HFEPR Studies of an Unusual Spin Triplet Six-coordinate Manganese(III) Complex

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Introduction

Six-coordinate (pseudo-octahedral symmetry) complexes of Mn(III) ($3d^4$) generally have spin quintet (S = 2) ground states. Such systems have been extensively investigated by HFEPR at NHMFL.[1] Recently, a six-coordinate Mn(III) complex with a triplet ground state has been reported: $[Tp_2Mn](SbF_6)$ and $[Tp^*_2Mn](SbF_6)$, where Tp = hydrotris(pyrazol-1-yl)borate, Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate.[2] We have been investigating such "scorpionate" complexes of other paramagnetic metal ions, and expanded our study to this unusual system.

Experimental

Both the Mm and Sub-mm Wave Facility and EMR Facility were used in this work. The former employs a range of tunable backward wave oscillators as sources, and a 25-T resistive magnet; the latter uses solid state sources and a 17-T superconducting magnet. Microcrystalline powder samples were loaded under inert atmosphere conditions.

Results and Discussion

HFEPR spectra of $[Tp_2Mn](SbF_6)$ and $[Tp^*_2Mn](SbF_6)$ clearly show the triplet ground state, with zero-field splitting (zfs) much larger, as shown in Fig. 1, than that for other six-coordinate S = 1 metal ion complexes, such as those of V(III).

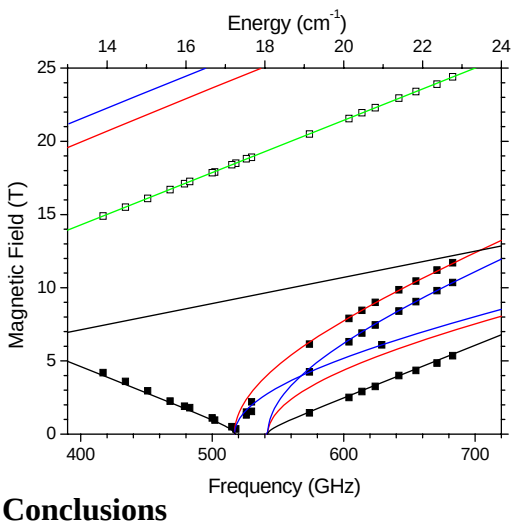

Figure 1. 2D field vs. frequency (energy) map of EPR resonances in polycrystalline $[Mn(Tp)_2]SbF_6$ at 4.2 K in the region of $|D - E|$ and $|D + E|$ zero-field transitions. Full squares are experimental turning points while curves were simulated using following spin Hamiltonian parameters: S = 1, $|D|$ = 17.67 cm^{-1}, $|E|$ = 0.42 cm^{-1}, $g_x = g_y$ = 2.1, g_z = 2.0. Red curves are turning points with B//x, blue curves – B//y, and black curves – B//z. Empty squares correspond to a Mn(II) impurity, which is simulated using S = 1/2 and g_{iso} = 2.00 (green line), and is very useful as a field marker. A positive sign of D was established by simulations of single-frequency experiments (not shown). Analogous experiments and analysis for $[Mn(Tp^*)_2]SbF_6$ gave the following parameters: S = 1, D = +15.90 cm^{-1}, $|E|$ = 0.09 cm^{-1}, g_{iso} = 2.1.

Conclusions

HFEPR is uniquely able to measure accurate spin Hamiltonian parameters, including the very large zfs, of these unusual Mn(III) complexes. The next step will be to combine these results with structural data and ligand-field and density function theory calculations to understand the role of the scorpionate ligands in promoting the S = 1 ground state for Mn(III).

Acknowledgements

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References

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