EPR Studies of a Mononuclear Co(II)(terpy)Cl_2 Single-Molecule Magnet

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Introduction

There is a great interest in the study of single-molecule magnets (SMMs) because of their potential application in molecular spintronics devices and their fascinating quantum properties. SMMs represent discrete molecular species that can retain a magnetic moment after removal of an applied magnetic field. The associated barrier to magnetization reversal usually originates from the action of negative uniaxial anisotropy (*D*) on a large spin ground state. SMMs were initially limited to multi-nuclear transition metal clusters. However, molecules containing a single lanthanide ion have recently been shown to exhibit slow magnetic relaxation at low temperature [1]. In these monometallic SMMs, the highly anisotropic ground state is generated by strong spin orbit coupling. By exploiting the inherent magnetic anisotropy of a high-spin cobalt(II) ion (S = 3/2), enhanced by controlling the metal coordination environment, it has been possible to realize SMM behavior in the Co(II)(terpy)Cl_2 complex (**1**). Preliminary micro-SQUID measurements show hysteresis at temperature below 0.3 K confirming SMM behavior.

Experimental

Constrained-powder EPR data were collected at 5 K in the EMR facility using a transmission probe and a 17 T superconducting magnet. High-frequency microwaves (50-430 GHz) were generated by a phase-locked Virginia Diodes solid-state source followed by a chain of multipliers. Preliminary high-field single-crystal measurements are also included in this report.

Results and Discussion

Powder EPR measurements provide a way to ascertain the effective *g*-anisotropy associated with the ground state Kramers doublet, as seen in **Figure 1**. The extreme spread in g_{eff} from 1.35 to nearly 8.0 indicates a considerable anisotropy. Single-crystal high-field measurements were also performed in an effort to look for evidence of the upper Kramers doublet. This approach has proven successful in the study of other anisotropic Co(II) complexes [2]. One of the tell-tale signatures is the deviation of the ground state Kramers resonance branches from linearity. The black data points in Figure 1 clearly lie on a curve; the dashed line represents the linear portion of the best fit 2nd-order polynomial. These measurements were performed in late Dec. 2012. Consequently, the results are still being analyzed.

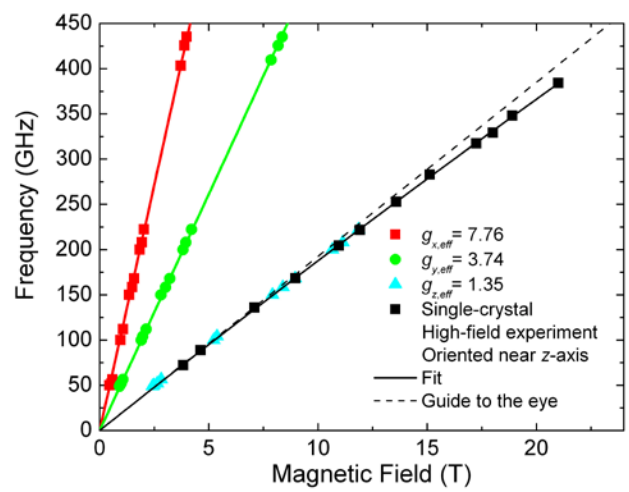

Figure 1. Powder and single-crystal EPR data for Co(II)(terpy)Cl_2 collected at ~5 K (see main text).

Conclusion

EPR studies have been performed on Co(II)(terpy)Cl_2, revealing significant *g*-anisotropy associated with the ground state Kramers doublet. The components of the effective *g*-tensors vary from 1.31 to 7.89. From initial analysis of single-crystal high-field/frequency EPR data, there is a curvature in the plot of frequency versus field that may be used to estimate the location of the upper Kramers doublet.

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References

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[2] Zadrozny, J., *et al*., Chem. Commun., **48**, 3927-3929 (2012).