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

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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) (d⁵, 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; ν > 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(OMAPz)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 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 (H₀) lies near the microwave quantum (ν), 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 gβH₀ = ν – Δ 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, H = βgH₀S + D(S² – S(S + 1)/3) + E(S₁² – S₂²) (eq 1).1 The energy levels for H₀ parallel or perpendicular to the principal zfs (c) axis of an S = 2 system can be calculated through use of analytic solutions18 to eq 1; their field dependence is described because they are mixtures of absorption and dispersion and may reflect passage effects.

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

Scheme 1

(1) Abbreviations used are as follows: TPP, 5,10,15,20-tetraphenylporphyrinate; OMAPz, 2,3,7,8,12,13,17,18-octakis(dimethylamino)porphyrinate; DTC, diethyldithiocarbamato.
(15) Compound I was purchased from Porphyrin Products, Inc., Logan, UT. Full details of the preparation of 2 and 3, including single-crystal structure determinations, are described elsewhere. Goldberg, D. P.; Montalban, A. G.; White, A. J. P.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. Inorg. Chem. Submitted. Sample size 1 to 3 mg.
(17) The field plotted (H₀) is that of the peak maximum (derivative zero-crossing point in Figure 1). The experimental line shapes are not well-defined because they are mixtures of absorption and dispersion and may reflect passage effects.

S0002-7863(97)01169-4 CCC: $14.00 © 1997 American Chemical Society
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 $|\bar{z}|$; dotted lines are for $|\bar{H}z|$. The arrow represents the microwave quantum as $338 \text{ GHz}$. (b) EPR transitions for $S = 2$ with resonant frequency and field each normalized by $D$. The dotted lines are for $|\bar{H}z|$; the dashed lines, $|\bar{H}|z|$; the solid line is the $|\bar{z}| \rightarrow |\bar{-z}|$ transition with $|\bar{H}|z|$. 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 $|\bar{H}|z|$ parallel and perpendicular to $z$ is shown in Figure 2b. A linear dependence of $H_r$ on $h\nu$ for the $\Delta M_z = \pm 1$ transitions is exhibited by molecules oriented with $|\bar{H}|z|$ parallel to the $z$ axis, but strong curvature at lower fields is predicted for molecules with $|\bar{H}|z|$ (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 signal near zero field at $X$ or $Q$ bands, confirms that $E \approx 0$. 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 $|\bar{H}|z|$, greatly simplifying the spectra and their analysis.

The spectra were taken at low temperature ($\sim 4 \text{ K}$) and high fields, where $g|\bar{H}|K$ and $\Delta K > 1$, 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 $|\bar{z}| \rightarrow |\bar{-z}|$ state is the ground state, so $g|\bar{H}|z|$ (Figure 2a), and only one parallel, ground-state transition is expected ($|\bar{z}| \rightarrow |\bar{-z}|$), 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 $g|\bar{H}|z| = h\nu - \Delta$, as seen in Figure 2a, where the zero-field intercept in Figure 2a would be $\Delta = -3D$. If instead $D > 0$, one again expects a single line $(0 \leftrightarrow +1)$ with this field-frequency variation for $h\nu > \Delta$, but for $h\nu < \Delta$ there must be a related transition $(0 \leftrightarrow -1)$ described by the following equation,

$$g|\bar{H}|z| = -h\nu + \Delta.$$

The lack of such a signal for $1$–$3$ supports the assignment of $D < 0$ for all three molecules.

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

<table>
<thead>
<tr>
<th>compd</th>
<th>$D$ (cm$^{-1}$)</th>
<th>$g$z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(TPP)Cl$(1)$</td>
<td>$-2.27(1)$</td>
<td>1.822</td>
</tr>
<tr>
<td>Mn(ODMAp)Cl$(2)$</td>
<td>$-2.33(1)$</td>
<td>1.984</td>
</tr>
<tr>
<td>Mn(OHMAp)DTC$(3)$</td>
<td>$-2.62(1)$</td>
<td>1.983</td>
</tr>
<tr>
<td>Mn(DP-IX-DME)Cl$(4)$</td>
<td>$-2.53(2)^a$</td>
<td>2.0</td>
</tr>
</tbody>
</table>

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

Figure 2c demonstrates the replacement of chloride as the axial ligand in $2$ with sulfur in $3$ occurs without additional change in the Mn(III) coordination geometry 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 National Institutes of Health (CA67527 and CA87766) for a Postdoctoral Fellowship (5-F32-CA66240) [L.C.B.].

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.

JA971169O

(18) Baranowski, J.; Cukierda, T.; Jezewska-Trzebiatowska, B.; Kozlowski, H. J. Magn. Reson. 1979, 33, 585–593. We note that there is an error on p 586; the variable $p_1$ is incorrectly set equal to $b_1$, and should be set to $b_1$. This change is necessary to obtain a correct energy level diagram as shown in Figure 2a.


(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 $z$ axis and $g$ tensors are colinear. As emphasized by a helpful reviewer, the experimental value of $g_z$ for $1$ is surprisingly low and needs further investigation.

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


(26) Behere, D. V.; Mitra, S. Inorg. Chem. 1980, 19, 992–995. In this work a single-crystal susceptibility measurement was also performed, and the sign of $D$ was determined to be negative.

(27) The manganese ion sits only 0.09 Å out of the plane of the pyrrolic nitrogen atoms in $1$ (see: Boucher, L. J. In Coordination Chemistry of Macrocyclic Compounds; Melson, G. A., Ed.; Plenum: New York, 1979; p 527 and references therein), but is displaced 0.33 (0.34) Å in $2$ (see ref 15).