32811-25-9; **28**, 40195-26-4; **29**, 75436-61-2; **30**, 31469-15-5; **31**, 40195-27-5; **32**, 88869-01-6; **33**, 75436-68-9; **34**, 75436-59-8; **35** (isomer 1), 88869-02-7; **35** (isomer 2), 88869-03-8; **36** (isomer 1), 88869-04-9; **36** (isomer 2), 88869-05-0; **37** (isomer 1), 88869-06-1; **37** (isomer 2), 88869-07-2; **38**, 75436-65-6; **39**, 84796-94-1; **40**, 75436-60-1; **41**, 88869-08-3; **42**, 88869-09-4; **43**, 75436-67-8; **44**, 88869-10-7; **45**, 15174-78-4; $SnCl_4$, 7646-78-8; $TiCl_4$, 7550-45-0; $AlCl_3$, 7446-70-0; Ti(OPr-*i*)$_4$, 546-68-9; 2-(2-oxobutyl)cyclohexanone, 29943-11-1; 2-(1-methyl-2-oxopropyl)cyclohexanone (isomer 1), 60415-91-0; 2-(1-methyl-2-oxopropyl)cyclohexanone (isomer 2), 60416-02-6; 2-methyl-2-(2-oxopropyl)cyclohexanone, 27943-50-6; 1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one, 39163-29-6; 3-methyl-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one, 24730-98-1; 7a-methyl-1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one, 16508-51-3; [(6-methyl-1-cyclohexen-1-yl)oxy]trimethylsilane, 19980-33-7; (1-cyclopenten-1-yloxy)trimethylsilane, 19980-43-9; 2,5-undecanedione, 7018-92-0; *cis*-1,6a-dimethyl-4,5,6,6a-tetrahydro-2(1*H*)-pentalenone, 74320-65-3; *trans*-1,6a-dimethyl-4,5,6,6a-tetrahydro-2(1*H*)-pentalenone, 74320-92-6; methyl 2,2-dimethyl-4-oxopentanoate, 66372-99-4; methyl 2,2-dimethyl-4-oxohexanoate, 15118-75-9; methyl 2-phenyl-4-oxopentanoate, 74457-44-6.

Crystal Field of Atypical Low-Spin Ferriheme Complexes†

J. C. Salerno*‡ and J. S. Leigh§

Contribution from the Department of Biology, Rensselaer Polytechnic Institute, Troy, New York 12181, and the Department of Biochemistry and Biophysics, University of Pennsylvania, Philadelphia, Pennsylvania 19104. *Received April 21, 1983*

Abstract: Recently reported heme model complexes including bis(piperidine) and bis(2-methylimidazole) complexes of (tetraphenylporphyrin)iron(III) and (protoporphyrin IX)iron(III) exhibit electron paramagnetic resonance spectra with unusually large values of g. Previous assignments of the other q values were incorrect, however; these led to the creation of a separate category of HALS (highly anisotropic low spin) complexes. Correct assignment of the g values leads to a crystal field model in which the low-spin complexes all fall into a single continuous category. The values of V/Δ are merely smaller for the so-called HALS species, due primarily to a decrease in V. The more axial nature of the bis(2-methylimidazole) complexes may be due to a difference in the orientation of the planar axial ligands between the bis(imidazole) and bis(2-methylimidazole) complexes.

Introduction

Ferric heme complexes with strong field axial ligands are low spin by EPR and magnetic susceptibility criteria. Griffiths[1] described these complexes by using a hole formulation that considered the low-lying t_{2g} set of d orbitals. Blumberg, Peisach, and co-workers[2,3] have classified low-spin heme complexes by using the tetragonal and rhombic splittings within the t_{2g} set.

Heme proteins such as cytochrome b_5 and cytochrome c are low spin in the native state at neutral pH.[4,5] Other heme proteins such as hemoglobin and myoglobin are low spin in the presence of exogenous ligands such as cyanide or azide.[6,7] The EPR spectra of these proteins is primarily determined by the nature of the axial ligands.[2,3] For example, the EPR spectrum of cytochrome b_5, in which both axial ligands are histidine residues, closely resembles that of (protoporphyrin IX) bis(imidazole)iron(III). Other heme proteins, such as the b cytochromes of the inner mitochondrial membrane, exhibit much greater apparent g tensor anisotropy.[8] Ligand identification in these proteins is uncertain.

Recently, Migata and Iwaizumi[9] reported the EPR parameters of a series of low-spin ferrihemes which they termed "HALS" (highly anisotropic low spin) complexes. These were distinguished from conventional low-spin complexes primarily by the large numerical value of g_z. Crystal field analysis indicated that the tetragonal and rhombic crystal field terms (Δ and V) were both smaller in HALS complexes than conventional low-spin complexes, while the ratio of V to Δ remained relatively constant. The sum of the squares of the coefficients of the basis set of t_{2g} orbitals in the ground-state doublet deviated significantly from unity, an anomaly which the authors attributed to configuration interaction.

In this paper we will show that the crystal field analysis in at least some (and presumably all) of the interesting HALS complexes described by Migata and Iwaizumi is based on an incorrect assignment of g values. The so-called LS and HALS groups are in fact part of a continuous distribution of low-spin complexes all of which are probably well approximated by the t_{2g} hole model.[1,10] The substituted imidazole complexes are of particular interest as models for the b cytochromes of mitochondria, although the analogies between steric hindrance in these complexes and possible restrictions on ligand rotation by a protein are far from perfect.

Experimental Section

(Protoporphyrin IX)iron(III) chloride and nitrogenous bases[11] were obtained from Sigma. (PPIX)$Fe^{III}Cl$ and (tetraphenylporphyrin)iron(III) chloride were the gift of Alan Adler. Dichloroethane, *N*,*N*-dimethylformamide, and dimethyl sulfoxide were used as solvents. Solutions of the complexes were prepared by dissolving the iron porphyrins in dichloroethane solutions of the bases. EPR spectra were recorded by using a Varian E-109 spectrometer. Low temperatures were obtained with an Air Products flowing helium cryostat.

Results

Addition of (PPIX) $Fe^{III}Cl$ and (TPP) $Fe^{III}Cl$ to dichloroethane solutions of imidazole produced red (PPIX) and green (TPP)

† Supported by NSF Grant PCM 78-16779 and by a grant from the Perkin Fund.

‡ Rensselaer Polytechnic Institute.

§ University of Pennsylvania.

(1) Griffiths, J. S. *Nature (London)* **1957**, *180*, 30-31.
(2) Peisach, J.; Blumberg, W. E.; Adler, A. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 310-327.
(3) Blumberg, W. E.; Peisach, J. In "Structure and Function of Macromolecules and Membranes"; Chance, B., Yonetoni, T., Mildvan, A., Eds.; Academic Press: New York, 1971; Vol. II, p 215.
(4) Peisach, J.; Blumberg, W. E.; Wittenberg, B. A.; Wittenberg, J. B. *J. Biol. Chem.* **1968**, *243*, 1871-1879.
(5) Mailer, C.; Taylor, C. P. S. *Can. J. Biochem.* **1972**, *50*, 1048-1055.
(6) Hori, H. *Biochim. Biophys. Acta* **1971**, *251*, 227-235.
(7) Gibson, J. F.; Ingram, D. J. *Nature (London)* **1957**, *180*, 29-30.
(8) Orme Johnson, N. R.; Hansen, R. E.; Beinert, H. *J. Biol. Chem.* **1974**, *249*, 1928-1939.
(9) Migata, C.; Iwaizumi, M. *J. Am. Chem. Soc.* **1981**, *103*, 4378-4381.
(10) (a) Taylor, C. P. S. *Biochim. Biophys. Acta* **1977**, *491*, 137-149. (b) Bohan, T. *J. Magn. Res.* **1977**, *26*, 109-118.
(11) Abbreviations used in this communication are as follows: PPIX, protoporphyrin IX; PPIXDME, protoporphyrin IX dimethyl ester; TPP, tetraphenylporphyrin; ImH, imidazole; 4-Me-ImH, 4-methylimidazole; 4-Ph-ImH, 4-phenylimidazole; N-MeIm, *N*-methylimidazole; 2-Me-ImH, 2-methylimidazole; EPR, electron paramagnetic resonance.

0002-7863/84/1506-2156$01.50/0

Table I. EPR and Ligand Field Parameters for Low-Spin Ferric Heme Complexes

ligand	g_z	g_x	g_y	a	b	c	Σg	V	Δ	g_c[h]	ΔE[i]
$(ImH)_2$[a]	−3.02	2.24	−1.51	0.874	0.133	−0.484	1.016	1.77	3.54	(3.83)[j]	2.07
$(ImH)_2$[b]	−2.93	2.27	−1.53	0.861	0.137	−0.456	1.006	1.97	3.29	(3.81)	2.23
$(4\text{-Me-ImH})_2$[c]	−2.87	2.26	−1.59	0.852	0.134	−0.501	0.996	2.00	3.29	(3.81)	2.24
$(4\text{-Ph-ImH})_2$[c]	−2.90	2.26	−1.54	0.856	0.125	−0.509	1.008	2.03	3.62	(3.84)	2.28
$(N\text{-MeIm})_2$[c]	−2.92	2.25	−1.53	0.860	0.133	−0.495	1.002	1.91	3.39	(3.82)	2.18
ImH/Im⁻[d]	−2.78	2.26	−1.72	0.837	0.105	−0.546	1.010	2.47	4.25	(3.87)	2.67
NMe/Im(OCH_3)[e]	−2.43	2.15	−1.92	0.780	0.050	−0.624	1.000	4.64	8.67	(3.97)	8.67
$(2\text{-MeImH})_2$	−3.51	1.7	(−0.55)	0.946	0.188	−0.260	0.999	0.68	2.82	3.75	1.32
$(2\text{-Me-ImH})_2$[f]	−3.41	1.85	(−0.75)	0.932	0.183	−0.183	0.997	0.84	2.82	3.75	1.41
piperidine[f]	−3.43	1.85	(−0.6)	0.94	0.02	−0.29	1.00	0.78	2.5	3.7	1.39
piperidine	−3.58	(1.5)	(−0.2)	0.96	0.02	−0.19	1.00	0.48	2.5	3.7	1.25
pyridine	−3.42	(1.8)	(−0.2)	0.94	0.025	−0.22	1.00	0.6	1.9	3.58	1.32

[a] Reference 12. [b] With PPIXDME, ref 13. [c] With PPIXDME, ref 14. [d] Peisach, J. and Mims, W. B. *Biochemistry* 1977, *16*, 2795–2799. [e] Tang, S. C.; Koch, S.; Papaefthymiou, G. C.; Foner, S.; Frankel, R. B.; Ibers, J. A.; Holem, R. H. *J. Am. Chem. Soc.* 1976, *98*, 2414–2434. [f] With TPP. [g] $\Sigma = a^2 + b^2 + c^2$. [h] g Value at low field cutoff ($V = 0$). [i] Energy above ground of first excited state. [j] Numbers in parentheses were calculated as described in text (g_c can sometimes also be directly observed in ImH_2 complexes). Complexes are with PPIX unless otherwise noted.

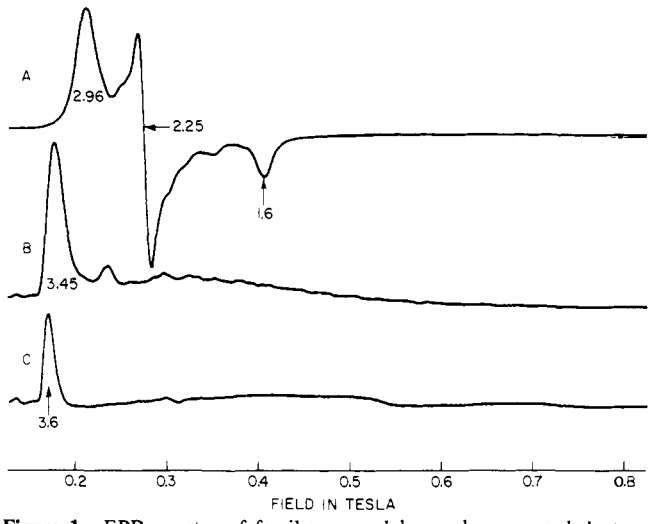

Figure 1. EPR spectra of ferriheme model complexes recorded at a sample temperature of 12 K and a microwave power of 1 mW. (a) Bis(imidazole)(protoporphyrin IX)iron(III) chloride. (b) 2-Me-Im-(PPIX)$Fe^{III}Cl$. (c) 2-Me-Im(TPP)$Fe^{III}Cl$.

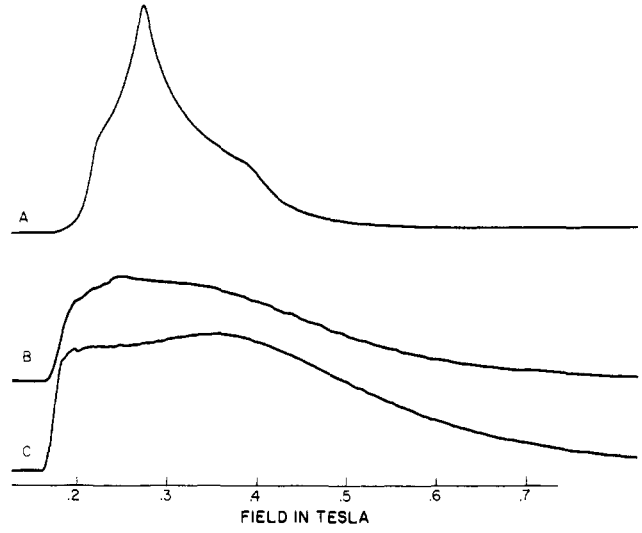

Figure 2. EPR spectra of ferriheme model complexes in the second harmonic out of phase mode; temperature = 8 K, microwave power = 20 mW. (a) Bis(imidazole)(protoporphyrin IX)iron(III) chloride. (b) 2-Me-Im(PPIX)$Fe^{III}Cl$. (c) 2-Me-Im(TPP)$Fe^{III}Cl$.

complexes with EPR spectra identical with those reported by previous workers.[12-15] Imidazoles substituted at other than the 2 position produced similar complexes; addition of base produced complexes identified as imidazole imidazolate by Quinn et al.[12] As these workers reported, the conversion of bis(imidazole) complexes to imidazole imidazolate complexes was characterized by the shift of g values from approximately 2.9, 2.26, and 1.5 to 2.7, 2.26, and 1.75.

When imidazole was replaced by 2-methylimidazole, the complexes formed had larger numerical values of g_z as reported by Migata and Iwaizumi.[9] However, as shown in Figure 1, the intermediate field features reported by them were not observed. Instead, in each case a broad derivative feature with a zero crossing point below $g = 2$ could be discerned. No "g_z" feature was observed at temperatures down to 5 K.

Addition of $(TPP)Fe^{III}$ to a solution of piperidine in dichloroethane produced a species with a large numerical value of g_z; pyridine produced a similar complex. The other features were too broad to observe by conventional slow-passage EPR spectroscopy at 5 K.

In order to obtain further information about the g tensors of these species, spectra were obtained by using the second harmonic feature of the EPR spectrometer under saturating conditions. This feature is often utilized to study tumbling of spin-labeled molecules (saturation transfer EPR). In a low-temperature glass, as the rotational correlation time becomes very long the line shape approaches the absorption line shape of the species if the saturation factor and relaxation times are reasonably constant across the spectrum; in effect, the 100 kHz modulation is used to obtain rapid passage conditions. This is advantageous in searching for broad features since a broad feature may have considerable absorption intensity but little slope and therefore little derivative intensity. If the passage conditions vary across the line, a distorted but still useful absorption line shape will be observed.

Figure 2 shows spectra of the heme complexes of Figure 1 in second harmonic mode under saturating conditions. Features near 2.9, 2.2, and 1.5 can be distinguished in the spectra of the bis-(imidazole) complexes. The pseudo absorption spectra of the bis(2-methylimidazole) complexes show a sharp rise at $g \sim 3.5$, broad peaks at $g \sim 1.9$ (TPP) or $g \sim 1.7$ (PPIX), and long tails that never return to the base line at fields of up to 10^4 G. The bis(piperidine) complex shows features at $g = 3.5$ and $g = 1.7$ plus a long sloping tail at high field (now shown). These results, in agreement with our derivative spectra, suggest that the so-called HALS complexes have numerical g_z values of above 3.0 as reported, but that the intermediate field features of these complexes are between $g = 1$ and $g = 2$ with very wide line widths and the high field features lie near or below $g = 1$ and are extremely broad.

Scrutiny of Figure 2 of Migata and Iwaizumi[9] shows that the broad "g_2" reported here is probably present, and that their "g_3"

(12) Quinn, R.; Nappa, M.; Valentine, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 2588–2595.
(13) Momenteau, M.; Mistpelter, J.; Lexa, D. *Biochim. Biophys. Acta* **1973**, *320*, 652–662.
(14) Ozaki, T.; Yoshimura, T. *Inorg. Chim. Acta* **1979**, *36*, L421–422.
(15) Hiroshi, H. (1971) *Biochim. Biophys. Acta* **1971**, *251*, 227–235.

is in fact the negative deflection of the real g_2 derivative signal. The g_2 they report is nearly as sharp as the g_z peak; if this were the g_2 feature, it should be of approximately equal amplitude t o the g_z peak. It is not nearly large enough to correspond to the g_z feature. This has been confirmed by computer simulation (not shown). It appears that the small features they assign to g_2 are due to either minority species or to impurities in their quartz tubes; in any case, they cannot correspond to the intermediate field features of the majority species.

Table I summarizes the data obtained from these experiments. The signs and ordering of the g values follows convention III of Bohan.[10b] In cases where the high-field g value is too small numerically to be experimentally determined, the number in parenthesis was calculated from the other two values, assuming $a^2 + b^2 + c^2 = 1$. The coefficients a, b, and c and the crystal field splittings were determined as described in the next section. The orbital reduction factor K in the expression $\beta H(KL + 2s)$ for the Zeeman interaction was taken as 1.0 if only two g values could be determined. Reasonable deviations from $K = 1.0$ caused by covalency and/or configuration interaction would change the values of the Δ and V terms somewhat but would not affect the conclusions of this paper. In addition, we will later justify the assumption that $K \sim 1.0$ by arguing that the line shape of the g_z feature is indicative of $0.95 < K < 1.05$.

Discussion

Crystal field calculations were carried out as described by Taylor[10a] and Bohan.[10b] The coordinate system chosen had the tetragonal axis along the z direction, which in all known cases corresponds to the normal to the heme. The ground-state doublet is of the form

$$\Psi^+ = a|+1,{}^1/_2\rangle + b|2+,{}^1/_2\rangle + c|-1,{}^1/_2\rangle$$

$$\Psi^- = a|-1,{}^1/_2\rangle - b|2+,{}^1/_2\rangle + c|+1,{}^1/_2\rangle$$

where $+{}^1/_2$ and $-{}^1/_2$ denote the orientation of S, $|2+\rangle = (|2\rangle - |+2\rangle)/2^{1/2}$ (denoting states with $L = 2$ by their M value), and $|+1, +{}^1/_2\rangle$ represents the state with $M = +1$, $M = +{}^1/_2$). When the ordering and signing of convention III of Bohan's paper[10b] is used in these complexes, $|g_z| = g_1$, $|g_y| = g_3$, $|g_x| = g_2$, and

$$g_x = -2(2^{1/2}a + b)(2^{1/2}c - b)$$

$$g_y = 2(2^{1/2}a + b)(2^{1/2}c + b)$$

$$g_z = -2(2^{1/2}a + b)(2^{1/2}a - b)$$

The perturbation Hamiltonian matrix with terms in crystal field parameters V and Δ (sometimes written R and T) and the spin–orbit coupling constant has been given by many authors and can be used to find V and Δ when g_z, g_x, and g_y are known. If $K = 1$ and $a^2 + b^2 + c^2 = 1$ (in other words, if the t_{2g} hole model is a good approximation), V and Δ (in units of λ) can be calculated if any two g values can be determined by experiment. Alternatively, the g values of a hypothetical complex with crystal field splittings V and Δ can be calculated by diagonalization of the matrix.

Table I shows the results of this calculation for the ferriheme complexes of Figures 1 and 2. Where g_y cannot be observed directly, the assumption $K = 1$, $a^2 + b^2 + c^2 = 1$ was used to evaluate g_y, V and Δ. In general, two physically distinct solutions exist for each pair $|g_z|$ and $|g_x|$. The value of g_x corresponding to a reasonable value of Δ for the axial ligands was chosen. The data are consistent with a nearly constant value of Δ for the bis(imidazole) and substituted imidazole complexes, and with $K = 1$, $a^2 + b^2 + c^2 = 1$. On the other hand, V varies from nearly the maximally rhombic value of ${}^2/_3$ in the bis(imidazole) complex to nearly the axial value of 0.

Figure 3 shows the variation of the absolute values of the three g values of a hypothetical low-spin heme complex with $\Delta = 3.32$ as V is varied from 0 to 2.4. The limiting value of $|g_z|$ is 3.81 at $V = 0$. Negative V corresponds to an interchange of x and y, and the plot in this region would correspond to a reflection about the vertical axis. As $|V|$ is decreased, g_z becomes insensitive to variations in V while the g_x and g_y values become more sensitive to V variations. Line-widths in these complexes are probably due to the existence of a distribution of possible crystal fields leading to a distribution of g values for each species. A distribution in V would lead to a much sharper line at g_z than at g_x or g_y as the axial case is approached. An additional factor due to the fact that the spectra are displayed on a field scale rather than a g-value scale increases this tendency. In the rhombic case, the line widths should be much more nearly equal at g_z, g_y, and g_x.

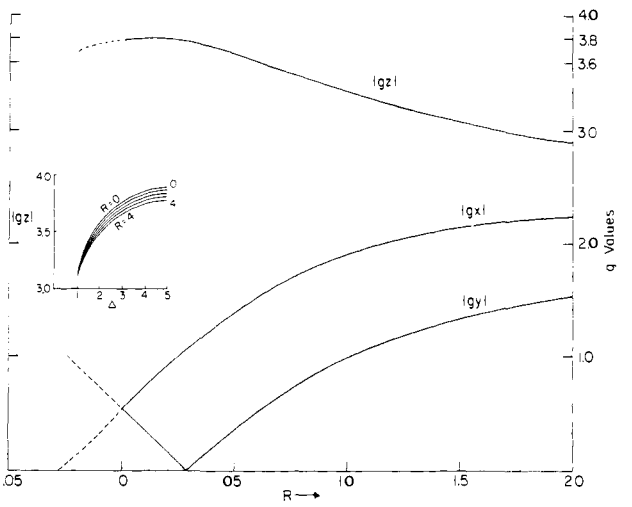

Figure 3. Plot of absolute g values vs. rhombic splitting of t_{2g} orbitals (in units of spin orbit coupling) for a tetragonal distortion of 3.3λ using the Griffiths model for a low-spin d^5 system. (Inset) Plots of $|g_z|$ vs. tetragonal distortion for rhombicities of 0, 0.1, 0.2, 0.3, and 0.4; both parameters in units of spin–orbit coupling.

The insert to Figure 3 shows the dependence of $|g|$ on Δ for several values of V. Variations of Δ of the same magnitude as variations of V produce smaller changes in g_z in this region. In axial low-spin heme complexes the intensity of the g_z peak falls rapidly to zero on the low-field side. This "cutoff" corresponds to the limiting g_z value as V approaches zero. The asymmetric low field peaks of the bis(2-mehylimidazole) complexes can be simulated by assigning a Gaussian distribution to the V parameter as the primary source of line width. The low-field cutoff does not occur in the right vicinity unless, as we earlier assumed, $K \sim 1.0$; the range is approximately 0.95 to 1.05.[16] The low-field EPR peak of cytochrome b_{566} in mitochondria has an asymmetric shape that can be simulated by using a similar distribution in V.[16] The cutoff on the low-field side of the b_{566} peak is sharper than in the bis(2-methylimidazole) complexes, however. This is primarily because V is larger in the bis(2-methylimidazole) complexes than in cytochrome b_{566}; therefore the center of the line is further from cutoff. In the model complexes steric hindrance between the 2-Me-ImH ligands and the porphyrin could cause a distribution in Δ as well as in V. This blurs the cutoff point although V is still the major source of line width. In this case V and Δ might be correlated with each other rather than being independently distributed. In the cytochrome, V is probably determined by external (protein induced) effects that need not couple Δ and V.

Walker et al.[17] recently reported the effects of a series of nitrogenous bases as axial ligands on the splitting of porphyrin proton NMR resonances in (TPP)Fe^{III} complexes. They found that although the mono(2-methylimidazole) complex had much more inequivalence in the shifts of the ring protons that the bis(imidazole) complex, the bis(2-methylimidazole) complex was nearly axial, since the ring protons had nearly identical chemical shifts. This is consistent with our results, since the bis(2-

(16) Salerno, J. C.; Kelley, S. E.; Ohnishi, T. *Biophys. J.* **1978**, *37*, 401a.
(17) Walker, F. A.; Lo, M.-W.; Ree, M. T. J. *J. Am. Chem. Soc.* **1976**, *98*, 5552–5560.

methylimidazole) complexes have a much smaller value of V than bis(imidazole) complexes.

Mims and Peisach[18] have discussed the effects of the orientation of planar ligands such as imidazole, pyridine, and pyrrole in heme model complexes. The determining factor in the value of V may be the orientation of the two imidazole planes. Steric factors could account for the differences between various substituted imidazoles as axial ligands. Blumberg and Peisach[2,3] have postulated that the tetragonality depends primarily on the strength of the axial ligands as Lewis bases. Methylation of the 2 position should not greatly change the basic strength of the imino nitrogen; the lack of large change in Δ therefore seems reasonable chemically. This picture is clouded by the uncertain effects of steric hindance on metal–imino nitrogen bond lengths; the moderate decrease in Δ from 3.0–3.5 for the other substituted imidazoles to 2.8 for the 2-Me-ImH complexes may reflect a longer metal–ligand distance. It is also not clear how much of the difference in V between complexes with different axial ligands is due to axial ligand induced ruffling of the porphyrin. It may be relevant to note that powder samples prepared by evaporation of solvent from solutions of bis(imidazole) hemes sometimes contain considerable amounts of a species with a broad g_z peak between 3.3 and 3.4.[19] Steric effects produced by packing might account for these species. It would be of interest to compare the value of g_z in bis(imidazole) heme crystals with varying orientations of the axial ligands.

Clearly, the conclusions of Migata and Iwaizumi[9] regarding correlations between Δ and V in the so-called HALS series are invalid since their values of Δ and V are severely in error. In addition, the correlation between Δ and g_z proposed by these workers is based on erroneous values of Δ and should be abandoned. We feel that the estimation of Δ from g_z only proposed by Brautigan et al.[20] for a series of cytochromes should be carefully reconsidered in light of the dominant effects of V on the spectra of these model complexes.

On the other hand, the position at which low-field cutoff of the g_z peak is observed can be used to estimate Δ (if $K \sim 1.0$). Cutoff for the 2-Me-Im complexes was at $g \sim 3.75$; this corresponds to $\Delta \sim 2.8$, slightly smaller than Δ for bis(imidazole) complexes. For the low-spin complexes formed from piperidine, cutoff occurs near $g = 3.7$, corresponding to $\Delta \sim 2.5$. For pyridine complexes, cutoff was observed near 3.58, which implies $\Delta \sim 1.9$. This series of decreasing values of Δ is in the order predicted by Blumberg, Peisach, and co-workers;[2-4,18,20] in general, weaker field ligands produce weaker tetragonal splittings. In the complexes observed by Brautigan et al.,[20] the expected tendency of V to decline with Δ in this case was apparently dominant. However, in some cases geometrical factors overwhelm overall field strength considerations; in these cases strong-field ligands can produce large numerical values of g_z.

In complexes not too far from the axial case, the cutoff can be used to estimate Δ. It is in just these cases that the g_x and g_y values are difficult to observe. Unfortunately, this estimate depends on K, and the range of cutoffs observed varies only from $g \sim 3.5$ to $g \sim 3.9$. Therefore the estimates are fairly crude, although we hope to improve them by simulating the line shape at g_z. The simulation of low-spin ferric heme EPR line shapes using only a single disorder parameter instead of a "line-width tensor" will be the subject of a separate communication.

Summary

(1) A number of low-spin heme model complexes have high numerical values of g_z; these include not only pyrroles, pyridines, and cyanides but also bis(2-methylimidazole) complexes.

(2) These complexes differ from the familiar bis(imidazole) complexes in having small values for the rhombic splitting parameter V but can have a wide range of Δ values.

(3) Analysis of the spectra shows that contrary to the assertions of previous workers, the orbital reduction factor K need not be very different from 1.0.

(4) These complexes are of possible interest as models for the mitochondrial *b* cytochromes. The spectral properties may be determined in part by the orientation of the planar axial ligands.

Registry No. 2-Me-Im(PPIX)$Fe^{III}Cl$, 88106-21-2; 2-Me-Im(TPP)-$Fe^{III}Cl$, 61056-69-7; bis(imidazole)(protoporphyrin IX)iron(III) chloride, 18661-46-6; bis(piperidine)(tetraphenylporphyrin)iron(III), 88106-22-3; bis(pyridine)(tetraphenylporphyrin)iron(III), 60542-64-5.

(18) Mims, W. B.; Peisach, J. *J. Chem. Phys.* **1976**, *64*, 1074–1091.
(19) Salerno, J. C.; Leigh, J. S., unpublished observation.
(20) Brautigan, D. L.; Feinberg, B. A.; Hoffman, B. M.; Margoliash, E.; Peisach, J.; Blumberg, W. E. *J. Biol. Chem.* **1977**, *252*, 574–582.