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MÖSSBAUER SPECTROSCOPY AND MAGNETOCHEMISTRY OF METALLOPORPHYRINS

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12.1. Mössbauer Spectroscopy

12.1.1. Introduction

Mössbauer spectroscopy, in contrast to electron paramagnetic resonance or magnetic susceptibility measurements, can give detailed information about electronic configurations of diamagnetic as well as paramagnetic states¹⁻³. A serious limitation of the method is that a nuclide having a low-lying isomeric nuclear energy must be employed as an absorbing nucleus and the excited state of that same nuclear isomer must be populated as a result of a nuclear reaction or decay. ⁵⁷Fe, ¹¹⁹Sn and ¹²⁹I Mössbauer studies have been used to probe the electronic environment in the vicinity of the coordinated metal ion or axial ligand in metalloporphyrin systems.

For ⁵⁷Fe Mössbauer spectroscopy, ⁵⁷Co sources with activities of 1 to 50 mCi are commercially available. The spectroscopic arrangement then consists of a source, an absorber, a detector of the transmitted 14.4 keV gamma radiation (a proportional gas counter or a scintillation counter), and some means of providing a relative velocity between the source and absorber (to vary the energy of the gamma ray). Both the source and absorber must be in solid form to insure that the recoil free gamma transition will be favored. The minimum in the transmission of 14.4 keV gamma rays will only occur at zero relative velocity when both the source and absorber are in the same identical chemical state. If however a 'standard' source material is used with a variety of absorbers, chemical information about the absorber can be obtained.

Porphyryns and Metalloporphyryns, ed. Kevin M. Smith

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Since the discovery of Mössbauer spectroscopy (MS) in 1958, several thousand research papers have appeared, most dealing with applications to solid-state physics, chemistry, geochemistry, and biochemistry. Introductory descriptions of Mössbauer spectroscopy are to be found in books by Frauenfelder⁴, Danon⁵ and Wertheim⁶; applications to chemistry are stressed in books by Goldanskii and Herber⁷, and by Greenwood and Gibb⁸. Monographs on specific applications of Mössbauer spectroscopy are found in the series edited by Gruverman⁹. A MS data index¹⁰ for the years 1958–1965 and an updated listing of biological MS publications¹¹ are available.

Information about the chemical surroundings of the Mössbauer nuclide is contained in the fact that small changes in the local symmetry and magnitude of electronic wave functions affect to an observable degree the energies of the nuclear energy levels connected by the Mössbauer absorption (or emission) line(s). The observation of these small energy shifts or splittings is made possible by the high monochromaticity of Mössbauer emission lines, typically $1 : 10^{13}$ for ^{57}Fe . Although the data are best discussed in terms of an appropriate 'spin-only' Hamiltonian, it is useful to describe Mössbauer spectra in terms of four distinct types of interactions. These are: the electric monopole interaction (isomer shift or chemical shift); the electric quadrupole interaction; the nuclear Zeeman interaction; and the nuclear hyperfine interaction.

The nuclear monopole interaction which gives rise to the isomer shift (δ_0) has its origin in the Coulombic interaction between electronic charge density at the Mössbauer nuclide position and the intranuclear charge distribution. As only s-orbitals have electron density at the nucleus, the relative isomer shift will be dependent on the extent of s-character of the electronic wave function. This is related to the shielding of s electrons by p and d electrons, and the bonding properties of ligands surrounding the nuclide. Both free atom¹² and covalency¹³ calculations have been made for ^{57}Fe .

The nuclear quadrupole interaction in ^{57}Fe occurs between the nuclear quadrupole moment of the $I = 3/2$ excited state ($^{57\text{m}}\text{Fe}$, 14.4 keV) and nonzero electric field gradients present at the nuclear position due to either atomic charge configurations, ligand charge configurations, or both¹⁴. In the absence of other interactions, materials displaying a nuclear quadrupole interaction show two Mössbauer absorption lines. The separation between lines, the quadrupole splitting (ΔE), is a measure of the energy difference between the $m_I = \pm 1/2$ and the $m_I = \pm 3/2$ nuclear energy states. The nuclear quadrupolar interaction is also described by the asymmetry parameter, η , which is defined as, $\eta = (V_{xx} - V_{yy})/V_{zz}$ where V_{xx} , V_{yy} , and V_{zz} represent the second derivatives of the electric potential along orthogonal crystal axes with the origin at the Mössbauer nuclide. The sign of η can be determined by the application of an external magnetic field of sufficient intensity (30 to 50 kG) to produce observable differences in the nuclear Zeeman interaction of the $m_I = \pm 1/2$ and $m_I = \pm 3/2$ states¹⁵.

The nuclear Zeeman interaction is the Mössbauer analog of the optical Zeeman Effect in which degenerate nuclear paramagnetic states show splittings in the presence of an applied magnetic field⁷. An additional magnetic interaction, the magnetic hyperfine interaction, occurs when there is unpaired spin density near the Mössbauer nuclide. The interaction is of the form $a\mathbf{I} \cdot \mathbf{S}$ where \mathbf{I} is the nuclear spin (1/2 and 3/2 for the ground and first excited state of ⁵⁷Fe), and \mathbf{S} is the unpaired electron spin. The nuclear hyperfine coupling constant, a , is a measure of the strength of the interaction⁷. Observation of the nuclear hyperfine interaction is facilitated by imposing a small external magnetic field either parallel or perpendicular to the direction of the Mössbauer gamma radiation; this magnetic field produces a polarization of electronic magnetic moments dependent on H/T . The external field strength can usually be chosen such that it does not produce an observable direct nuclear Zeeman splitting.

In general all four interactions may be present in a Mössbauer spectrum; judicious use of external parameters such as sample temperature and applied magnetic field are often necessary to sort out the interactions and to determine which electronic configurations might give rise to the observed spectrum. Calculation of expected Mössbauer spectra is in many cases essential to an understanding of the experimental data. There may be important time dependencies in the effects of these interactions, particularly for the nuclear hyperfine component. It is well to remember that Mössbauer spectroscopy senses the energy of nuclear energy levels for times of the order of 10^{-9} to 10^{-6} sec. ⁵⁷Fe Mössbauer spectroscopy has a characteristic time of 10^{-7} sec, the lifetime of the ⁵⁷Fe excited state. Time dependencies such as those due to electronic-spin relaxation can often be seen by working in the liquid helium range.

With ⁵⁷Fe, spectra taken in zero magnetic field can only sort out high-spin Fe(II) from the other spin states of Fe(II) and Fe(III), as the quadrupole splittings and isomer shifts for the other three common spin states lie too close to each other and can be identical for many combinations of ligand symmetry and ligand-field strength. In the case of high-spin Fe(III)porphyrins, the spin state (⁶S_{5/2}) is well-established by other techniques, particularly the observation of electron paramagnetic resonance spectra¹⁶ with g -values of 6,6 and 2 and low temperature susceptibility data⁷. Therefore the important role of Mössbauer spectroscopy of high-spin iron-porphyrins is to supply precise values of the nuclear isomer shift and the nuclear quadrupole interaction coupling constant for comparison with theoretical values calculated on the basis of modern quantum mechanical methods for the electronic configuration of the iron-porphyrin structure¹⁸⁻²¹.

12.1.2. High-spin ferric porphyrins

Mössbauer spectra of protohemin chloride have been obtained almost from the beginning of the chemical application of this spectroscopy²²⁻³⁰.

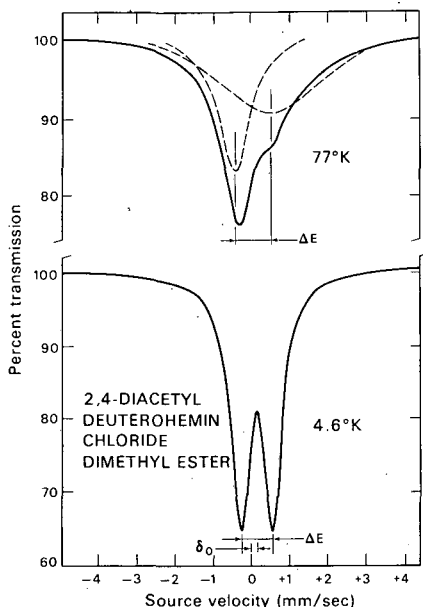


Fig. 1. Typical Mössbauer spectra of a high-spin five coordinated ferric porphyrin. The dashed lines show the computer resolution of the unresolved quadrupole doublet at 77°K. ΔE is the quadrupole splitting and δ_0 is the isomer shift, relative to sodium nitroprusside ($\delta_0 = 0.00$ mm/sec). See Ref. 27.

The most striking feature of the spectra is that a quadrupole doublet is only observed at temperatures below about 10°K. Above this temperature, the lines have equal absorption areas, and widths approach the ratio 3 : 1 (Fig. 1). Blume³¹ has explained this phenomenon as arising from electron spin-spin relaxation as a consequence of the large zero field splitting (D) for such ferric porphyrins³². ($2D$ is ~ 10 cm^{-1} rather than ~ 0.1 cm^{-1} as is usually found for high-spin ferric complexes). The crystal field produces three doublets; the ground $S_z = \pm 1/2$ state, an intermediate $S_z = \pm 3/2$ level and the upper $S_z = \pm 5/2$ state, which are separated by $2D$ and $4D$, respectively. D can be obtained very accurately in the far infrared³², and approximate values are found by Mössbauer³⁰ and PMR measurements. At helium temperatures, the spin relaxation is fast in the $\pm 1/2$ state, and the effective field at the nucleus averages to zero. Thus no magnetic hyperfine spectra are expected, and a well resolved quadrupole doublet is obtained. As the temperature increases, the $\pm 3/2$ and $\pm 5/2$ states become occupied. These states have slower relaxation rates than the $\pm 1/2$ level, and produce asymmetric spectra. Thus as the temperature increases, states that produce asymmetric behavior increase, and the quadrupole lines broaden³¹. The sign of the electric field gradient is positive since the highest energy peak displays the broadening at 300°K.

Johnson²⁸ has demonstrated the existence of an internal field in protohemin chloride. For Mössbauer measurements at high H/T (30 kG, 1.6–4.2°K), the doublet splits into six hyperfine components. 10^{-3} M protohemin chloride in tetrahydrofuran at 4.2°K is magnetically dilute, and shows a hyperfine spectrum which was better resolved in an applied magnetic field³³.

Other high-spin ferric porphyrins behave in essentially the same manner as protohemin chloride (Table 2). Work has been done with TPP^{34–36}, (*p*-Cl)³⁷, (*p*-F)³⁷, (*p*-NO₂)³⁴ and (*p*-OMe)TPP³⁷, various substituted deuterohemins^{27,30,38} and *meso*-tetrapyridylporphyrin²⁹ coordinated by different axial ligands. At about 5°K, the isomer shifts (with respect to sodium nitroprusside) range from 0.58–0.77 mm/sec, and average³⁷ to ~0.67 mm/sec. This is typical for high-spin ionic Fe(III) in a five coordinate environment. With a given porphyrin type, δ_0 increases in the order $I^- > CH_3CO_2^- > N_3^- \sim NCS^- \sim Br^- > CF_3CO_2^- \sim Cl^- > F^-$, which parallels their pi-bonding interactions with iron³⁷.

In general, the quadrupole splitting with hemins increases slightly with decreasing temperature, and values at 4°K are about 10–15% greater than at 300°K. For chloro, bromo and iodo complexes, ΔE increases³⁷, as (*p*-OMe)TPP > (*p*-F)TPP > (*p*-Cl)TPP > TPP. The axial ligand also affects ΔE , and the trend with (*p*-OMe)TPP³⁷ is $I^- > CF_3CO_2^- > Br^- > Cl^- > CH_3CO_2^- > N_3^- > F^-$. Similar results^{30,38} have been found with Deuterio-IX-DME. The order follows the directly observed³² zero-field splitting parameters found for the deuterohemin complex: $I^- (D = 16.4 \text{ cm}^{-1}) > Br^- (11.8) > Cl^- (8.95) > N_3^- (7.32) > F^- (5.55)$. Such D values can also be determined by computer simulation of the temperature dependence of the spectrum, which was assumed to be composed of three pairs of Lorentzian lines representing thermal populations of the three zero-field states³⁰. The origin of the frequently observed reversal in intensities of the quadrupole lines as the temperature decreases has been attributed to a thermally induced change in the magnetic field direction^{35,37}.

MS studies on Fe(III)Hemato-IX and a hematoheme–internal histidine complex with the axial ligand ¹²⁹I⁻ indicated that the Fe–I bond is extremely covalent in both derivatives³⁹. While the net charge on F⁻ in the ionic (P)Fe–F is ~0.95e⁻, that of I⁻ in (P)Fe–I is ~0.1e⁻. This charge is localized in the porphyrin ring, not on the iron. The electron capture decay of ¹²⁵I was used to produce a ¹²⁵Te axial ligand in hematoheme.

Low spin bis-amine hemichromes show quadrupole-split doublets at 300°K, which increase slightly in width at lower temperatures^{36,40,41}. The asymmetric d⁵ S = 1/2 configuration produces ΔE values in the range 1.9 to 2.5 mm/sec, much larger than found with the symmetric S = 5/2 ferric porphyrins (0.4–1.3 mm/sec). The pyridine hemichromes have a smaller ΔE than the imidazoles, which are better pi donor ligands and ΔE is insensitive to the counter ion⁴⁰. The isomer shifts range from 0.37 to 0.47 mm/sec

TABLE 1

Mössbauer parameters for selected iron porphyrins

Spin State	Porphyrin	Isomer shift (δ_0 , mm/sec) ^a	Quadrupole splitting (ΔE , mm/sec) ^a	Temp. ^b	Ref.
Fe(III), S = 5/2	Fe(Proto-IX)Cl	0.61	0.83	H	30
	Fe(Meso-IX)Cl	0.58	0.93	H	30
	Fe(TPP)I	0.72	0.75	H	37
	Fe(<i>p</i> -Me · TPP)I	0.76	1.33	H	37
	Fe(<i>p</i> -Me · TPP)-CF ₃ CO ₂	0.65	1.10	H	37
	Fe(<i>p</i> -Me · TPP)-Br	0.65	1.07	H	37
	Fe(<i>p</i> -Me · TPP)-Cl	0.64	1.03	H	37
	Fe(<i>p</i> -Me · TPP)-CH ₃ CO ₂	0.73	0.92	H	37
	Fe(<i>p</i> -Me · TPP)-N ₃	0.71	0.67	H	37
	Fe(<i>p</i> -Me · TPP)-NCS	0.69	0.63	H	37
Fe(III), S = 1/2	(<i>p</i> -OMe · TPP)Fe(Im) ₂ ^c , Cl	0.44	2.06	A	40
	(<i>p</i> -OMe · TPP)Fe(Im) ₂ , Br	0.43	2.05	A	40
	(TPP)Fe(Im) ₂ , Cl	0.40	2.11	A	40
	(<i>p</i> -Cl · TPP)Fe(Im) ₂ , Cl	0.42	2.11	A	40
Fe(II), S = 0	(<i>p</i> -OMe · TPP)Fe-(Pip) ₂ ^c	0.69	1.49	A	40
	(<i>p</i> -Me · TPP)Fe-(Pip) ₂	0.69	1.53	A	40
	(Pip) ₂ -Fe(Proto-IX)	0.67	1.47	A	40
	(Py) ₂ -Fe(Proto-IX)	0.63	1.27	A	40
	(Eim) ₂ -Fe(Proto-IX)	0.64	1.03	A	40
	(Morp) ₂ -Fe(Proto-IX)	0.68	1.52	A	40
Fe(III), S = 5/2	[(<i>p</i> -OMe · TPP)Fe] ₂ -O	0.68	0.63	N	46
	[(<i>o</i> -OMe · TPP)Fe] ₂ -O	0.59	0.65	N	46
	[2-PyridylPFe] ₂ -O ^d	0.70	0.64	N	46
	[3-PyridylPFe] ₂ -O	0.69	0.63	N	46
	[4-PyridylPFe] ₂ -O	0.69	0.67	N	46

^a Reported with respect to sodium nitroprusside, $\delta_0 = 0.0$ mm/sec.^b H, 4.2–6°K; A, 295–300°K; N, 77–80°K.^c Im, imidazole; Pip, piperidine; Py, pyridine; Eim, ethylenimine; Morp, morpholine.^d *meso*-tetrakis(2-Pyridyl)porphyrin.

(versus nitroprusside), and are consistent with hexacoordination. δ_0 is rather insensitive to porphyrin basicity. The pi-bonding characteristics of low spin ferric porphyrins, where the iron is in the porphyrin plane, might suggest that the iron delocalizes added charge into both the porphyrin and ligand orbitals, and maintains an effective electroneutrality.

The spectra of protohemin chloride have been studied in applied pressures up to 170 k bar⁴². Both δ_0 and ΔE increase with pressure, indicating reduction of the initial Fe(III) to intermediate or mixed spin states of Fe(II). At

high temperatures and low pressures, the bis-imidazole(Proto-IX)chloro complex is 30% reduced to low spin Fe(II), while high pressures favor low and intermediate Fe(II) states. The complex itself is in a mixed spin state⁴¹ at 300°K.

12.1.3. Ferrous porphyrins

Low spin bis-amine hemochromes are readily prepared due to the spontaneous reduction of the Fe(III) form in many amine solvents. Well defined quadrupole doublets are obtained at 300°K, and ΔE is fairly insensitive to temperature^{36,40}. For a number of porphyrin types and axial substituents, δ_0 (300°K) is in the narrow range 0.64–0.72 mm/sec; an indication that the Pauling electroneutrality principle outlined for the hemichromes may also apply to the d^6 hemochromes. With a given porphyrin, ΔE depends somewhat on the coordinated ligand, and values from 1.2 to 1.6 mm/sec are common for related nitrogenous bases⁴⁰. Little variation of ΔE is found for the same ligand with various (*p*-X)TPP complexes. Some work has been done on $S = 2$ Fe(TPP) and Fe(TPP)(THF)₂ complexes⁴³ and with mono-amine ferrous porphyrins that carry molecular oxygen⁴⁴.

12.1.4. Oxy-bridged ferric porphyrin dimers

The MS parameters^{38,45,46} of these $S = 5/2$ antiferromagnetically coupled μ -oxy dimers were essentially the same for seven different *meso*-tetra-arylporphyrin types⁴⁵. $\delta_0 = 0.70 \pm 0.02$ mm/sec (nitroprusside) and $\Delta E = \sim 0.67 \pm 0.05$ mm/sec at both 77° and 4.2°K.

Twelve Sn(IV) derivatives in the *meso*-tetra-arylporphyrin series with bis-chloro, fluoro or hydroxy ligands were studied by ¹¹⁹Sn spectroscopy⁴⁷. Only in the case of Sn(*p*-Me)TPP(OH)₂ was a quadrupole splitting observed. The isomer shifts varied with the electronegativity of the axial group, and the corresponding phthalocyanines had larger quadrupole interactions. Other tin porphyrin work has been reported in relation to the sitting-a-top complex problem⁴⁸. Doublets have been found in the Sn(*p*-X)TPP(Cl)₂ series¹¹⁵.

12.2. Magnetic susceptibility

12.2.1. Introduction

Magnetic susceptibility measurements are routinely used by inorganic chemists to probe the stereochemistry and electronic state of metal ions in coordination compounds. Many excellent monographs have been devoted to this subject^{49–53}. The susceptibility of solids or solutions can be measured on large (>100 mg) samples by the Gouy method. The Faraday technique, however, is more useful for porphyrin studies, where only a limited amount of solid material (<5 mg) is available. Balances for measurements from ambient temperatures to 77°K can be inexpensively constructed^{54,55}. Either method requires a standard of known susceptibility and Hg[Co(SCN)₄]⁵⁶

has been most widely used. Several groups^{54,57} have shown that the temperature dependence of the susceptibility of this complex when measured by the Faraday method differs from that obtained by the Gouy technique.

Many workers determine metalloporphyrin susceptibilities in solution by the Evans⁵⁸ PMR method⁵⁹. The shift of a proton resonance line of an inert reference substance due to a paramagnetic species is given by $(\Delta H/H) = (2\pi/3)\Delta\kappa$, where $\Delta\kappa$ is the change in volume susceptibility. The same precision⁶⁰ in the measurement of the paramagnetic susceptibility can be obtained by a PMR study on 50 mg of material at 60 MHz as with the Gouy method on 400 mg. At 220 MHz only 7 mg is required under favorable conditions.

When the observed susceptibility is corrected for ferromagnetic impurities, temperature independent paramagnetism and diamagnetic contributions, the temperature dependence of the molar paramagnetic susceptibility (χ_p) usually follows the Curie law, $\chi_p = C/T$ or the Curie-Weiss law, $\chi_p = C/(T + \theta)$. C is the Curie constant. The Weiss constant, θ , does not often have a simple interpretation⁵². The effective magnetic moment (μ_{eff}) in units of Bohr Magnetons (BM) is given by the expression

$$\mu_{eff} = 2.83 (\chi_p T)^{\frac{1}{2}} \quad (1)$$

and results should be reported in this form⁵². The aim of most metalloporphyrin susceptibility measurements is to confirm or establish the oxidation state of the metal ion, and to find if any peculiar magnetic interactions are present. For this purpose, μ_{eff} is compared with the 'spin only' value computed from the equation $\mu_{so} = (N(N + 2))^{\frac{1}{2}}$, where N is the number of unpaired electrons. Many tabulations show the range of μ_{eff} values to be expected from a particular magnetically dilute metal ion in a given environment⁵⁰. More information can of course be obtained from susceptibility studies at low temperatures and high field strengths, using single crystals. In the following sections, we will briefly describe magnetic studies on porphyrin compounds under the general categories (A) oxidation state determinations, (B) testing theoretical predictions, and (C) spin-state equilibria and magnetic exchange phenomena.

12.2.2. Oxidation states

Most metalloporphyrins⁶¹ obey the Curie law to 77° K, and the resulting magnetic moments (Table 2) are fairly unambiguous indications of the metal ions' oxidation state. Earlier work in this area has been reviewed^{62,63}. Phthalocyanines⁶⁴ have more complicated magnetic properties. Difficulties arise when the purity⁶⁵ or form of the complex is in question. The low moments for protohemin both in basic solution and as solids isolated under basic conditions⁶⁶ could arise from aggregation and oxy-bridge dimerization^{45,67}. Decarboxylation of protohemin chloride at high temperatures¹⁷

TABLE 2

Representative magnetic susceptibility results for metalloporphyrins

Con- figura- tion	Complex ^a	Coordi- nation num- ber	Unpair- ed elec- trons	μ (spin only)	μ (obs.)	Temp. ^b	Ref.
d ⁹	Cu(II)Hemato-IX-DME	4	1	1.73	1.93	N	61
	Ag(II)Hemato-IX-DME	4	1	1.73	1.94	N	61
d ⁸	Ni(II)Hemato-IX-DME	4	0	0	diam	N	61
	Pd(II)Hemato-IX-DME	4	0	0	diam	N	61
	Pt(II)Etio-I	4	0	0	diam	N	61
	Na[Co(I)TPP]	4	0	0	diam	R	101
	Ag(III)OEP	4	0	0	diam	R	102
	H[Rh(I)TPP]	4	0	0	diam	R	103
	Ni(II)TPP-Pip	5	0	0	diam	R	114
	Ni(II)TMPyP-(Im) ₂	6	2	2.84	3.3	R	73
d ⁷	Co(II)Meso-IX-DME	4	1	1.73	2.89	N	61
	Na[Fe(I)TPP]-(THF) ₂	6	3	3.87	c	N	104
	Fe(I)TPP	4	1	1.73	1.8	R	104
	Rh(II)TPP	4	1	1.73	1.2	R	103
d ⁶	Fe(II)TPP	4	4	4.89	4.85	R	105
	Fe(II)TPP(Py) ₂	6	0	0	diam	R	106
	Fe(II)TPP(THF) ₂	6	4	4.89	5.02	R	75
	Fe(II)TPP(NO)	5	4	4.89	4.75	R	107
	Rh(III)TPP(CO,Cl)	6	0	0	diam	R	108
	Ir(III)Hemato-IX-DME- (Cl,CO)	6	0	0	0.4	R	109
	Rh(III)Meso-IX-DME(Cl)	5	0	0	0.4	R	109
	Co(III)Hemato-IX(Cl,H ₂ O)	6	0	0	0.23	N	61
d ⁵	Fe(III)Proto-IX-Cl	5	5	5.92	5.89	N	17
	Fe(III)TPP-(Im) ₂	6	1	1.94	2.36	H	36
	Mn(II)TPP-(Py) ₂	6	5	5.92	6.02	R	106
	Rh(IV)TPP-(C ₆ H ₅ ,Cl)	6	1	1.94	1.95	R	110
	K[Ru(III)TPP](CN) ₂	6	1	1.94	1.9	N	65
d ⁴	Mn(III)Hemato-IX-Cl	5	4	4.89	4.88	N	61
	Fe(IV)TPP ⁺	?	4	4.89	c	R	111
	Cr(II)TPP	4	4	4.89	4.9	R	70
d ³	Cr(III)TPP-OCH ₃	5	3	3.87	3.61	N	112
	Mn(IV)Hemato-IX-(OH) ₂	6	1	1.73	2.0	R	113
d ¹	VO-Hemato-IX-DME	5	1	1.73	1.79	N	61
	O=MoTPP-Cl	6	1	1.73	1.71	N	113

^a Im, imidazole; Py, pyridine; THF, tetrahydrofuran.^b N, 77-300°K; R, 298°K; H, 4.2-50°K.^c Observed magnetic moment not reported.

could account for the unusual magnetic behavior found in this range^{6,8}. The low moment of 2.84 BM shown by Cr(II)Meso-IX-DME in the solid state^{6,9} indicates magnetic interactions that are absent in solution, where $\mu_{\text{eff}} = 5.19$ BM. This interaction is not found with solid Cr(II)TPP ($\mu_{\text{eff}} = 4.9$ BM) where the phenyl rings may inhibit close contact between the metal centers^{7,0,71}. Magnetic measurements have elucidated the equilibria in nickel-porphyrin solutions due to complexation by pyridine^{7,2} or water^{7,3} molecules (see Chapter 6).

The high spin-low spin transition and the resulting movement of the iron atom upon oxygen addition to ferrous hemoglobin may account for the cooperative subunit interactions^{7,4}. Both diamagnetic^{4,4} ($\text{O}_2\text{-Fe(II)P-(1-MeIm)}$) and paramagnetic^{7,5} ($\text{O}_2\text{-Fe(II)P-THF}$) dioxygen complexes have been synthesized. In the coboglobin system where only a formal spin change is realized upon dioxygen formation (low spin $d^7 \rightarrow d^6$), the doming of the entire porphyrin framework has been suggested as the stereochemical trigger.

The following molar diamagnetic susceptibilities have been reported. $\text{H}_2(\text{TPP})^{6,5} = -386 \times 10^{-6}$ cgs units, $\text{H}_2(\text{Proto-IX-DME})^{7,6} = 585 \times 10^{-6}$ and $\text{H}_2(\text{Meso-IX-DME})^{7,6} = 595 \times 10^{-6}$ cgs units.

12.2.3. Theoretical predictions

Figure 2 shows that protohemin chloride deviates markedly from Curie behavior below 40°K, and the Curie-Weiss law with $C = 7.09 \times 10^{-3}$ and $\theta = 3.1$ is a good representation of the data^{1,7}. Such deviations may be a reflection of differing populations of the 6A_1 , zero-field states with temperature, and the Kotani^{7,7}-Griffith^{1,6} equation shows a relationship between the observed moments (μ^2) and the zero-field splitting parameter D , where $x = D/kT$.

$$\mu^2 = \frac{19 + [6x^{-1} \exp(-2x)(19-11x^{-1})] + \exp(-6x)(25-5x^{-1})}{1 + \exp(-2x) + \exp(-6x)} \quad (2)$$

At high temperatures where $kT \gg 2D$, the moment will reach the spin-only value of 5.92 BM, and at low temperature where only the $\pm 1/2$ state is populated ($2D \gg kT$), μ should approach 4.36 BM. Studies of protohemin chloride by several groups^{1,7,7,8} show that $\mu = 5.92$ or 5.89 BM at 293°, 5.86 BM at 77°K, and 4.58 BM at 4°K. The chloride, bromide and SCN salts of Fe(III)TPP behave in a similar fashion^{7,8}. With the exception of possibly Fe(TPP)Br, the observed results are not well represented by the Kotani-Griffith equation for any value of D , and similar deviations at low temperature are found for other hemiproteins^{7,9}. The origin of these deviations has been discussed^{1,7,7,8}. The temperature dependence of the moments are in fair agreement with the Harris-Loew calculations^{1,8}. At high values of H/T (22 kG, 2°K), 90% magnetic saturation was demonstrated for protohemin chloride^{1,8}.

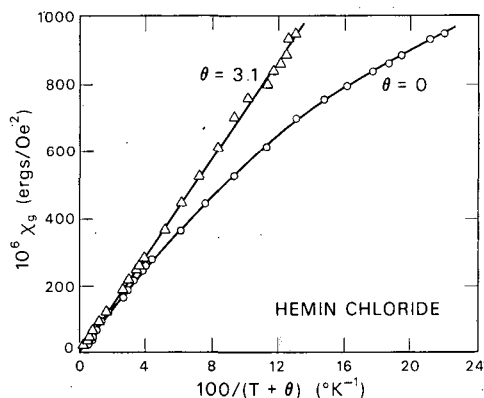


Fig. 2. Temperature dependence of the magnetic susceptibility of Cl-Fe(III)-Protoporphyrin-IX, (hemin chloride) from 4.5 to 300° K. The results are expressed in terms of the Curie-Weiss law, $\chi = C/(T + \theta)$. $\theta = 0$ is the observed data and $C = 7.09 \times 10^{-3}$, $\theta = 3.1$ are the best-fit parameters to the equation. See Ref. 17.

12.2.4. Spin state equilibria and magnetic exchange

The magnetic susceptibility⁸⁰ of the protohemin dimer [μ -oxy-bis(Proto-IX-DME)Fe(III)] was studied from 1.5 to 300° K at field strengths from 2 to 18 kG. Antiferromagnetism was indicated, as the moments increased with increasing temperature ($\mu^2 = 2.4$ BM at 296° K, 1.5 at 213°, and 0.09 at 78° K). By using the Heisenberg $2JS_1S_2$ model, a coupling constant $2J$ of 380° was found for the interaction between two high spin ($S = 5/2$) ferric ions in the dimer. The temperature dependence of the Knight shifts of the pyrrole protons of ferric porphyrin dimers⁸¹ was used to determine isotopic exchange parameters ($-J$) of 309 cm^{-1} for O-[Fe(III)TPP]₂ and 335 cm^{-1} for O-[Fe(III)(*p*-Me·TPP)]₂. However, PMR results on related porphyrin⁸² dimers indicate that dipolar interactions and zero field splitting parameters are not negligible, and thus the TPP dimer results⁸¹ are probably inaccurate.

Mn(III)⁸³, Mo and W⁸⁴ porphyrins also form oxybridged adducts. The nature of the interactions have not been studied in detail. Several solid vanadyl porphyrins have low room temperature moments, which have been attributed to antiferromagnetic interactions⁸⁵.

The magnetic properties of an aligned crystal⁸⁶ of Cu(TPP) has been determined at low temperature. The hyperfine interactions between the nuclear and electronic spins of copper affect the perpendicular susceptibility, and the parallel susceptibility obeyed the Curie-Weiss law above 20° K with $\theta = 3^\circ$.

The spin-state equilibrium behavior found in many heme proteins⁸⁷ and inorganic complexes⁸⁸ has also been observed with iron porphyrins. PMR measurements have demonstrated that bis-pyridine Fe(III)Proto-IX may be

an ($S = 1/2 \rightarrow S = 3/2$) system^{8,9}, with the singlet state predominant at low temperature. Similar results^{9,0} are found with substituted pyridines in methanol solutions. Low spin bis-pyridine Fe(II) and Fe(III) complexes exchange electrons rapidly^{9,1}, and the addition of CO to form (CO-Fe(II)P-Py) blocks the exchange. The higher spin ferric forms do not exchange electrons with the low spin complexes^{9,1,9,2}. The [H₂O-Fe(III)-P-Py] Proto-IX derivative^{9,3} is about 20% in the $S = 5/2$ form at 300°K, and the monoimidazole complex of Fe(III)/TPP may be high spin^{9,4}. The nature of the species present in pyridine solutions of ferric porphyrins are not well understood. The high spin complex [Py-Fe(III)P-Cl] is present at 300°K in pure pyridine^{3,8}, in agreement with monopyridinate stability constant results^{9,5}. The transformation of metmyoglobin-hydroxide between its high and low spin states was found to be a very rapid process^{9,7}. Therefore the much slower rates that have been attributed to spin state equilibrium in porphyrin systems^{9,1,9,3} may in fact involve axial ligand substitution at the iron center.

In the solid state, monoamine adducts of Fe(III)OEP-ClO₄ have been prepared^{9,8}. The monopyridinate is low-spin between 77° and 240°K, while the 4-CHO and 4-CN pyridine derivatives have moments higher (4.3 and 3.3 BM) than the low spin value of 2.2 BM at 77°K. The perchlorate complex itself had a moment of 4.8 BM, and ClO₄⁻ was probably coordinated to the iron. The solid bis-imidazole [Fe(III)Proto-IX] chloride^{4,1} is low spin at 77°K, and 23% in the assumed $S = 5/2$ spin state at 300°K. Upon heating to 530°K, only one imidazole is lost, and the resulting complex was shown to be high spin. In contrast, the bisimidazole (Meso-IX) and (Deut-IX) derivatives are low spin at 300°K.

In a novel approach, 2 moles of Fe(III)TPP-N₃ and 1 mole of Fe(II)TPP were reacted to form 2 : 1 complexes that could be represented^{9,9} as either [-Fe(III)-NNN-Fe(II)-NNN-Fe(III)-], [N₃-Fe(III)-Fe(II)-Fe(III)-N₃] [Fe(III)-N₃-Fe(II)-N₃-Fe(III)] (-N-configuration). The magnetic moment was unchanged from 77° to 300°K, with $\mu_{eff} = 5.0$ BM. The interpretation was that Fe(II) is diamagnetic, and each Fe(III) has a normal spin-only moment of four unpaired electrons ($S = 2$). The fifth electron from each ferric ion was paired in an orbital that extended across the entire system. The polymer [-Fe(TPP)-(imidazolate)-]_n has been shown by magnetic techniques to involve spin coupling through the imidazolate ion^{1,0,0}.

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