

EPR Spectra from “EPR-Silent” Species: High-Field EPR Spectroscopy of Manganese(III) Porphyrins

David P. Goldberg,[†] Joshua Telser,[‡] J. Krzystek,[§]
Antonio Garrido Montalban,[⊥] Louis-Claude Brunel,[§]
Anthony G. M. Barrett,[⊥] and Brian M. Hoffman^{*,†}

Department of Chemistry, Northwestern University
Evanston, Illinois 60208
Chemistry Program, Roosevelt University
Chicago, Illinois 60605
Center for Interdisciplinary Magnetic Resonance
National High Magnetic Field Laboratory
Florida State University, Tallahassee, Florida 32310
Department of Chemistry
Imperial College of Science, Technology and Medicine
London, UK SW7 2AY

Received April 14, 1997

EPR spectroscopic methods at conventional microwave frequencies (X-band: ~ 9 GHz (0.3 cm $^{-1}$); Q-band: ~ 35 GHz (1.2 cm $^{-1}$)) have long played a central role in defining the structural and electronic environments of half-integer spin (Kramers) paramagnets. In general, these methods are not applicable to “EPR-silent” systems with integer-spin ground states where the zero-field splitting (zfs) is larger than the microwave quantum, and in particular where the zfs interaction approaches axial symmetry.¹ High-spin manganese(III) (d^4 , $S = 2$) is archetypical of such non-Kramers ions. Mono- and polynuclear Mn(III) is of central importance in biological systems such as superoxide dismutase,² catalase,³ and photosystem II,⁴ while Mn(III) porphyrins⁵ and phthalocyanines⁶ have been used as building blocks in the construction of molecule-based magnets.

High-frequency, high-field EPR (HF-EPR; $\nu > 90$ GHz) methods have proved to be effective complements to conventional studies of Kramers systems.⁷ We illustrate here their value for probing non-Kramers centers,^{8–10} with an HF-EPR investigation of the Mn(III) ion incorporated into the three complexes depicted in Scheme 1: Mn(TPP)Cl (**1**), Mn(ODMAPz)-Cl (**2**), and Mn(ODMAPz)DTC (**3**).¹¹ The first of these is a classical metalloporphyrin, and the other two are tetraazaporphyrin (porphyrazine) complexes newly prepared as part of our

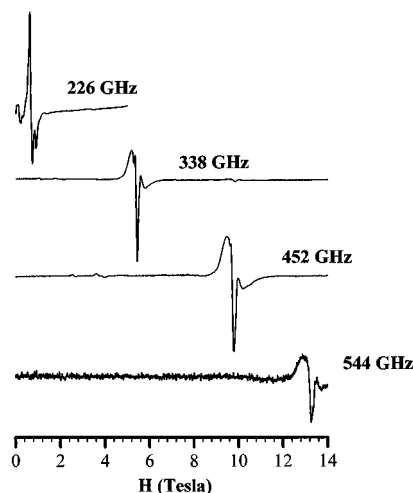
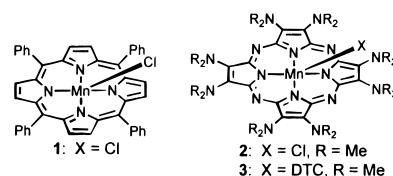


Figure 1. HF-EPR spectra obtained at 4 K for **1** at selected frequencies.

Scheme 1



broader effort to synthesize novel porphyrazine macrocycles.¹² All three compounds are EPR-silent at conventional microwave frequencies.

The HF-EPR spectrometer employed generates numerous microwave frequencies (25–3000 GHz (~ 100 cm $^{-1}$)) and is capable of continuous field sweeps over a broad range (0–17 T).^{13,14} Sets of field-dependent spectra at multiple frequencies were collected at 4 K from samples of **1–3**,¹⁵ so as to generate full field-frequency relationships of their EPR transitions.¹⁶ Figure 1 is a selection from the data for **1** at four different frequencies. The spectra show one main feature whose resonant field (H_r) shifts linearly with the microwave quantum ($h\nu$), as shown by the field-frequency plot of Figure 2a.¹⁷ The spectra for **2** and **3** are similar, and for all three molecules the frequency dependence of this transition can be well fit to the linear relationship $g\beta H_r = h\nu - \Delta$ with a value of Δ between 7 and 8 cm $^{-1}$ (see Figure 2a).

The magnetic properties of an ion with $S = 2$ can be described by the standard spin Hamiltonian comprised of Zeeman and zfs terms, $\mathbf{H} = \beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} + D(S_z^2 - S(S+1)/3) + E(S_x^2 - S_y^2)$ (eq 1).¹ The energy levels for \mathbf{H}_0 parallel or perpendicular to the principal zfs (z) axis of an $S = 2$ system can be calculated through use of analytic solutions¹⁸ to eq 1; their field dependence

[†] Northwestern University.

[‡] Roosevelt University.

[§] Florida State University.

[⊥] Imperial College of Science, Technology and Medicine.

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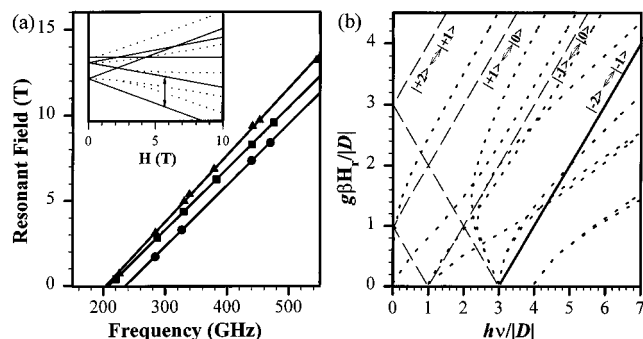


Figure 2. (a) Resonance field versus microwave frequency of the major feature for **1** (triangles), **2** (squares), and **3** (circles) plus the best linear fits (solid lines). Inset: Energy level diagram for an $S = 2$ with $D = -2.273 \text{ cm}^{-1}$, $E = 0$, and $g = 1.822$. Solid lines are for $\mathbf{H}_0||z$; dotted lines are for $\mathbf{H}_0\perp z$. The arrow represents the microwave quantum as 338 GHz. (b) EPR transitions for $S = 2$ with resonant frequency and field each normalized by D . The dotted lines are for $\mathbf{H}_0\perp z$; the dashed lines, $\mathbf{H}_0||z$; the solid line is the $|2, -2\rangle \leftrightarrow |2, -1\rangle$ transition with $\mathbf{H}_0||z$. The parallel transitions are labeled for $D < 0$.

is shown in the inset to Figure 2a for a system with $D < 0$, $E = 0$. A plot of transition fields versus the microwave frequency calculated for both \mathbf{H}_0 parallel and perpendicular to z is shown in Figure 2b. A linear dependence of H_r on $h\nu$ for the $\Delta M_s = \pm 1$ transitions is exhibited by molecules oriented with \mathbf{H}_0 parallel to the z axis, but strong curvature at lower fields is predicted for molecules with $\mathbf{H}_0\perp z$ (Figure 2b). As a result, the major feature in Figure 1 is assigned to a “parallel” transition. This absence of even weak curvature, combined with the absence of a so-called “integer-spin” EPR signal¹⁹ near zero field at X or Q bands,²⁰ confirms that $E \cong 0$. The lack of additional, “perpendicular” features in the experimental data indicates that the crystallites had reoriented in the large fields so that the z axis is parallel to \mathbf{H}_0 , greatly simplifying the spectra and their analysis.²¹

The spectra were taken at low temperature ($\sim 4 \text{ K}$) and high fields, where $g\beta H/kT$ and $\Delta/kT > 1$, and thus the peak observed in Figure 1 should arise from a transition involving the ground spin state of the $S = 2$ manifold. If $D < 0$, the $|2, -2\rangle$ state is the ground state for $\mathbf{H}_0||z$ (Figure 2a), and only one parallel, ground-state transition is expected ($|2, -2\rangle \leftrightarrow |2, -1\rangle$); highlighted by the arrow in the inset of Figure 2a), in agreement with the single major resonance observed for **1–3**. The field-frequency variation of this transition is predicted to be, $g\beta H_r = h\nu - \Delta$, as seen in Figure 2a, where the zero-field intercept in Figure 2a would be $\Delta = -3D$.²² If instead $D > 0$, one again expects a single line ($|0\rangle \leftrightarrow |1\rangle$) with this field-frequency variation for $h\nu > \Delta$, but for $h\nu < \Delta$ there must be a related transition ($|0\rangle \leftrightarrow |-1\rangle$) described by the following equation, $g\beta H_r = -h\nu + \Delta$. The lack of such a signal for **1–3** supports the assignment of $D < 0$ for all three molecules.

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(21) For completeness we have attempted to obtain true powder spectra by hindering the crystallite reorientation through grinding the samples and pressing them. This procedure indeed introduces additional features in the spectra, but has so far failed to give a truly random distribution of crystallite orientations. The g values presented in Table 1 can be considered as the $g_{||}$ component of the true g tensor, under the assumption that the zfs and g tensors are colinear. As emphasized by a helpful reviewer, the experimental value of $g_{||}$ for **1** is surprisingly low and needs further investigation.

Table 1. Magnetic Parameters for Mn(III) Porphyrinic Compounds^a

compd	$D \text{ (cm}^{-1}\text{)}$	$g_{ }$
Mn(TPP)Cl (1)	$-2.27(1)$	1.822
Mn(ODMAPz)Cl (2)	$-2.33(1)$	1.984
Mn(ODMAPz)DTC (3)	$-2.62(1)$	1.983
Mn(DP-IX-DME)Cl ^b	$-2.53(2)^c$	2^d

^a Pure powder samples were used. ^b DP-IX-DME refers to deuteroporphyrin IX dimethyl ester. ^c As determined by far-IR absorption.⁸ ^d An isotropic g value of 2.0 was assumed.

As confirmation of this analysis, we successfully modeled the spectra of **1–3** through use of a program that employed full-matrix diagonalizations of eq 1 to calculate the spectra of oriented samples ($\mathbf{H}_0||z$). Intensities of the transitions were weighted for both the Boltzmann population of the states involved in the transition and the magnetic dipole transition probabilities.²³ The parameters used in the simulations were $D = -\Delta/3$ and $g_{\perp} \equiv g_{||}(g_z)$, as derived from the best-fit lines in Figure 2a and given in Table 1, with $E = 0$; the absence of any detectable curvature in the plots of Figure 2a requires that $|E/D| < 0.05$ (see Figure S1, Supporting Information). Measurements of D for Mn(III) porphyrin-type molecules by bulk magnetic susceptibility^{24–26} have given $1.5 < |D| < 3.0 \text{ cm}^{-1}$, compatible with D for the compounds studied here. We explicitly note that the bulk measurements do not have the precision to make detailed comparisons among related molecules, do not give the sign of D , and are insensitive to E .

The Mn(III) ions of compounds **1** and **2** both have a chloride ion as the axial ligand, but the coordination geometries imposed by the two macrocycles are strikingly different in the displacement of the metal ion from the porphyrin plane.²⁷ Thus it is surprising that the zfs parameters for the two compounds are essentially the same ($D \approx -2.30(5) \text{ cm}^{-1}$). The replacement of chloride as the axial ligand in **2** with sulfur in **3** occurs without additional change in the Mn(III) coordination geometry²⁷ but with a significant increase in the magnitude of D ($D = -2.62(1) \text{ cm}^{-1}$). These results suggest the axial ligand is dominant in determining D . Such magnetostructural correlations obtained from high-precision, variable-frequency HF-EPR measurements will also be possible for other heretofore EPR-silent metal ion systems.

Acknowledgment. This work was supported by the NSF (CHE9408561 [A.G.M.B. and B.M.H.]; DMR9523228 [B.M.H.]), The Human Frontier Science Program (RG-349/94) [L.C.B.], and the NHMFL [J.K. and L.C.B.]. D.P.G. is grateful to the NIH (National Cancer Institute) for a Postdoctoral Fellowship (5-F32-CA66240) and the NHMFL User Program. We thank Dr. Luca Pardi and a reviewer for helpful remarks.

Supporting Information Available: One figure illustrating the effect of non-zero E/D (1 page). See any current masthead page for ordering and Internet access instructions.

JA9711690

(22) More generally, $\Delta = -3[D + |E| + E^2/D]$.

(23) Intensities are treated by: Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*; John Wiley & Sons, Inc.: New York, 1994. For both oriented and powder samples, uncertainties in the experimental line shapes (see ref 17) preclude precise simulations of spectra.

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