HFEPR and Luminescence Studies of a Six-coordinate Manganese(IV) Complex

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Introduction

As described in a separate report,[1] we have been investigating six-coordinate Mn(III) complexes with triplet ($3d^4$, $S = 1$) ground states. These are "scorpionate" complexes such as $[Tp_2Mn](SbF_6)$, where Tp = hydrotris(pyrazol-1-yl)borate,[2] and $[(PhB(MeIm)_3)_2Mn](OTf)$,[3] where the ligand is phenyltris(1-methyl-imidazol-2-ylidene)borate and OTf^- is trifluoromethyl-sulfonate. Mn(IV) ($3d^3$, $S = 3/2$) analogs of these can also be prepared and studied by EPR, preferably in its high-frequency and -field version. Mn(IV) complexes are of interest to us for two reasons: this ion has been implicated in photosynthesis,[4] and isoelectronic Cr(III) shows some interesting photochemistry/physics.[5] Despite this, Mn(IV) has been little investigated by either magnetic resonance or luminescence techniques. We have thus begun an effort to correct this deficiency.

Experimental

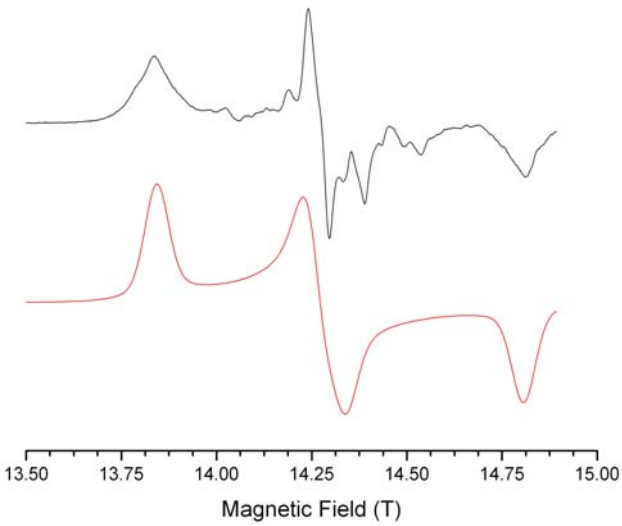

Figure 1. Representative EPR spectrum of polycrystalline $[(PhB(MeIm)_3)_2Mn^{IV}](OTf)_2$ at 400 GHz and 5 K (black trace) and its simulation (red trace) using spin Hamiltonian parameters: $S = 3/2$, $D = 0.225$, $E = 0.075$ cm^{-1}, $g_x = 2.004$, $g_y = g_z = 1.995$. The structure around $g = 2$ is an artifact due to imperfect powder pattern and not reproduced in the simulation.

The EMR Facility with a 17-T superconducting magnet was used in this work. Both microcrystalline powder and acetonitrile frozen solution samples were used for HFEPR studies. Optical spectroscopic measurements were made on powders, single crystals, and fluid solutions.

Results and Discussion

$[(PhB(MeIm)_3)_2Mn](OTf)_2$ exhibits EPR spectra over a wide range of frequencies and temperatures (Fig. 1). Preliminary analysis of the data suggests zero-field splitting of D ~0.225 cm^{-1} and a maximum rhombicity of the zfs tensor (E/D ~ 1/3) The complex exhibits a strong absorption at 500 nm and two strong, broad emission lines at 680 and 820 nm (not shown).

Conclusions

This work is still at a preliminary stage. However, it has been demonstrated that a Mn(IV) "scorpionate" complex can exhibit well-defined EPR spectra in solution and in the solid state, at room temperature as well as at low temperature as well as steady-state luminescence over a wide temperature range. The combined techniques have the potential to explain fully the electronic structure of this system, which may have photochemical/physical applications.

Acknowledgements

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References

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