High-Frequency and -Field EPR of a Co^{II}-Y^{III} Single-Molecule Magnet with Positive Axial Zero-Field Splitting

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Introduction

Single-Molecule Magnets (SMMs) have been suggested for applications in molecular spintronics, ultra-high density magnetic information storage, quantum computing at molecular level and magnetic refrigeration. Until recently, SMMs were based on polynuclear clusters characterized by a large spin number *S*. Bolstered by recent reports of mononuclear metal complexes having similar SMM properties, we have synthesized a binuclear complex $[Co^{II}(\mu\text{-L})(\mu\text{-OAc})Y^{III}(NO_3)_2]$ (**1**) where H_2L = N,N',N"-trimethyl-N,N"-bis(2-hydroxy-3-methoxy-5-methylbenzyl)diethylenetriamine (Fig. 1). Since Y^{III} is diamagnetic, the magnetic properties of that complex correspond to those of the mononuclear Co^{II} which is in a high-spin (S = 3/2) state, and they indicate SMM behavior. Only two examples of mononuclear Co^{II} complexes with $D > 0$ exhibiting SMM behavior have been reported (with either pseudotetrahedral or octahedral rhombic geometries) and none of them was measured by HFEPR [1]. The purpose of the EPR study was to confirm the (positive) sign of the zero-field splitting (zfs) of the Co^{II} ion, and estimate its rhombicity.

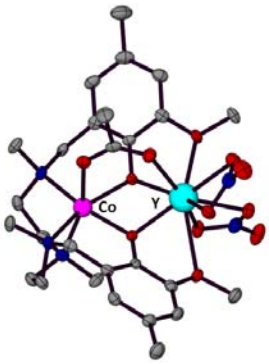

Figure 1. A perspective view of the structure of **1**.

Experimental

The EMR Facility at the NHML Tallahassee was used including its 15/17 T SC magnet.

Results and Discussion

Complex **1** produced a strong EPR response, which is typical for (quasi)octahedral high-spin Co^{II} (Fig. 2). The zfs in such spin systems is too large to be determined by HFEPR but its magnitude was independently measured by Inelastic Neutron Scattering (INS), and estimated by magnetometry. The zfs parameters were then used to simulate the HFEPR spectra in case of both positive, and negative sign. The results point unequivocally at the positive sign, and the rhombicity of the zfs up to $|E/D| \sim 0.09$.

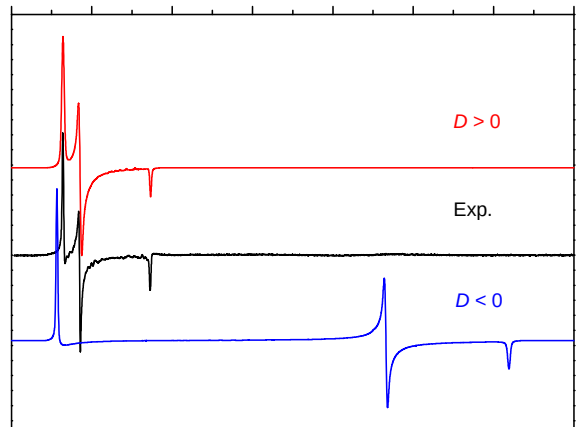

Figure 2. HFEPR spectrum of **1** at 5 K and 101.2 GHz (black trace). The colored traces were simulated using the magnitude of *D* obtained by INS (47.6 cm^{-1}), while adjusting $|E/D|$ to 0.09, and (intrinsic) *g* values to: $g_{||} = 2.150$, $g_{\perp} = 2.495$.

Conclusions

The combination of HFEPR measurements with dc and ac magnetic susceptibility, INS and *ab initio* quantum computing has demonstrated that in **1**, with an easy-plane anisotropy ($D > 0$), the spin-phonon relaxation does not take place through a Orbach thermally activated process but through a dominant optical acoustic Raman process [1].

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References

[1] E. Colacio., *et al*., Angew. Chem. Int. Ed., **52**, 9130-9134 (2013).