High Field EPR Study of a Mn(IV) Monomer

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Introduction

Mn(IV) complexes have been in use for some time as building blocks of single molecular magnets SMMs (the very famous Mn12 SMM [1]), therefore it is vital to understand the magnetic nature of a single Mn(IV) ion. In this work we are interested in exploring the magnetic anisotropy associated with a mononuclear Mn(IV). The crystal structure indicates a P 21/c space group, with indications of two different orientations in the unit cell.

Experimental

The magnetic properties of the complex were probed via single crystal high field EPR studies using the heterodyne spectrometer with a 12.5 Tesla superconducting magnet. The sample was mounted on single axis goniometer for both the continuous wave and the pulsed EPR study, with the rotation axis either parallel or perpendicular to the long axis of the crystal.
The orientation and temperature dependence [5 to 70 K] of the EPR spectrum was studied at two available frequencies 240 GHz and 336 GHz. For the pulsed experiment very short pulses were used at low temperature 1.5 K to observe the echo. The samples under study were provided by Muhammad Ali at Jadavpur University, India.

Results and Discussion

Mn(IV) is normally expected to have a small anisotropy [2], however in this sample we observed a relatively large anisotropy of about 5 Tesla (as seen in **Figure 1**). We observe two orientations as predicted by the crystal structure. Furthermore, with pulsed EPR experiments in high frequency quasi-optical spectrometer at low temperature (~1.487K) a spin echo could be observed and we were able to observe the variation of the T_2 times as a function of the magnetic field orientation (inset of Figure 1).

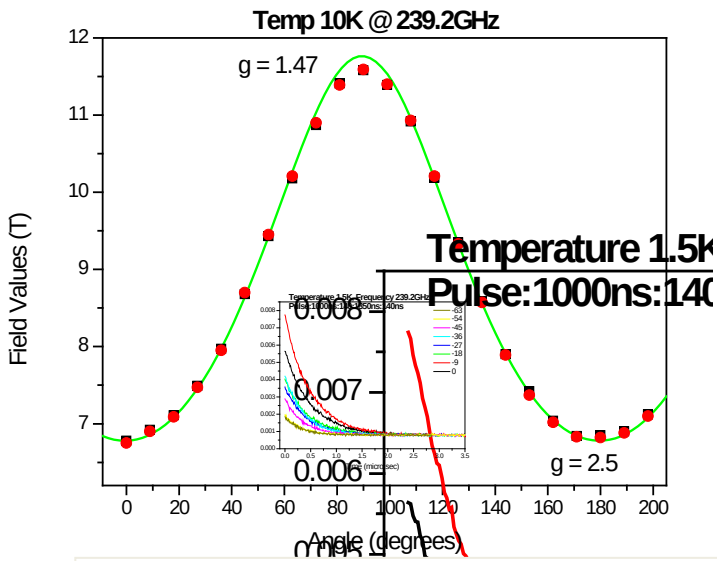

Figure 1: A highly anisotropic behavior is observed when the sample is rotated at 10K, with the initial position of the sample's long axis perpendicular to magnetic field. The inset shows the T_2 decay observed for short applied pulses for the same frequency and orientation.

Conclusions

Mononuclear Mn(IV) is known to exhibit very small magnetic anisotropies (few GHz), however in the current sample we are able to provide evidence of significant anisotropy (approximately 50 GHz), the anisotropy is extremely dependent on the mounting of the sample with respect to the magnetic field). The high frequency EPR was also able to provide insight into the two orientations of monomer present within the unit cell. The origin of the anisotropy requires further investigation.

Acknowledgements

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References

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[2] Duboc, C., *et al.,* Chem. Commun., 2715-2717 (2009).