

High-frequency EPR of octahedral Mn(II) compounds with large zero-field splittings

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The use of HF-EPR to determine large zero-field splittings in distorted octahedral, high-spin d⁵ ions is demonstrated with two Mn(II) coordination polymers, giving detail on both electronic and geometric structure.

The extension of electron paramagnetic resonance (EPR) spectroscopy towards higher operating frequencies (90 GHz and above) has arguably been the most exciting development of the technique in the last decade. In addition to the hugely enhanced spectral dispersion at very high frequencies and magnetic fields, allowing much better resolution of *g*-values, HF-EPR has also allowed the study of multiple unpaired electron species (*S* > 1/2) with large zero-field splittings (ZFSs). Such species are often EPR silent under conventional microwave conditions because the exciting microwave quantum *hν* is much smaller than the ZFS [e.g. *hν* ≈ 0.3 cm⁻¹ at X-band (ca. 9 GHz) and ca. 3 cm⁻¹ at W-band (ca. 90 GHz)].¹ Thus EPR spectra have now been observed for pseudo-octahedral Ni(II),² V(III)³ (both *S* = 1), Mn(III),⁴ Cr(II)⁵ (both *S* = 2), and tetrahedral Fe(II)⁶ (*S* = 2) ions. In this work we demonstrate the use of HF-EPR to probe the electronic structures of two Mn(II) species. The Mn(II), high-spin d⁵ ion is often thought of as essentially isotropic with very small ZFS. Under these conditions its EPR spectra are dominated by the ⁵⁵Mn hyperfine interaction (*I* = 5/2) giving rise to a sextet hyperfine structure centred at *g* = 2.0. However, even slight distortions from a regular octahedral environment can give rise to significant ZFS in Mn(II) and highly complicated EPR spectra. To the best of our knowledge the work in this communication is the first application of HF-EPR to determine the large ZFS in molecular, magnetically dilute *S* = 5/2 species.

The synthesis and characterisation of Mn[O(Pr₂SiOCH₂)₂]₂Cl₂ (**1**) and Mn[O(Pr₂SiOpy)₂]₂Br₂ (**2**) have been reported recently.⁷ Both **1** and **2** have chain polymer structures with Mn(II) ions bridged by siloxypyridine ligands, which coordinate *via* the pendent pyridyl moieties. The Mn(II) ions are well separated (ca. 10 Å in **1**) such that they are magnetically dilute. The local coordination environment around the Mn(II) ions is *trans*-[Mn(pyridyl)₄X₂] [X = Cl (**1**), Br (**2**)].

X-Band EPR spectra of powdered samples of **1** and **2** at room temperature (Fig. 1a and Fig. 2a) are highly complicated and spread over almost the full field range of the electromagnet (0–2 T), which is clear evidence for the ZFSs being comparable to, or larger than, *hν* at this frequency. At Q-band (ca. 34 GHz, 1.2 cm⁻¹) the spectrum of **1** becomes recognisably that of a *S* = 5/2 ion with an approximately axial symmetry (Fig. 1b).⁸ The most intense features are the “perpendicular” transitions arising from orientations of the molecular *z* axis perpendicular to the magnetic field. The separations of these transitions are ca. 0.2 cm⁻¹ and this can be used as a good initial approximation of the axial ZFS parameter, *D*. The Q-band spectrum of **2** contains only four transitions within the available magnetic

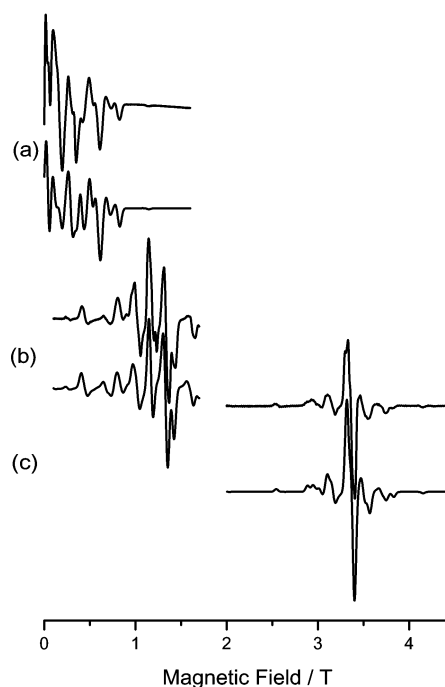


Fig. 1 Room temperature EPR spectra of powdered samples of **1** at (a) X-band, (b) Q-band and (c) W-band: experimental (upper), simulations (lower) with the parameters in the text and isotropic Gaussian linewidths of 400 G at each frequency.

field range (Fig. 2b), which indicates that *D* is much larger for this compound than for **1**.

Room temperature W-band EPR spectra (93 GHz) are in Figs. 1c and 2c. These spectra have a much simpler appearance than the lower frequency spectra, indicative of a “first order” regime where *D* ≪ *hν*. This makes estimation of the *D* values, and therefore the simulation of the data at *all* frequencies much easier. The lineshapes of the “perpendicular” transitions for **1** suggest that the system is not strictly axial, but is slightly rhombic. Simulation⁹ of the spectra of **1** at all three frequencies gives *D* = 0.188(1) cm⁻¹, the rhombic ZFS parameter *E* = 0.011(1) cm⁻¹ (and hence “rhombicity”, λ = *E/D* = 0.06), and *g_{xx}* = *g_{yy}* = *g_{zz}* = 2.00 (Fig. 1).

The W-band spectrum of **2** (Fig. 2c) is complicated by the presence of an impurity¹⁰ in the *g* = 2 region (ca. 3.3 T), but is clearly indicative of a very nearly axial *S* = 5/2 ion. Using the separations of the perpendicular transitions as an initial estimate of *D*, there are good simulations of the spectra at all frequencies with *D* = 0.650(1) cm⁻¹, *E* = 0.0065(5) cm⁻¹ (λ = 0.01) and *g_{xx}* = *g_{yy}* = *g_{zz}* = 2.00 (Fig. 2). The very slight rhombicity (λ) is apparent from the shoulders on the “perpendicular” transitions in the X-band spectrum. Note the similarity in

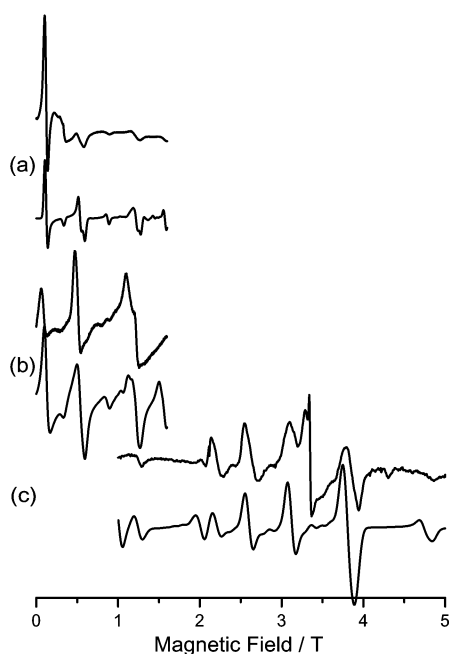


Fig. 2 Room temperature EPR spectra of powdered samples of **2** at (a) X-band, (b) Q-band and (c) W-band: experimental (upper), simulations (lower) with the parameters in the text and isotropic Gaussian linewidths of 300 (X), 500 (Q) and 900 G (W).

appearance of the spectra of **1** at Q-band (Fig. 1b) and **2** at W-band (Fig. 2c): this arises because $D/h\nu$ is similar for the two spectra, and highlights the importance of recording spectra at more than one frequency. There is no evidence for resolution of metal hyperfine or quadrupole structure, and there was no need to include these parameters in the spectrum simulations.

The ZFS in an $S = 5/2$ ion arises from mixing of excited states into the 6A ground state *via* spin–orbit coupling. Thus the much larger axial ZFS, D , in **2** compared to **1** could be anticipated on the grounds of the higher spin–orbit coupling constant of bromide *vs.* chloride.¹¹ Dowsing *et al.*¹² and Jacobsen *et al.*¹³ have observed this previously in *trans*-[Mn(Nhet)₄X₂] (Nhet = N-donor heterocycle; X = Cl, Br, I) although these studies were limited to X- and Q-band frequencies. The significantly larger rhombicity in **1** than in **2** is unexpected on these grounds. Single-crystal X-ray diffraction of **1**⁷ reveals the Mn(II) coordination sphere to be rhombic with Mn–N distances of 2.330(3) and 2.370(3) Å, Mn–Cl distances of 2.4687(9) Å, and N–Mn–N bond angles of 84.69(9) and 95.31(7)° in the equatorial plane. Thus the approximate C_{2h} local symmetry with respect to the MnN₄Cl₂ coordination sphere is consistent with the rhombic EPR symmetry, and the principal axis of the ZFS tensor is expected to be parallel to the Cl–Mn–Cl vector. The X-ray structure of **2** has not been determined as suitable single crystals could not be grown. However, the much lower

rhombicity of the EPR parameters of **2** must reflect a local symmetry at Mn(II) that is nearer axial, effectively D_{4h} , *i.e.* a more regular arrangement in the MnN₄ plane with N–Mn–N angles much nearer to 90° and/or more similar Mn–N distances.

In summary, we have shown the use of HF-EPR to record “first order” powder EPR spectra of **1** and **2**. This simplifies the simulation and interpretation of the spectra at all frequencies considerably. In addition to the electronic structural information, the spin-Hamiltonian parameters obtained give symmetry information. This demonstrates the sensitivity of EPR to the site symmetry of paramagnets and this can be invaluable when it is not possible to obtain an X-ray crystal structure and the paramagnetism precludes use of NMR spectroscopy.

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- 9 The simulated spectra are iteratively fitted by eye, using software described in ref. 8 (ch. 16) and based on the spin-Hamiltonian:

$$\hat{H} = \beta B \cdot g \cdot \hat{S} + D[\hat{S}_z^2 - S(S+1)/3] + E[\hat{S}_x^2 - \hat{S}_y^2].$$
- 10 EPR can detect very small amounts of Mn(II) when $|D|$ is small. The sensitivity of detection increases as $h\nu$ increases, hence we do not observe the impurity in significant amounts in the X- or Q-band spectra. The impurity may result from residual starting material, but in any case only amounts to a small percentage of the total signal. The much narrower linewidth of the impurity compared to the resonances from **2** gives it an artificially large significance in relation to its concentration (estimated as <3%).
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