A High-Frequency EPR Study of a High Spin Fe(II) Complex

Greer, S.M.; Arroyave, A.; Shatruk, M. (FSU, Chemistry); Stoian, S.A. (NHMFL); Hill, S. (FSU, Physics)

Introduction

The phenomenon of spin crossover (SCO) was first observed in an Fe(III) complex in 1931; since then the vast majority of spin crossover complexes reported have contained Fe(II).[1,2] The complex in this report, [(bpte)FeII(NCS)$_2$], **1** (bpte = S,S'-bis(2-pyridylmethyl)-1,2-thioethane and NCS = thiocyanate) shows an incomplete SCO which allows it to be studied using electron paramagnetic resonance (EPR). Relatively few EPR studies have been performed on Fe(II) SCO complexes. The reason for this is two-fold: First the low spin state is S = 0 and second, the high spin S = 2 state has historically been considered "EPR silent". The incomplete spin transition of **1** coupled with the unique facilities available at the National High Magnetic Field Laboratory, permits us to study this partial SCO complex with EPR.

Fig. 1. Crystal structure of **1**.

Experimental

A series of high-field EPR measurements was conducted on a single crystal of **1** using a Quantum Design Physical Property Measurement System and accompanying 7 T magnet at the NHMFL. Additional measurements were performed on a ground solid sample of **1** using the homodyne, quasi-optical EPR instrument outfitted with a 15/17 T superconducting magnet of the EMR facility.[3]

Results and Discussion

A series of EPR spectra of **1** were recorded at multiple frequencies, and the observed resonance fields are plotted versus the applied frequency (Fig. 2). The lines in Fig. 2 correspond to the transitions resulting from a model Hamiltonian fit to the experimental data. The model Hamiltonian shows a strong rhombic component, which is formally allowed in the C2 point group of **1**.

Single crystal EPR spectra recorded at 251.1 GHz with the plane of rotation parallel to the applied magnetic field are shown in Fig. 3. By combining the information obtained in Figs. 2 and 3 we can place the magnetic anisotropy tensor onto the molecular frame of **1**.

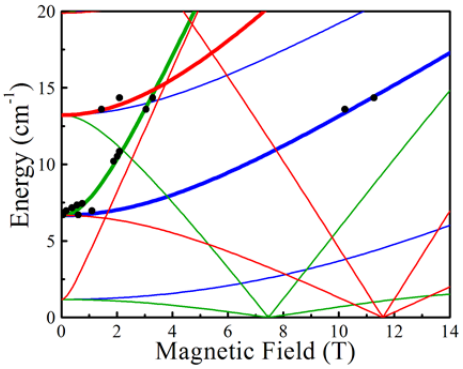

Fig. 2. Observed resonance positions (black) along with model Hamiltonian transitions with observed transitions shown in bold.

Conclusions

1 was found to have a significant rhombic component to its magnetic anisotropy.

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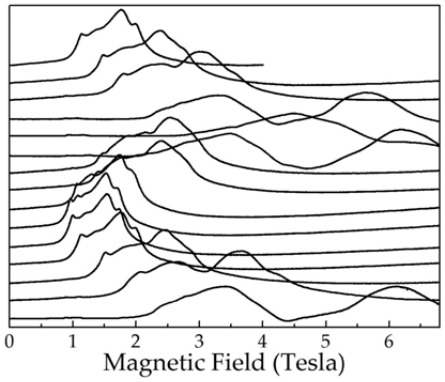

Fig. 3. Single crystal EPR spectra at varying angles rotated with the magnetic field applied perpendicular to the rotation axis.

References

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