High-Field EPR Studies of the Mononuclear $[Co(II)(SPh)_4]^{2-}$ Single-Molecule Magnet

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Introduction

Single-Molecule Magnets (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 ($D < 0$) on a large spin ground state. Therefore, most work in this field has focused on multi-nuclear transition metal clusters with the goal of achieving high-spin ground states. However, recent work has demonstrated that SMM behavior can be realized in mononuclear species with relatively small spin values, but with strong spin-orbit anisotropy. High-field/frequency EPR represents an essential tool for determining the anisotropy in these compounds, due to the very large zero-field energy splittings that are generated by the strong spin-orbit coupling.

Experimental

Angle-dependent, single-crystal high-field EPR measurements were carried out on $[Co(SPh)_4]^{2-}$ (**1**) in a 35 T, narrow bore (32 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

Magnetization measurements of this compound have been previously reported [1]. However, the obtained D value (70 cm^{-1}) is not consistent with the barrier to magnetization reversal (20 cm^{-1}) determined from ac susceptibility measurement. Thus, high-field, single-crystal EPR measurements were performed in order to independently evaluate the D parameter. Representative high-field EPR spectra of **1** are shown in **Figure 1**. These experiments were performed with the field applied in the hard plane of the molecule. The best simulation was achieved with $D = -79$ cm^{-1}, while fixing $E = 0$ and $g = 2.57$. The obtained D value is in good agreement with the previous magnetic measurements ($D = -70$ cm^{-1}).

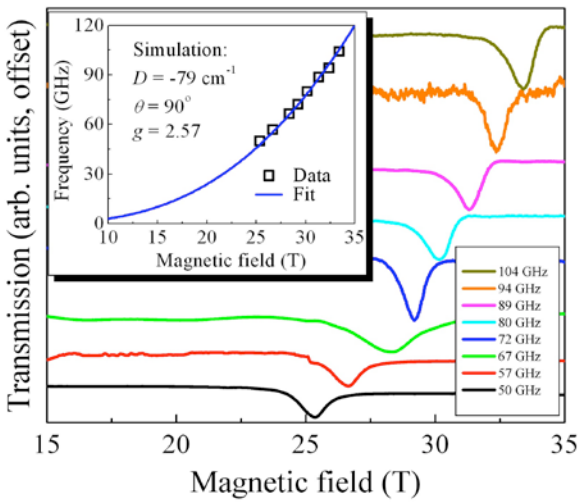

Figure 1. Hard plane high-field EPR spectra for **1**, at a temperature of 1.3 K. The inset shows the frequency dependence of the resonance position, together with the corresponding fit to the data and the obtained parameters.

Conclusions

High-field EPR studies have been performed on $[Co(SPh)_4]^{2-}$ confirming a previously reported D value determined from magnetic measurements [1]. Therefore, the 20 cm^{-1} barrier evaluated from ac susceptibility studies suggests that the low temperature slow relaxation in this compound does not does not involve the usual over-barrier Arrhenius mechanism.

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References

[1] Zadrozny, J.M., *et al.*, J. Am. Chem. Soc., **133**, 20732-20734 (2011).