifth coordination site with its oxygen being coordinated to the iron. The iron is slightly out of the plane but to a lesser extent than in the high-spin. The relevant structural data listed in Table IV for the perchlorates and some high- and low-spin porphyrins bring out the 'intermediate' structural features of these perchlorato porphyrins. This is also reflected in their physical properties as seen in the table. The distinctive features of their novel electronic structure are reflected in the temperature-dependence of their solid state magnetic moment (Fig. 7), which clearly brings out the most unusual characteristics.[28] That these properties are not related to any solid-state effect is borne out by the unusual temperature-dependence of the solution proton nmr measurements[32] which show that the isotropic shift varies from down-field to upfield as the temperature is changed. It is thus clear that the unusual and remarkable properties of the perchlorato iron(III) porphyrins are intramolecular in origin and arise from their novel electronic structure.

TABLE IV

Structural and magnetic properties of perchlorato and some other ferric porphyrins

Spin state	Temp (K)	Fe(TPP) ClO_4 Spin-mixed Predo. $S = 3/2$	Fe(OEP) ClO_4 Spin-mixed Predo. $S = 3/2$	Fe(TPP) Br High-spin $S = 5/2$	Fe(TPP) $(MeIm)_2$ ClO_4 Low-spin $S = 1/2$
Fe–N(Å)		2.001	1.994	2.069	1.971
Fe–Ct(Å)		0.28	0.26	0.49	0
(BM)	290	5.00	4.80	5.85	2.42
	80	4.60	4.20	5.80	2.20
	4.2	3.60	3.16	4.60	—
(mm/sec)	295	2.79	3.16	—	2.23
	4.2	3.50	3.57	0.72	—
I.S. (mm/sec)	295	0.30	0.29	—	0.23
(w.r.t. metallic iron)	4.2	0.38	0.37	0.45	—

Using again a crystal field model the electronic structure of these complexes can be deduced from their physical properties. Results of such a calculation are included in Table V for the two perchlorato iron(III) prophyrins. It is seen that the formal ground state is predominantly $^4A_2$ which lies very close to the excited state $^6A_1$. The two components of $^4A_2$ ($\pm$ 1/2, $\pm$3/2) are significantly spin-mixed

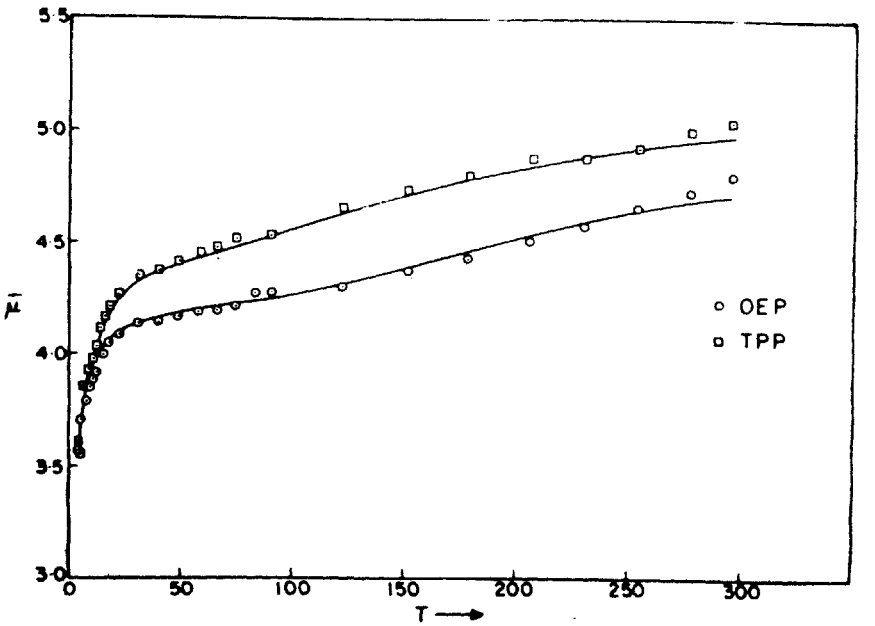

FIG 7 Variable temperature μ for the spin-mixed Fe(TPP) ClO_4 and Fe(CEP) ClO_4. Note the unusual behaviour of μ. The solid lines are theoretically calculated ones using parameters discussed in the text.[28]

TABLE V

Electronic structure of perchlorato iron(III) porphyrins[28,32]

	Fe(TPP) ClO_4 Energy (cm^{-1})	Fe(OEP) ClO_4 Energy (cm^{-1})
$^4A_2 \mid \pm 1/2 >$*	0	0
$^4A_2 \mid \pm 3/2 >$*	38	18
$^6A_1 \mid \pm 5/2 >$	275	264
$^6A_1 \mid \pm 3/2 >$*	405	313
$^6A_1 \mid \pm 1/2 >$*	445	332

*Designates states which are spin-mixed. The ground state wave function is spin-mixed with components of $^6A_1$ to the extent of 35 per cent and 18 per cent in the TPP and OEP complexes recpectively.

with $^6A_1$ ($\pm 3/2$) and $^6A_1$ ($\pm 1/2$), and all the five spin states lie within 500cm^{-1}. The ground state ($^4A_2$) is spin-mixed with $^6A_1$ to the extent of about 40 per cent in the OEP and 20 per cent in the TPP complex.[28,32]

The novel feature of the electronic structure of perchorato ferric porphyrins lies in their spin-mixed ground state. This mixing is through spin-orbit coupling with the low-lying $^6A_1$. The mixing is so extensive especially in the OEP complex that the ground state cannot be designated by a specific spin state as is usually done. How the coordination of perchlorate helps in lowering the energy of $^4A_2$ and $^6A_1$ and bring them both so close, is not clearly understood except in a semi-quantitative manner within the above crystal field model. It is interesting that such a spin-mixed ground state has been speculated for the ferric ion in ferricytochrome C' and suspected to be a more widespread phenomenon in the heme proteins than is at present believed.[9]

IRON(II) PORPHYRINS

The iron(II) porphyrin chromophore obviously plays the most important role in the biological functions of heme proteins like hemoglobin and myoglobin. The ferrous ion in these porphyrins can have three possible ground states: $S = 2$, $S = 0$ and $S = 1$. The first two spin situations are the most abundant ones in heme proteins, and the last one is known only in a few synthetic planar iron(II) porphyrins. Detailed knowledge of the electronic structure of high-spin ($S = 2$) ferrous porphyrins is very vital but little is known in this regard beyond that their ground electronic state is a spin-quintet with substantial ZFS as expected. Table VI lists some typical magnetic data for the ferrous hemes, which are normal as expected. The large quadrupole splitting for the 'diamagnetic' HbO_2 may seem surprising for $S = 0$ iron(II) hemes but then the electronic structure and formal oxidation state of iron in HbO_2 is still a matter of debate and controversy.[21,33]

S = 1 Iron(II) Porphyrins

As in the case of the ferric porphyrins, the intermediate spin state ($S = 1$) is a rarity for the iron(II) porphyrins and has been demonstrated only in a very few

TABLE VI

Magnetic properties of iron(II) porphyrins and proteins

Complex	μ^*_{BM}	Temp (K)	ΔE (mm/sec)	δ† (mm/sec)	spin-state
Fe(TPP) $(THF)_2$	5.2	77	2.66	0.95	$S = 2$
Fe(TPP) (2MeIm) (EtOH)	5.3	77	2.67	1.02	,,
Hb		4.2	2.40	0.91	,,
Fe(TPP)	4.3	300	1.52	0.42	$S = 1$
Fe(OEP)	4.7	295	1.49	0.52	,,
Fe(PC)	3.9	4.2	2.49	0.48	,,
Fe(TPP) $(py)_2$	0	77	1.25	0.45	$S = 0$
Fe(Proto) $(py)_2$	,,	77	1.21	0.45	,,
HbCO	,,	195	0.36	0.18	,,
HbO_2	,,	195	1.89	0.20	,, (?)
		77	2.19	0.26	

*value at 295 K
†w.r.t. metallic iron

planar iron(II) porphyrins.[34,35] This spin state has no proven analogue in the iron(II) heme proteins though its existence has been speculated in certain heme proteins.[36] The constraints involved in stabilising this rare spin state is expected to import unusual characteristics to their physical properties and electronic structure.

The best known example of intermediate spin iron(II) porphyrin is the Fe (TPP). The molecule is planar with iron being strictly in the plane of the porphyrin core.[35] The molecule can be prepared by particularly two different methods. Originally[37] it was prepared by heating Fe(TPP) $(py)_2$ in vacuum for several hours giving an 'amorphous-looking' highly air-sensitive powder with $\mu = 4.75$ BM at room temperature. A crystalline and relatively less air-sensitive Fe(TPP) can be prepared[35] by chromous reduction of Fe(TPP) Cl, which is suitable for detailed studies. Experimental results[34] of measurements on polycrystalline and single crystal samples of the latter preparation are included in Figs. 8 and 9. Three features of the results are noteworthy. , First is the high room temperature magnetic moment for an $S = 1$ ground state (see Table VI). This is a common feature with all planar iron(II) porphyrins and analogous iron(II) phthalocynine.[38] All these planar $S = 1$ iron(II) compounds show room temperature magnetic moment lying between 4.0-4.8 BM. What is the origin of such large orbital contribution in these cases ? Answer must lie in their electronic structure. Second is the temperature-dependence[34] of which shows sharp decrease in below 50 K and appears to suggest the existence of very large ZFS of the ground state. Third is the observation of large anisotropy $(K_\perp - K_\parallel)$ of the molecule.[34] Here K refers to molecular susceptibility.

A search into conditions which favour spin triplet as ground state can be made within the crystal field theory.[34] Fig. 10 spans regions of parameter space delineat-

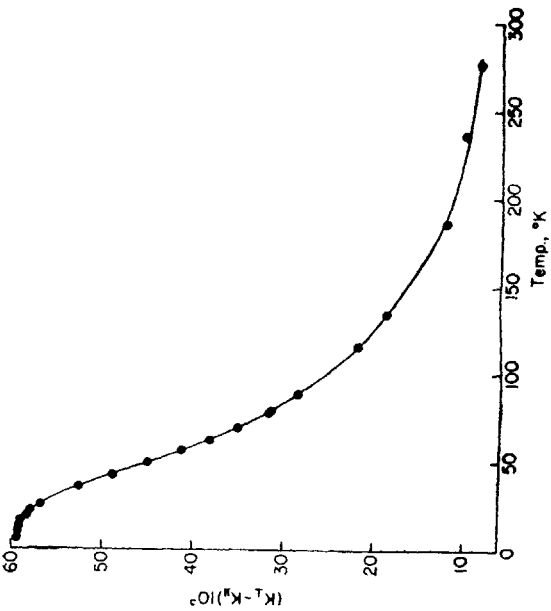

FIG 9 Temperature-dependence of the molecular anisotropy $(K_\perp - K_\parallel)$ of the single crystals of $S = 1$ Fe^{II}(TPP).[34] Here $K_\parallel$ and $K_\perp$ refer to the principal susceptibilities parallel and perpendicular to the symmetry axis of the molecule, respectively.

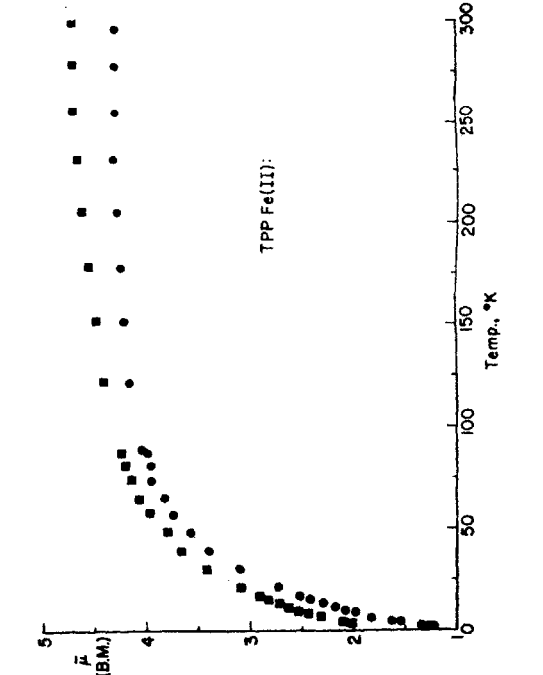

FIG 8 Temperature-dependence of μ for $S = 1$ Fe^{II}(TPP). The data[7,34] were collected on samples prepared by two different methods. Rectangles refer to the Kobayashi method while circles to the Collman method (*see the text for details*).

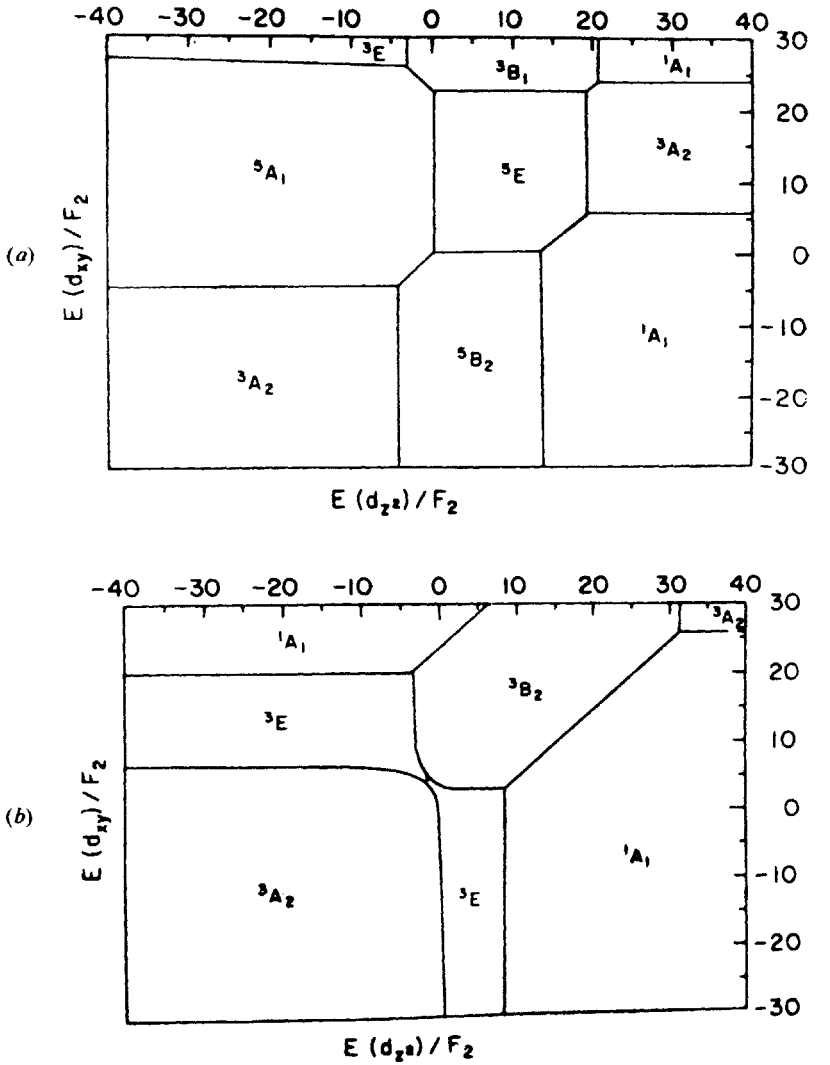

FIG 10 Parameter space diagram defining the different ground states for a d^6 electron configuration in D_4 symmetry : (top Figure) $E(x^2 - y^2) = 15{,}000\text{cm}^{-1}$, $E(xy, yz) = 0$; (bottom one) $E(x^2 - y^2) = 35000\text{cm}^{-1}$, $E(xz, yz) = 0$; $F_2 = 1000\text{cm}^{-1}$ and $F_4 = 100\text{cm}^{-1}$.[7,24]

ing different ground states for a ferrous ion in D_{4h} symmetry for two values of the energy of the $d_{x^2-y^2}$ orbital, $E(x^2-y^2)$. It is seen that for the lower value of $E(x^2-y^2)$, spin-quintets are favoured as ground states, while for larger value of $E(x^2-y^2)$, spin-triplets become the most likely possibility. The $S = 1$ ground state can thus be stabilised when $d_{x^2-y^2}$ orbital lies very high in energy i.e. when the tetragonal distortion is very large as in the limiting case of planar stereochemistry in the Fe(TPP). An additional point is the 'cross over' region in Fig. 10(*b*) where $^3A_2$, ^3E and $^3B_2$ come close together. The calculation shows that in this region the

high value of magnetic moments may be reproduced suggesting that the planar iron(II) porphyrin actually lies in this crossover region. The analysis of the magnetic data yields a scheme of the electronic structure for the Fe(TPP), which is shown in Fig. 11.

There are several features in the electronic structure scheme of Fig. 11, which deserve a mention here. First is the one-electron orbital scheme. It is shown[34] that unless the d_{z^2} orbital lies lowest in energy, the existing physical properties of these planar iron(II) porphyrins cannot be explained. Significantly, all the orbitals lie close together except the $d_{x^2-y^2}$ which must lie very high in energy (to stabilise $S = 1$ ground state). Second, several spin states lie very close within 2000cm^{-1}. This arises from the proximity of various spin triplets (^3E and $^3B_1$) to the ground state $^3A_2$. In fact these triplets must be so extensively mixed that the ground state

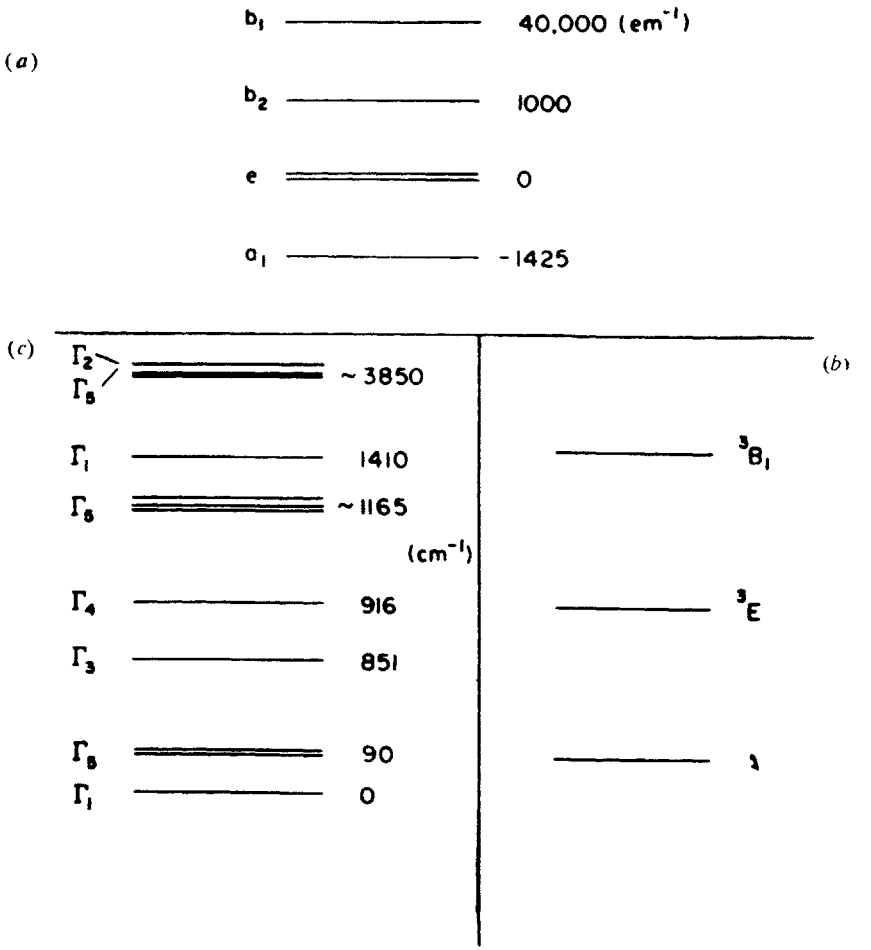

FIG 11 One-electron energies[1] (*a*) terms (*b*) and spin-states (*c*) deduced from the magnetic data of Fe(TPP).[34]

may not be strictly given one particular electron configuration. Finally, we observe that the ground state $^3A_2$ has a large ZFS of 90cm^{-1}. Such large ZFS has not been observed in any other iron complexes. Evidently the existence of such large ZFS in Fe(TPP) is a consequence of the ferrous ion being in the crossover region in Fig. 10, which accounts for the interesting feature of its electronic structure.

MANGANESE(III) PORPHYRINS

Electronic structure of manganese porphyrins is important because of direct and indirect involvement of these molecules in various biological processes. Manganese (III) porphyrins are hign-spin ($S = 2$) and isoelectronic with the high-spin iron(II) porphyrins, which makes the knowledge of their electronic structure more interesting. An interesting aspect of their study is the determination of the ZFS of the ground state and its comparison with iron porphyrins.

The ground electronic state of the manganese(III) porphyrins (d^4 electron configuration) is $^5B_1$ arising from $d^1_{xy}\ d^2_{xy\cdot xz}\ d^1_{z^2}$ configuration. The ZFS of this spin-quintet is shown in Fig. 12, where the ZFS parameter D is positive for Ms = 0 lying lowest. The sign and magnitude of this ZFS parameter in a number of high-spin manganese(III) porphyrins have been determined by variable temperature magnetic susceptibility measurements on single crystal and polycrystalline samples.[39–40] A typical set of experimental results on Mn(TPP) Cl is shown in Figs. 13 and 14, and in Table VII. All maganese(III) porphyrins show a room temperature magnetic moment of 4.9 BM which is almost the spin-only value for $S = 2$, suggesting no orbital contribution at all. The magnetic moment remains, nearly constant down to about 20 K, below which it decreases fast. The latter decrease is indicative of the ZFS of the ground spin-quintet. The effect of this ZFS is more pronounced in Fig. 14 which shows increasing anisotropic character of

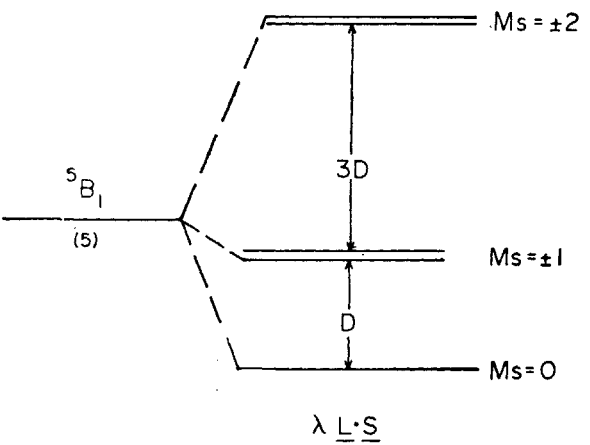

FIG 12 The zero-field splitting diagram for the high-spin manganese(III) porphyrins (d^4 electron configuration).

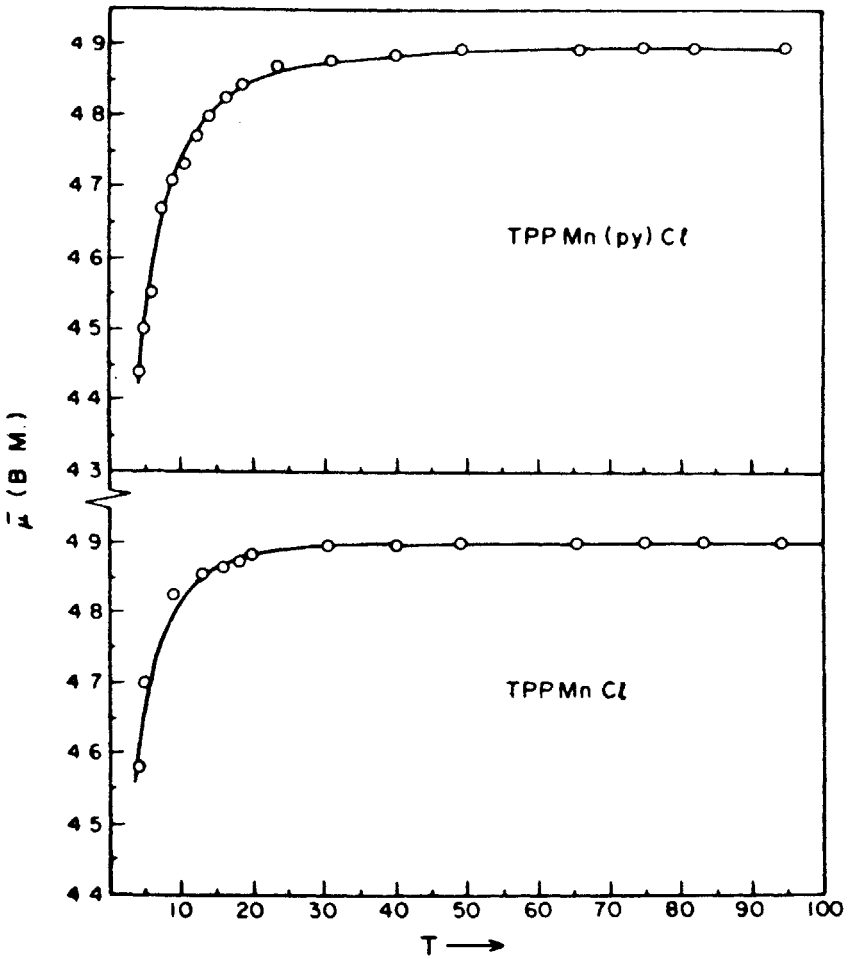

FIG 13 Temperature-dependence of the average magnetic moment (μ) for two typical high-spin manganese(III) porphyrins.[39]

the molecule at lower temperatures because of ZFS. The unusual change in the sign of the anisotropy around 160 K is due to the competing diamagnetic and paramagnetic anisotropies of the molecule, the latter dominating at lower temperatures. Using the experimental results of this type, ZFS in several manganese(III) porphyrins have been determined which are listed in Table VII.

Two observations are noteworthy. First the ZFS parameter in manganese(III) porphyrins is negative (i.e. $M_s = \pm 2$ lying lowest) and its magnitude is small lying between 1–3cm^{-1}. Second, in the five coordinated complexes of the general formula Mn(III) (Por) X(X = Cl, Br, I) the magnitude of the ZFS decreases in going from chloro to the bromo complex. Both these observations are in fact opposite to the known behaviour of the ZFS in analogous five-coordinated high-spin iron(III)

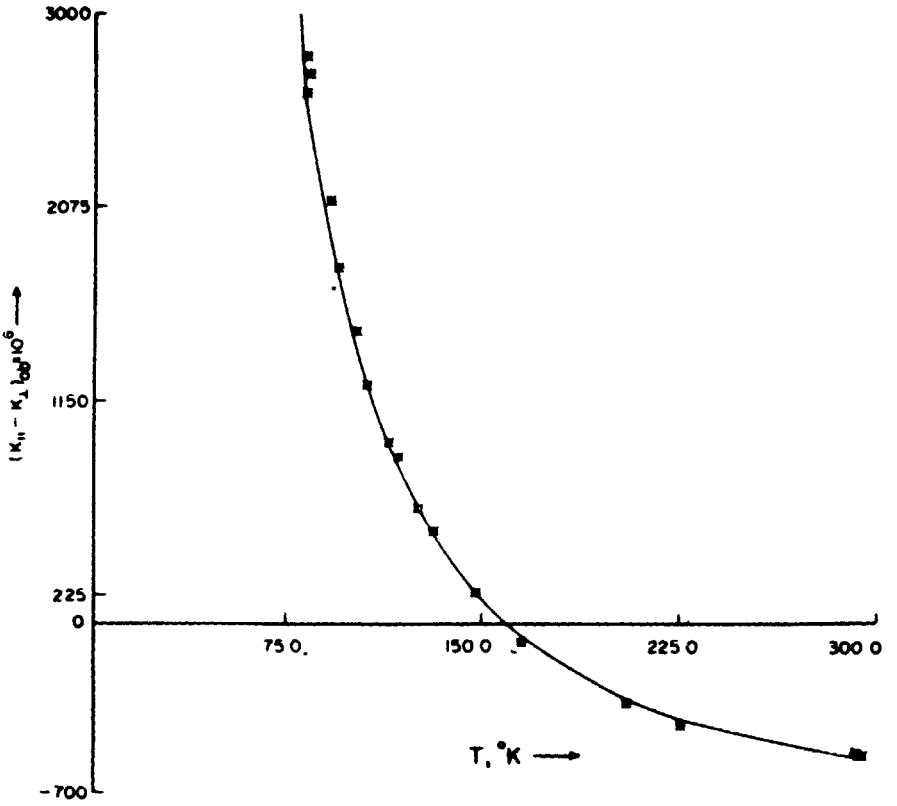

FIG 14 Temperature dependence of the magnetic anisotropy of Mn(TPP) Cl. Note the change in sign of the anisotropy around 160 K, which occurs because the diamagnetic anisotropy of the molecule is of opposite sign and comparable to its paramagnetic counterpart at high temperature.

porphyrins (see Table II for comparison). It is evident that the electronic structure of the manganese(III) porphyrins must be quite different from the iron(III) porphyrins to account for this difference in their ZFS behaviour.

The origin of the ZFS in manganese(III) porphyrins has recently been investigated, which gives some insight into their electronic structure. In C_{4v} symmetry, the energy and electronic configuration of various low-lying states are given in Table VIII. With the energies as given in the table the ^3E can lie very low in energy for smaller values of the tetragonal distortion, and can mix with the ground state $^5B_1$ through spin-orbit coupling. Using second-order perturbation theory following expression for D can be obtained :

$$D = \frac{\zeta^2}{16}\left[\frac{1}{^5E - {}^5B_1} - \frac{4}{^5B_2 - {}^5B_1} - \frac{4}{^3E - {}^5B_1}\right],$$

where ζ is the one-electron spin-orbit coupling parameter. The negative sign and small magnitude of D is now easy to understand. Since the contributions from the

TABLE VII

ZFS in high-spin manganese(III) porphyrins

Complex	μ (295 K) (BM)	D (cm^{-1})	Ref
Mn(TPP) Cl	4.90	—2.3	39, 40
Mn(TPP) (*py*) Cl	4.90	—3.0	39, 40
Mn(TPP) ClO_4	4.95	—2.0	41
Mn(TPP) 1-$(MeIM)_2$ ClO_4.THF	5.0	—2.5	41
Mn(DPDME) Cl	—	—2.5	22
Mn(DPDME) Br	—	—1.1	22

TABLE VIII

The energies and electronic configurations of various low-lying states in manganese(III) porphyrins

State	*Energy*
$^5A_1(b_2e^2b_1)$	δ_2
$^5E(b_2ea_1b_1)$	$\Delta - \delta_1$
$^5B_2(e^2a_1b_1)$	Δ
$^3E(b_2e^3)$	$6B + 5C - \Delta + \delta_1 + \delta_2$
$^3A_2(b_2^2e^2)$	$6B + 5C - \Delta + \delta_2$

Here $\delta_1 = e - b_2$, $\delta_2 = b_1 - a_1$, $\Delta = b_1 - b_2$. B and C are the Racah parameters.

second and third terms are negative and four times that of the positive first term, the negative sign of D is most likely. The magnitude of D depends upon the competing contributions of the positive and negative terms in the above equation. From Table VIII, the energy of ^5E is expected to be moderate if δ_1 is large. This would make the positive term in the equation significant and hence magnitude of D small. The variation in D is expected to be mainly due to the position of ^3E which depends on both δ_1 and δ_2.

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