Large Zero-Field Splitting in the Tetrahedral Complex $[Co(SPh)_4]^{2-}$

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Introduction

Recent discoveries have shown that mononuclear transition metal complexes can display single-molecule magnet behavior under an applied dc magnetic field as a result of large, negative zero field splittings.[1,2] Further progress showed that such an observation can be made under zero applied dc field if the spin is half-integer, in accordance with Kramers' theorem. This latter concept was demonstrated with the $(Ph_4P)^+$ salt of $[Co(SPh)_4]^{2-}$, which possesses an effective spin reversal barrier, U_{eff}, of 21(1) cm^{-1}.[3] Of particular interest here is the fact that the reported D values ($D \approx -70$ cm^{-1})[3,4] indicate a theoretical energy requirement for spin reversal that is greater ($U_{calc} = 2D = 140$ cm^{-1}) than the observed value. A critical eye toward the initial D values, obtained from either magnetization fitting,[3] which often yield imprecise results, or the original X-band EPR spectrum, which features nearly vanishing signals,[4] suggests that the disagreement between U_{eff} and U_{calc} is due to an incorrect assessment of the magnitude of D. To resolve this discrepancy, High-Field EPR was applied.

Experimental

High-frequency EPR measurements on single crystals of $(Ph_4P)_2[Co(SPh)_4]$ were performed in a spectrometer that enabled in-situ rotation of the sample about a fixed axis.[6] The magnetic field was generated by a 36 T resistive magnet at the National High Magnetic Field Laboratory at FSU, Tallahassee. Variable-frequency (49.92-104.16 GHz) and variable-temperature measurements were conducted with the field aligned nearly orthogonal to the molecular z-axis.

Results and Discussion

The EPR spectrum of **1** reveals a single resonance which intensifies with decreasing T, indicating that the resonance corresponds to a ground state transition. Further, at 1.3 K this resonance shifts to higher fields with higher applied microwave frequencies (see **Figure 1**). The field and frequency dependences of the observed resonance were successfully simulated with the Hamiltonian $\hat{H} = D\hat{S}_z^2 + \mu_B g \boldsymbol{S} \cdot \boldsymbol{H}$, revealing a D value of -79 cm^{-1}.

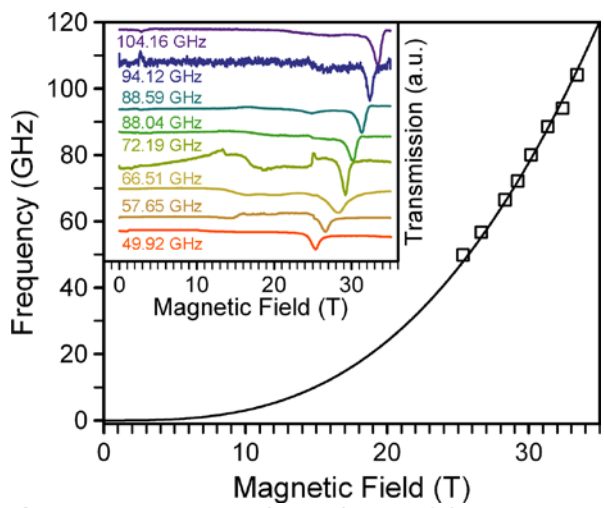

Figure 1. Frequency dependence of the intrakramers resonance and simulation with $D = -79$ cm^{-1} and $g = 2.57$. Inset: Variable frequency EPR spectra of **1** at 1.3 K.

Conclusions

The determined D value is in the range of the D values obtained by X-band EPR and magnetometry, indicating that the discrepancy between the magnitudes of the theoretical and experimental spin reversal barriers is not due to errors in the determination of D. Importantly, the D value reported here is larger than those determined via magnetometry and X-band EPR. These results highlight the utility of HF-EPR in the quantitative determination of magnetic anisotropy in mononuclear single-molecule magnets.

Acknowledgements

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References

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