Giant Ising-type Magnetic Anisotropy in Trigonal Bipyramidal Ni(II) Complexes

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Introduction

High-field, high-frequency electron paramagnetic resonance measurements performed on a single crystal of $[Ni(Me_6tren)Cl](ClO_4)$ (**1**) reveal a giant uniaxial magnetic anisotropy with an experimental D_{exp} value [zero-field splitting (zfs) between the $M_S = \pm 1$ and $M_S = 0$ components of the ground spin state $S = 1$] estimated to be between -120 cm^{-1} and -180 cm^{-1} [1]. Theoretical studies shows that, for an ideally trigonal Ni(II) complex, the orbital degeneracy leads to a first order spin-orbit coupling that results in a splitting of the $M_S = \pm 1$ and $M_S = 0$ components of *ca.* -600 cm^{-1}. In spite of the Jahn-Teller (JT) distortion that removes the ground term degeneracy and reduces the effects of the first order spin-orbit interaction, the *D* value remains very large. A good agreement between theoretical and experimental results (theoretical D_{th} between -100 cm^{-1} and -200 cm^{-1}) is obtained [1].

Experimental

Angle-dependent, single-crystal high-field EPR measurements were carried out on **1** in a 31 T, wide bore (50 mm) resistive magnet at the DC field facility in Tallahassee. A Millimeter Vector Network Analyzer and several different multipliers were used as a microwave source and detector.

Results and Discussion

The extreme zfs of this compound precludes detection of the usual $M_S = \pm 1$ to $M_S = 0$ transitions that enable a straightforward and precise evaluation of D_{exp}. However, by rotating the applied magnetic field into the hard plane ($\perp$ to easy-axis), one can observe nominally forbidden transitions within the $M_S = \pm 1$ doublet, as seen in **Figure 1**. The JT distortion breaks the trigonal symmetry of **1**, giving rise to a rhombic anisotropy, *E*, as seen from the clear zero-field intercept (= 2*E*) of the data in the figure. Although the local trigonal symmetry is broken, the average crystallographic symmetry remains trigonal, i.e., the JT distortion gives rise to three differently oriented molecules – hence the observation of more than one EPR signal (**A** and **B** resonances). Fits to the two resonance branches enable an estimate of D_{exp}.

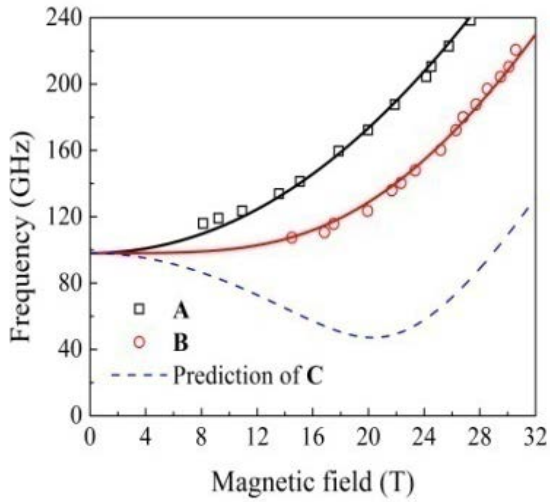

Figure 1. EPR peak positions observed with the field aligned in the hard plane of the **A** (black squares) and **B** (red circles) molecules. The solid lines are fits to the data; the dashed line represents the predicted positions of the EPR transitions associated with the **C** molecules.

Conclusions

Theory combined with EPR results and structural analysis at 10 K lead to the important conclusion that the JT effect only weakly distorts the structure of complex **1**. As a consequence a giant axial anisotropy parameter is found, resulting from a non totally quenched orbital angular momentum.

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References

[1] Ruamps, R., *et al.*, J. Am. Chem. Soc. (undergoing revisions).