HFEPR Investigation of a $Mn^{III}O_6$-Containing Complex Exhibiting Field-Induced Slow Magnetic Relaxation

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Introduction

The $[Mn\{(OPPh_2)_2N\}_3]$ complex (**1**) has recently been shown to exhibit field-induced slow relaxation of its magnetization [1]. Almost concurrently reported, similar behavior has also been observed in two additional high-spin $S = 2$ Mn^{III}-containing complexes [2,3]. These Mn^{III} compounds belong to a distinct class of mononuclear metal complexes exhibiting properties akin to single molecule magnets (SMM), mainly comprising cobalt and iron complexes. Complex **1** has been previously investigated by SQUID magnetometry and parallel mode X-band EPR spectroscopy, which provided estimates of its zero-field splitting (zfs) parameters [1]. In an effort to further elucidate the underlined electronic factors conferring a SMM behavior to complex **1**, in the work reported herein, spin Hamiltonian parameters of **1** were accurately determined by HFEPR spectroscopy.

Experimental

HFEPR experiments on **1** were performed in the EMR Facility using its 15/17 T SC magnet and both the homodyne and the BWO-based instrument. A crystalline sample of **1** was used "as is". A second, less crystalline sample was carefully ground, mixed with *n*-eicosane, and pressed into a pellet.

Results and Discussion

It was necessary to study the pellet-sample of **1**, since its more crystalline form was strongly oriented (torqued) in the magnetic field. Having assured that the pellet effectively immobilized the crystallites, a standard field vs. frequency two-dimensional map was constructed, using resonances both from the "as is" and the pellet samples (Fig. 1). The "parallel-mode" resonance that had been previously obtained at X-band [1] was also included in the map at 9.33 GHz. The fits using the SPIN software afforded the following spin Hamiltonian parameters at 10 K: $S = 2$, $|D| = 3.917(5)$ cm^{-1}, $|E| = 0.018$ cm^{-1}, $g = [1.994(5), 1.996(4), 1.985(4)]$, $B_4^0 = B_4^2 = 0$, $B_4^4 = 36(17)\times10^{-4}$ cm^{-1}.

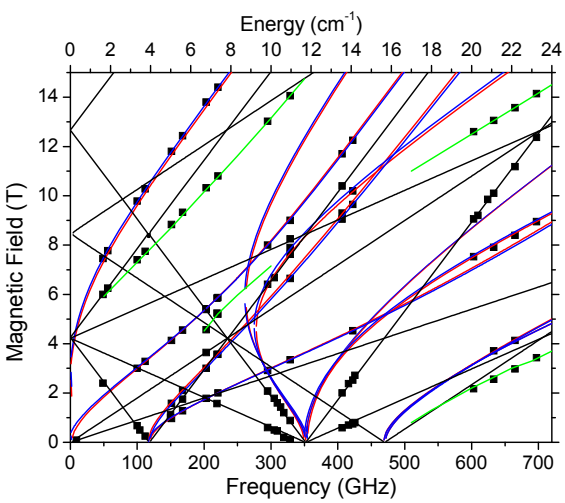

Figure 1. The 2D field vs. frequency map of resonances for **1**. The squares are experimental points, while the lines were drawn using best-fitted spin Hamiltonian parameters, as in the text. Red lines: turning points with $B_0 \parallel x$, blue lines: $B_0 \parallel y$, black lines; $B_0 \parallel z$, green lines: off-axis turning points.

The accuracy of the spin Hamiltonian parameters was confirmed by also simulating single-frequency spectra, which, in addition, made possible to unequivocally establish the negative sign of *D* for **1**.

Conclusions

The HFEPR study of **1** made possible to accurately determine its spin Hamiltonian parameters, including fourth-order zfs. This would allow i) to use these data as a reference for the currently performed quantum chemical calculations on the electronic structure of **1**, ii) to reliably comment on the possible quantum tunneling mechanisms underlying the slow magnetic relaxation of **1**.

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References

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