the C_6H_{10} ions except the elimination of H_2 take place from a similar state. If the elimination of $CH_3\cdot$ and H_2 were the only reactions considered for the metastable abundance probe, it would be concluded that the reacting C_6H_{10} ions in each spectrum were different.

The results for the coumarin–benzofuran system in Table III may be used to clarify the contradictory results[3,4] obtained previously. The results show that the elimination of CO and $CHO\cdot$ from the C_8H_6O ions occurs from reacting states common to both coumarin and benzofuran, but the elimination of C_2H_2[13] occurs from dissimilar states. Thus, both the consideration of ion energetics[3] and the metastable abundance probe indicate that the elimination of CO occurs from the same state of the C_8H_6O ion in each spectrum. The postulation that those C_8H_6O ions which eliminate a molecule of CO in the spectra of coumarin, benzofuran, and *o*-ethynylphenol are similar is also supported by the results presented in Table III.

In conclusion, changing the origin of an ion, either by changing the compound from which it is derived or by changing the energy distribution of the molecular ions by using a different ionizing energy, can result in changes in the metastable abundance ratios even though the structure of the ion is the same for each origin. Insufficient data on energy distribution functions and the dependence of rate constants with excess energy preclude calculation of the magnitude of the change, but the experimental results presented here indicate that a variation of 30–50% is not unusual. In those cases where the metastable abundance probe shows that two reactions of an ion occur from different states, it is advisable to determine a second ratio in order to find which reactions occur from states common to all origins.

Experimental Section

All metastable abundance data were obtained from a CEC 21-110 mass spectrometer using the defocusing method[14,15] for detecting metastable ions. To minimize changes in abundance ratio due to changes in instrumental operating conditions, all data for a given ionic species were determined in the shortest practicable time, 2 hr or less for the full range of precursor compounds. A four-figure digital voltmeter, which measured a fixed fraction of the ion accelerating voltage, was used to check the mass of the reacting ions.

Except for *o*-ethynylphenol, which was prepared from benzofuran, all compounds studied were commercially available samples. The mass spectra of the samples indicated some diethyl ether in the *o*-ethynylphenol but no impurities in the other compounds.

Acknowledgment. The author wishes to thank D. W. Smith for the numerical calculations presented in this paper.

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[13] The relative concentration of *m/e* 92 is low both in the first field-free region and at the collector; it is a minor species in each of the three spectra.

[14] M. Barber and R. M. Elliott, ASTM Conference on Mass Spectrometry, Montreal, June 1964.

[15] For metastable ions observed under normal conditions, the time for a metastable ion to travel from the ion source exit to a point in the first field-free region will be independent of the mass of the daughter ion. For metastable ions observed by the defocusing method, this time can be shown to be proportional to the square root of the mass of the daughter ion. Consequently, there may be differences in the metastable abundance ratios determined by the two methods; however, the general conclusions presented in this paper are applicable to metastable ions observed by either method.

Thermomagnetic Analysis of Hemin and Related Compounds

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Abstract: The magnetic susceptibility from 2.2 to 200°K was measured for hemin and the related $\alpha,\beta,\gamma,\delta$-tetraphenylporphiniron(III) chloride, thiocyanate, bromide, and iodide. All were found to be high-spin with the $^6A_1$ ground state predominating over the temperature range studied. An analytical expression for the susceptibility as a function of temperature and zero-field splitting, *D*, could not describe the data with reasonable values of *D* in all cases. At 2.2 and 4.2°K, and varying values of the applied field, the compounds approached 90% of paramagnetic saturation. A compound which has been formulated to date as the hydroxide derivative of $\alpha,\beta,\gamma,\delta$-tetraphenylporphiniron(III) was found to be diamagnetic at low temperatures.

Hemin, protoporphyrin(IX)iron(III) chloride, is a pentacoordinate complex formed by oxidizing heme, the prosthetic part of hemoglobin, during the removal of globin. Monovalent anions other than chloride can occupy the fifth coordination position, *e.g.*, Br^-, I^-, SCN^-, etc. Structural data[1] reveal that the coordinating nitrogens lie nearly in a plane with the iron ion displaced from this plane by about 0.5 Å. The microstructure about the iron ion in $\alpha,\beta,\gamma,\delta$-tetraphenylporphiniron(III) chloride, a synthetic analog of the naturally occurring hemin, is similar.[2]

Static magnetic susceptibility measurements have indicated that the iron in these pentacoordinate complexes is trivalent and high-spin, necessitating the assignment of a $^6S_{5/2}$ ground state.[3] Electron spin resonance (esr) studies on hemin[4,5] and the related myoglobin fluoride[6,7] have shown that the degeneracy of this symmetrical ground state is removed by the axial crystalline

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[3] J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964.

[4] G. Schoffa, O. Ristau, and F. Jung, *Naturwissenschaften*, **10**, 227 (1960).

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[6] J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discussions Faraday Soc.*, **26**, 72 (1958).

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field. The Kramers levels which arise within the ${}^6S_{5/2}$ manifold correspond to $|\pm 1/2\rangle$, $|\pm 3/2\rangle$, and $|\pm 5/2\rangle$. The measured values, $g_{\parallel} \simeq 2$ and $g_{\perp} \simeq 6$, for the ${}^6A_1$ $(\pm 1/2)$ ground state and the inaccessibility of the next higher state using esr with microwave radiation have suggested that the energy separation between the ${}^6A_1$ $(\pm 1/2)$ and ${}^6A_1$ $(\pm 3/2)$ states must be >7°K. A simplified spin-Hamiltonian, $\mathcal{H} = DS_z^2$, has been used to show that the energy separations between the Kramers levels should be $2D$ and $4D$, where D is the zero-field splitting.[8,9] Richards[10] and coworkers measured these energy separations for hemin using infrared radiation (ir) and found $|\pm 1/2\rangle \rightarrow |\pm 3/2\rangle$ to be 20°K and $|\pm 3/2\rangle \rightarrow |\pm 5/2\rangle$ to be 40° K.

These splittings are very large when one considers that zero-field splittings for S-state ferric ions in inorganic complexes rarely exceed a few tenths of 1°K. The origin of this splitting is not well understood because the presence of an electric field, regardless of its symmetry, cannot remove any degeneracy in an S state. Present theory accounts for such splitting by the combined effects of crystal field and spin–orbit coupling *via* excited states, mainly the ${}^4T_1$ state.

Thermomagnetic analysis (tma) data for a series of pentacoordinate iron porphyrin complexes (hemin and $\alpha,\beta,\gamma,\delta$-tetraphenylporphiniron(III) chloride, bromide, iodide, and thiocyanate) are reported in this paper. A compound previously assumed to be the hydroxide derivative of $\alpha,\beta,\gamma,\delta$-tetraphenylporphiniron(III) was also studied. The susceptibilities of these compounds were measured in the temperature range 2.2–200°K. Similar data for hemin or other related iron prophyrin complexes have never been reported, but Kotani[12] and coworkers have used the results of similar measurements for an understanding of the chemical bonding in a series of heme proteins.

Experimental Section

Starting Materials. All solvents were reagent grade and were used without further purification. $\alpha,\beta,\gamma,\delta$-Tetraphenylporphin, H_2TPP, was prepared according to the method of Adler, *et al.*,[13] washed with copious amount of acetone and ether, and dried under vacuum at 100°. Hemin, obtained from Nutritional Biochemicals Corp. of Cleveland, Ohio, was dried under vacuum at 100°.

Anal. Calcd for hemin, $C_{34}H_{32}N_4O_4FeCl$: Cl, 5.45. Found: Cl, 5.45.

$\alpha,\beta,\gamma,\delta$-Tetraphenylporphiniron(III) Hydroxide, TPPFeOH. Approximately 40 ml of glacial acetic acid containing 3 ml of deionized water was deaerated by refluxing under a gentle stream of nitrogen for 0.5 hr. Finely powdered iron metal (50 mg, 0.0009 mole) taken onto a magnetized microstirring bar was added to this solution. After complete dissolution of the iron, the ferrous acetate solution was added to a refluxing solution of 500 mg (0.0008 mole) of H_2TPP, in 250 ml of glacial acetic acid under nitrogen. After refluxing gently with stirring for 1.5–2 hr, the heating was discontinued and the solution stirred for an additional 0.5–1 hr under nitrogen. The cooled solution was added to 300 ml of benzene in a separatory funnel. Deionized water was added to remove most of the inorganic impurities; the benzene layer was retained and further washed with several portions of water. This solution containing the crude iron porphin was stirred with dilute aqueous sodium hydroxide for several hours to convert the acetate, TPPFeOAc, to the hydroxide, TPPFeOH. Again the benzene layer was washed thoroughly with water, then dried overnight with anhydrous sodium sulfate. The solution was filtered, concentrated on a steam bath at reduced pressure, and chromatographed on a column prepared with silica gel (Baker Chemical Co., No. 3405) and cyclohexane. Unreacted free base (pink band) was eluted first with cyclohexane–benzene, initially 1:1 by volume, with increasing amounts of benzene. The desired product, TPPFeOH, appeared as a brown band strongly absorbed at the top of the column, and was eluted with a benzene–cyclohexane mixture containing a small amount of ethanol. The solution containing TPPFeOH was evaporated to dryness on a steam bath at reduced pressure and the resulting solid redissolved in dichloromethane. The filtered solution was placed over ether in a desiccator. The lustrous blue crystals which slowly formed were collected, washed well with ether, and dried under vacuum at 100°.

Anal. Calcd for $C_{44}H_{29}N_4OFe$: C, 77.08; H, 4.23; N, 8.18. Found: C, 77.44; H, 4.32; N, 8.39.

$\alpha,\beta,\gamma,\delta$-Tetraphenylporphiniron(III) Chloride, Bromide, and Iodide. Pure TPPFeOH, dissolved in the required amount of benzene, was added with stirring to 6 *N* hydrohalic acid saturated with the corresponding sodium halide. The stirring was continued until all of the TPPFeOH was converted to TPPFeX; the progress of the reaction was checked spectrophotometrically (*vide infra*). The benzene layer, after separation, was washed with several portions of water, dried overnight with sodium sulfate, and evaporated to dryness on a steam bath at reduced pressure; the resulting solid was recrystallized from dichloromethane and ether in the same way as TPPFeOH. The crystals were collected, washed with ether, and dried under vacuum at 100°.

Concentrated hydriodic acid was required to fully convert TPPFeOH to TPPFeI. During the course of conversion a finely divided bluish substance precipitated which was removed by filtering through glass wool. This appeared to be chlorin from its strong absorption at 690 mμ.

Anal. Calcd for TPPFeCl, $C_{44}H_{28}N_4FeCl$: Cl, 5.12. Found: Cl, 5.29. Calcd for TPPFeBr, $C_{44}H_{28}N_4FeBr$: Br, 10.61. Found: Br, 10.56. Calcd for TPPFeI, $C_{44}H_{28}N_4FeI$: I, 15.97. Found: I, 16.07.

$\alpha,\beta,\gamma,\delta$-Tetraphenylporphiniron(III) Thiocyanate, TPPFeSCN. A solution of TPPFeOH in benzene was added with stirring to a concentrated aqueous solution of sodium thiocyanate made acidic with sulfuric acid. The product was isolated as above. (No significance should be attached to the formulation as TPPFeSCN because it is presently unknown which atom is bonded to iron.)

Anal. Calcd for $C_{45}H_{28}N_5FeS$: S, 4.41. Found: S, 4.19.

Characterization of Synthetic Analogs of Hemin. These compounds are identified easily by their visible spectra.[14] The compound thought to be the hydroxide derivative of TPPFe has only two absorption bands in the visible region, at 612 and 572 mμ neglecting the Soret band at shorter wavelengths. By observing the disappearance of these bands and the gradual growth of a band at 510 mμ, the extent of conversion to the halide and thiocyanate derivatives was determined.

Instrumentation. All visible spectra were obtained using a Cary Model 14 recording spectrophotometer.

The Faraday method was used for magnetic measurements with equipment and techniques which are now standard in this laboratory.[15] Forces exerted on the samples were measured with an automatic recording servo-balance which was calibrated with standard weights after each measurement. Resistance thermometry, consisting of a carbon thermometer for the temperature range 4.2–20°K and a platinum thermometer for 20–300°K, was utilized for all temperature measurements except those below 4.2°K where the temperature was determined from the vapor pressure of the liquid helium. For sizable pulls (*e.g.*, high-spin ferric compounds), the precision and accuracy is about 1%, at least to 200°K.

Each investigation involved the measurement of the magnetic susceptibility as a function of magnetic field intensity at fixed temperatures of 2.2 and 4.2° K. Above 4.2°K, the sample was warmed slowly at a constant field intensity of about 18 kG, and the susceptibility was recorded simultaneously with temperature. The

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[9] M. Kotani, *Progr. Theor. Phys., Suppl.*, **17**, 4 (1961).

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[14] M. Zerner, M. Gouterman, and H. Kobayaski, *Theoret. Chim. Acta*, 32, 476 (1967).

[15] R. A. Butera, R. S. Craig, and L. V. Cherry, *Rev. Sci. Instr.*, 32, 708 (1961).

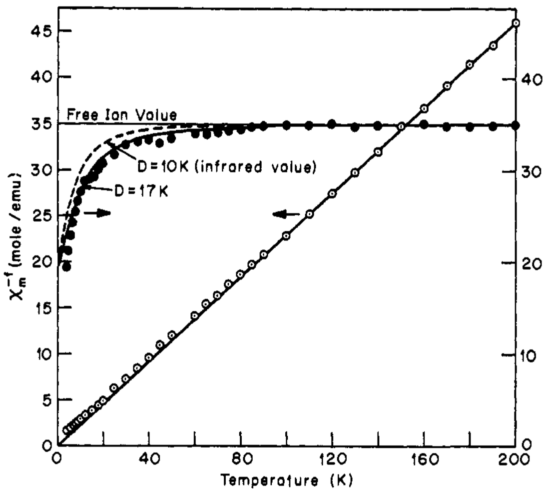

Figure 1. Plots of χ_m^{-1} and μ_{eff}^2 vs. T for hemin. The arrows designate the correct axes. For the μ_{eff}^2 vs. T plot the horizontal line through 35 corresponds to the free ion value. The line through the experimental data is computed from eq 2 and corresponds to a zero-field splitting, D, of 17°K. The dashed line is also computed from eq 2 and corresponds to D = 10°K which has been measured by Richards.[10]

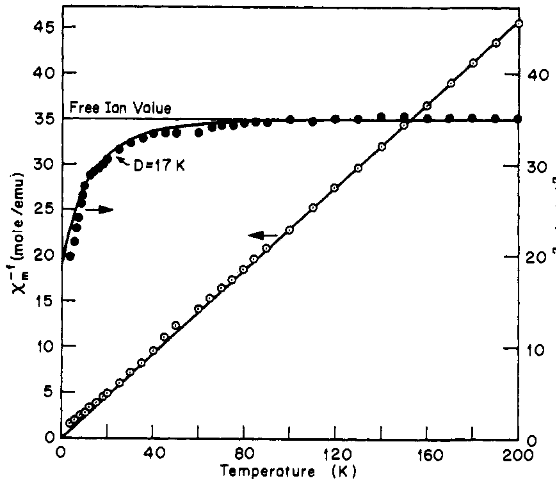

Figure 2. Plots of χ_m^{-1} and μ_{eff}^2 vs. T for TPPFeCl.

field intensity varied with each experiment, depending upon the position of the sample between the pole faces, but the actual intensity was always known to 1%.

Susceptibility data are reported on a molar basis in cgs units; effective moments are reported in Bohr magnetons as well as the molar magnetization

$$M = \chi_m H/N\beta \qquad (1)$$

where N is Avogadro's number, χ_m is the molar susceptibility, H is the applied field, and β is the Bohr magneton.

The data were corrected for the weak paramagnetism of the copper sample holder and the diamagnetism of the free base. All measurements were repeated at least once on different days, and the values obtained were reproducible within experimental error.

Microanalyses. All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results

Plots of reciprocal molar susceptibility, χ_m^{-1} (mole/electromagnetic unit), and effective magnetic moment squared, μ_{eff}^2 (Bohr magnetons^2), vs. temperature for each of the ferric ions contained in hemin and $\alpha,\beta,\gamma,\delta$-tetraphenylporphiniron(III) chloride, bromide, thiocyanate, and iodide are shown in Figures 1–5. The arrows designate the correct axes.

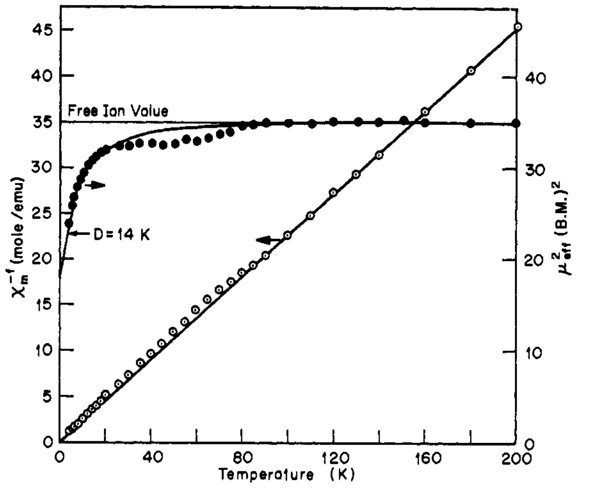

Figure 3. Plots of χ_m^{-1} and μ_{eff}^2 vs. T for TPPFeSCN.

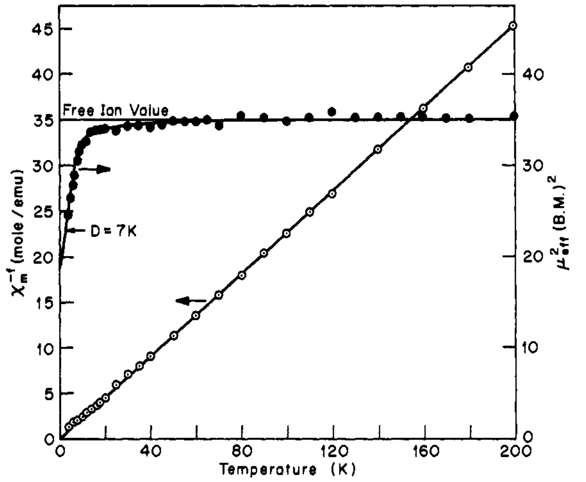

Figure 4. Plots of χ_m^{-1} and μ_{eff}^2 vs. T for TPPFeBr.

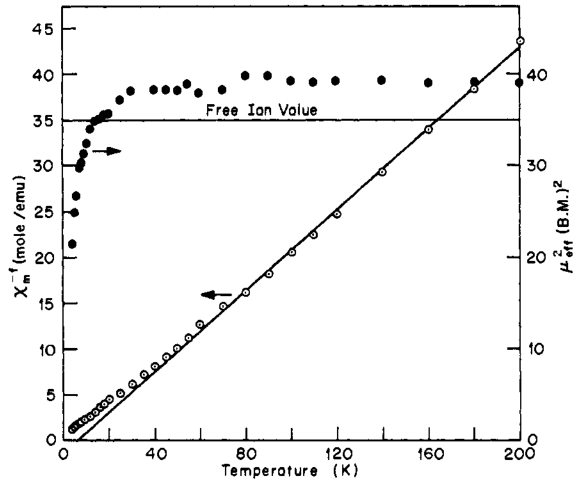

Figure 5. Plots of χ_m^{-1} and μ_{eff}^2 vs. T for TPPFeI.

Effective moments were determined from the slope of the linear portion of the χ_m^{-1} vs. T plots and have the following values (BM): hemin, 5.92; TPPFeCl, 5.92; TPPFeBr, 5.94; TPPFeSCN, 5.91; TPPFeI, 6.04. All

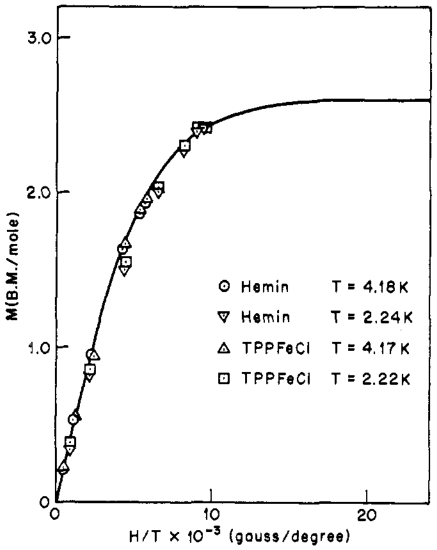

Figure 6. Magnetization *vs.* H/T for hemin and TPPFeCl. The smooth line is computed from eq 3 using $\bar{g} = 5.2$ and $M_s = {}^1/_2$.

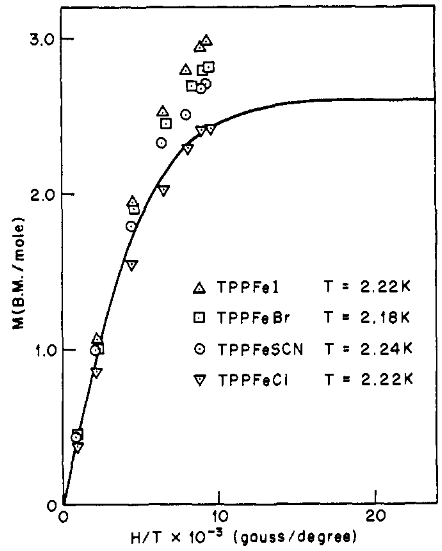

Figure 7. Magnetization *vs.* H/T for the synthetic analogs of hemin. The smooth line is computed from eq 3 using $\bar{g} = 5.2$ and $M_s = {}^1/_2$.

had a Weiss constant Θ of 0°K, except for TPPFeI, with $\Theta = 6$°K.

Plots of magnetization (Bohr magnetons/mole) *vs.* H/T (gauss/degree) for hemin and TPPFeCl are shown in Figure 6. Similar plots for the synthetic analogs of hemin demonstrating the effect of varying the fifth ligand are shown in Figure 7.

Discussion

Effective magnetic moments of complexed metal ions obtained from tma data remove, in part, the inherent ambiguity present when only static susceptibility measurements are used to deduce the electronic state of a paramagnetic ion. These results clearly show that the iron ions in hemin and the related derivatives of $\alpha,\beta,\gamma,\delta$-tetraphenylporphiniron(III) are high-spin, d^5, with the $^6A_1$ ground state predominating over the temperature range of study.

The strong deviation from Curie behavior, more obvious from the μ_{eff}^2 *vs.* T plots, is indicative of the relatively large zero-field splitting, D. When the susceptibility is measured at a temperature such that $2D > kT$, the only contribution to the total measured moment of the ferric ion should be due to the $^6A_1$ ($\pm{}^1/_2$) spin state which is the only one appreciably populated at this temperature. Conversely, when $2D < kT$, μ_{eff} approaches the free ion value of 5.92 BM. All of the high-spin complexes studied exhibited this marked deviation.

From the eigenvalues obtained using the spin-Hamiltonian, $\mathcal{H} = DS_z^2 + 2\beta S \cdot H$, Kotani[9] and Griffith[8] derived an analytical expression for μ_{eff}^2 as a function of $x = D/kT$.

$$\mu_{\text{eff}}^2 = \frac{19 + 16x^{-1} + e^{-2x}(19 - 11x^{-1}) + e^{-6x}(25 - 5x^{-1})}{1 + e^{-2x} + e^{-6x}} \tag{2}$$

Pure sextet wave functions ($M_s = {}^5/_2, {}^3/_2, \ldots, -{}^5/_2$) were used as the basis set, and axial symmetry was assumed for the derivation of this equation. Each eigenvalue was calculated to second order and expanded in a power series in applied magnetic field. Only those terms linear with magnetic field intensity were retained. The permanent magnetic moment carried by each electronic spin state was obtained by differentiating the corresponding eigenvalues with respect to applied field and temperature averaged according to Boltzmann's statistics by the usual method of Van Vleck.[16]

Equation 2 predicts that the effective moment of the chelated ion approaches its free ion value of 5.92 BM at high temperatures where the $^6A_1$ multiplets are narrowly separated relative to kT. At very low temperature eq 2 predicts that μ_{eff} should be about 4.36 BM. Because eq 2 seems to describe the expected deviation of the magnetic susceptibility from Curie behavior, especially at reduced temperatures, Kotani, Griffith, and later Weissbluth[17] suggested that its use could afford values of D of reasonable accuracy. Of course, this suggestion was made before Richards' ir data were available.

The fitted curve to the tma data for hemin corresponds to $D = 17$°K which is about 1.5 times the value measured directly using infrared radiation. The experimental data for TPPFeCl and TPPFeSCN also correspond to a D of this order of magnitude. For the ferric ion contained in hemin, μ_{eff} does not reach the free ion value of 5.92 BM up to 100°K. Equation 2 predicts that for $D = 10$°K the ion's moment should reach the upper limit at least at 75°K which corresponds to an amount of energy about 15°K in excess of the over-all splitting of $6D$ within the ground state. The fitted curve for the tma data of TPPFeBr corresponds to $D = 7$°K which we believe is more compatible with the ir values[10] of related compounds. Because the measured effective moment of the ferric ion in TPPFeI was slightly high with a positive Weiss constant, no effort to fit these data was made.

Factors which could be responsible for our inability to fit the tma data of hemin with a value of D which approximates the ir value of Richards include (1) contribu-

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(16) J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932.

(17) M. Weissbluth, *Struct. Bonding* (Berlin), 2, 1 (1967).

tions from higher excited states to the moment of the ground state, (2) magnetic field induced mixing of the Kramers levels within the ground state, and (3) the failure to include any departures from axial symmetry in the spin-Hamiltonian.

The next higher electronic state above the $^6A_1$ ground state is a $^4T_1$ state which itself is split by the crystal field into $^4E_1$ and $^4A_1$. The $^4A_1$ state is expected to interact more strongly with $^6A_1$ because it lies lower than $^4E_1$.[18,19] Such a contribution can be ruled out, however, on the basis of the values of measured effective moments for ferric ions in these complexes. Any magnetic mixing of the ground state with the higher $^4A_1$ state would result in a lower measured effective moment because the multiplicity of the latter is less by a factor of $^1/_3$.

In a subsequent theoretical treatment of high-spin iron porphyrin complexes, Harris[20] has indicated that magnetic fields above 10 kG can cause significant mixing of the Kramers levels within the $^5/_2$ manifold differing in M_s by ±1. Equation 2 makes no allowance for any field dependency to the susceptibility because energy terms higher than second order are neglected in its derivation. This magnetic field mixing which would change the permanent magnetic moment of each level is more important when the zero-field splitting is small and the applied magnetic field is large. For anions which exert weaker ligand fields in these complexes (*e.g.*, Cl^-), the effect of the magnetic field causing mixing is expected to be more appreciable. Also the magnetic field will change the center of gravity of the zero-field eigenvalues. The magnitude of these shifts will be inversely proportional to D, and the magnetic field would be less of a perturbation in the sense that the importance of higher order corrections to the zero-field eigenvalues with applied field decreases as D increases.

Conceivably, the occurrence of magnetic field induced mixing could explain the improved fit to the tma data for TPPFeBr using eq 2, because the bromide ion has been shown to exert a stronger ligand field in these complexes. Of several hemin compounds with various anions (*e.g.*, F^-, Cl^-, Br^-, OMe^-, N_3^-, I^-) studied by Richards, the iodide ion was shown to exert the strongest ligand field. For the same reasons one could expect better reliability using eq 2 to describe the data for TPPFeI. Unfortunately, the tma data for TPPFeI could not be fitted to eq 2 because these data showed a positive Weiss constant of 6°K.

If the molecular axes of these iron porphyrin complexes do not coincide with the crystal field axes, the inclusion of the term $E(S_x^2 - S_y^2)$ in the spin-Hamiltonian is warranted. This term essentially mixes $|\pm{}^1/_2\rangle$ with $|\pm{}^5/_2\rangle$ in zero field while the $|\pm{}^3/_2\rangle$ remains relatively pure. Numerical inclusion of this effect would invalidate use of eq 2, but at this time neither the magnitude nor the relative sign of E is known.

In most cases the Zeeman splitting in magnetic fields practically attainable is so small that at room temperature the energy differences between M_s states are small compared to kT. The available spin states, then, show no appreciable population imbalance at these temperatures, and the number of atoms with spins parallel and antiparallel with applied field is nearly the same.

Because the zero-field splitting for the ferric ion contained in hemin is relatively large, the only spin state that should be populated appreciably at 2.2°K is the $|\pm{}^1/_2\rangle$. The magnetic field splitting factors for this state have been calculated to first order to be $g_{\parallel} = 2$ and $g_{\perp} = 6$. These g's are proportionality constants between the energy separation and the field intensity, *i.e.*, $\Delta E = g\beta H$. For a field intensity of 22 kG, the intraseparation of the $|\pm{}^1/_2\rangle$ levels can be calculated to be 3 and 9°K for $H_{\parallel}$ and $H_{\perp}$, respectively. For a crystalline powder containing molecules with axial symmetry the weighted average to the magnetization for $H_{\perp}$ is $^2/_3$ and $H_{\parallel}$ is $^1/_3$, and because spin population imbalance increases with increasing field and decreasing temperature, saturation effects are expected. Figure 6 is a plot of the molar magetization *vs.* H/T for hemin and TPPFeCl and indicates about 90% saturation at 2.2°K and 22 kG.

The smooth line drawn through the data points is computed from

$$M = \frac{Ng\beta}{2} \tanh \frac{g\beta H}{2kT} \tag{3}$$

Equation 1 for magnetization is a defining relationship and holds for the high-temperature limit when the multiplet levels are very narrow with respect to kT. Equation 3 is a form for M when $D/kT \ll 1$ and, as such, is for the specific multiplet $^6A_1$ $(\pm{}^1/_2)$.[21]

The magnetization should level at a point which corresponds to $\bar{g}M_s$, as predicted by eq 3, where $\bar{g}$ is the average splitting factor for the spin state, M_s, which is populated at that particular temperature. The esr results for hemin are contradictory:[4,5] $g_{\parallel}$ varies from 2.0 to 2.6 and the resonance line at $g_{\perp} \simeq 6$ is broad and poorly resolved. Using the average of the g values and weighting $^1/_3$ and $^2/_3$ for $g_{\parallel}$ and $g_{\perp}$, respectively, g is angle averaged to 5.2. Figure 6 suggests good correspondence, but Figure 7 indicates the approximate nature of eq 3.

Figure 7 is a plot of the molar magnetization *vs.* H/T for the synthetic analogs of hemins, demonstrating the differences in extrapolated leveling points. There is correlation between the heights of the curves and the strength of the ligand fields the anions exert on the ferric ion based upon the ir data of Richards.[10] If first-order perturbation theory is used to describe the energy differences of the spin states within the ground state of the ferric ions contained in all these complexes, then nearly the same magnetization curves would be expected. Equation 3 is used assuming the maintenance of the purity of $|-{}^1/_2\rangle$ and $|+{}^1/_2\rangle$ and, as such, does not incorporate any magnetic field mixing of the multiplet levels. This same magnetic field mixing that invalidated the use of eq 2 for the acquisition of reasonable values of D would accordingly invalidate the use of eq 3 for any sort of quantitative description of the magnetization plots. Furthermore, the linearity of g with magnetic field intensity can no longer be assumed if the purity of the sextet wave functions is destroyed. Harris[19] calculated that $g_{\perp}$ for the $^6A_1$ $(\pm{}^1/_2)$ ground state in zero field should decrease with increasing ligand field strength because of the increasing proximity of the $^4T_1$ to the $^6A_1$ state. These same calculations revealed that $g_{\perp}$ de-

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[18] G. Harris, *Theoret. Chim. Acta*, 10, 119 (1968).

[19] G. Harris, *ibid.*, 10, 155 (1968).

[20] G. Harris, *J. Chem. Phys.*, 48, 2191 (1968).

[21] A. D. Morrish, "The Physical Principles of Magnetism," John Wiley and Sons, Inc., New York, N. Y., 1965, p 70.

creases nonlinearly with decreasing values of D as expected.

In order to include the contribution of magnetic field mixing the entire expressions for μ_{eff}^2 and M must be reformulated and a calculation made of the magnetic field energy of each contributing state which is not necessarily linear with field. These theoretical refinements would incorporate the additional field dependency in the susceptibilities and should describe the tma data more satisfactorily.[22]

Magnetic susceptibility measurements on the compound which has been formulated to date as TPPFeOH were also made. These as well as Mössbauer[23] and proton magnetic resonance measurements[24] performed in this laboratory have shown "TPPFeOH" to have distinctly different properties from those of the other TPPFeX compounds. Between 2.2 and 20°K this compound exhibited no measureable paramagnetism. Solution susceptibility using nmr techniques at 310°K[24] has shown, however, that $\mu_{\text{eff}} \simeq 1.7$ BM, which is still below the expected 2.2–2.5 BM for low-spin iron(III). These data strongly suggest dimerization with a bridging oxygen to permit superexchange between iron ions.[25]

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[22] Such calculations were suggested by one of the referees.

[23] C. Maricondi, D. K. Straub, and L. M. Epstein, manuscript in preparation.

[24] C. Maricondi, D. Davis, and D. K. Straub, manuscript in preparation.

[25] The X-ray crystal structure of this complex is presently being determined by J. L. Hoard at Cornell University.[26]

[26] Note Added in Proof. Fleischer has now reported the dimeric structure [E. B. Fleischer and T. S. Srivastava, *J. Am. Chem. Soc.*, **91**, 2403 (1969)].

The Ring-Current Effect of the Phthalocyanine Ring[1,2]

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Abstract: Some simple classical current loop calculations have been carried out on the phthalocyanine ring. Data for the calculations have been supplied by some single-ring and multi-ring silicon and germanium phthalocyanines. Possible structural uses are forseen for the results.

In 1959 and 1960 Bradley and Becker[3] and Ellis, Jackson, Kenner, and Lee[4] reported observing ring-current effects in the nmr spectra of porphyrins. Since then the nmr ring-current effects of these systems and the ring-current effects subsequently found in similar systems have attracted attention both because of their size and because of the importance of the macrocycles supporting them.

Several attempts have been made to develop quantitative descriptions applicable to these effects. Two were described by Bradley and Becker in their 1959 paper.[3] One was based on a model in which the magnetic effect of the ring was approximated by a magnetic dipole. The other was based on a model in which the magnetic effect was approximated by the magnetic effect of a pair of current loops.

Another attempt to describe the ring-current effects of such systems was made by Jackson, Ellis, Kenner, and Lee in their 1960 paper.[4] In this attempt a current-loop approach was also used. Abraham,[5] in much more detailed work, applied both the current-loop and magnetic dipole approaches. Extensions of this work were made by Abraham, Burbidge, Jackson, and Macdonald,[6] and further similar work was carried out by Katz, Strain, Leussing, and Dougherty.[7]

All of this work was patterned after similar work on benzene and related aromatic systems which was carried out by Pople,[8] Waugh and Fessenden,[9] and Johnson and Bovey.[10] Pople's work furnished the basis for the magnetic dipole calculations while that of the others provided the basis for the current-loop calculations.

In this paper the problem of a quantitative treatment of the ring-current effect in the porphyrin-like phthalocyanine ring is taken up. As in most of the previous related ring-current effect work, the current-loop approach is used.

The data on which the work is based come from some single-ring silicon and germanium siloxy compounds previously described and from some newly synthesized multi-ring compounds. Taken together the single-ring

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[2] The term ring-current effect is employed solely for convenience and is not to be construed as implying physical reality.

[3] E. D. Becker and R. B. Bradley, *J. Chem. Phys.*, **31**, 1413 (1959).

[4] J. Ellis, A. H. Jackson, G. N. Kenner, and J. Lee, *Tetrahedron Letters*, 2, 23 (1960).

[5] R. J. Abraham, *Mol. Phys.*, 4, 145 (1961).

[6] R. J. Abraham, P. A. Burbidge, A. H. Jackson, and D. B. Macdonald, *J. Chem. Soc., B*, 620 (1966).

[7] J. J. Katz, H. H. Strain, D. L. Leussing, and R. C. Dougherty, *J. Am. Chem. Soc.*, 90, 784 (1968).

[8] J. A. Pople, *J. Chem. Phys.*, 24, 1111 (1956).

[9] J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, **79**, 846 (1957).

[10] C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).