EPR Investigation of the Role of Spin-Orbit Coupling/Zero-Field Splitting in the Properties of Vandium(III) Compounds

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Introduction

We recently synthesized a family of mononuclear axially-distorted anions in the form of the salts A[Tp*VX_3] where Tp, Tp* = *tris*(*3*,*5*-dimethyl-*1*-pyrazolyl)borohydride), A = PPN^+, Et_4N^+ or $^nBu_4N^+$ and X= Cl, Br or F. The main motivation is to design new single-ion single-molecule magnets (SI-SMMs) with strongly anisotropic metal ions, in particular V(III), in order to gain insight into the complex interplay between metal ion and ligand effects on the properties of these materials. V(III) ion is known to exhibit very strong ferromagnetic interactions in dimeric species [1] and very large zero-field splitting (zfs) [1,2]. Reduced magnetization studies on the A[Tp*VX_3] family revealed axial zfs parameters as large as D = -30 cm^{-1} and the beginning of an out-of-phase signal in the AC susceptibility data for the PPN^+ salt. However, high-field EPR studies are crucial for precise evaluation of the zfs parameter which is responsible for Ising (or easy-axis) type anisotropy. We measured three compounds in this family to systematically study the changes in anisotropy.

Experimental

Multi-frequency EPR measurements based on a cavity perturbation technique were performed at magnetic fields up to 35 T. The sample was placed in a rotating cavity to obtain the required orientation of the single crystal with respect to the applied magnetic field. The EPR measurements were performed at a temperature of 4.2 K.

Results and Discussion

High-frequency EPR studies were performed on three members of the *S* = 1 V(III) family, i.e., PPN[Tp*VCl_3], TBA[Tp*VCl_3] and PPN[TpVCl_3]. After carefully orienting the magnetic field close to the hard plane of these anisotropic crystals, the shift of the resonance field for various frequencies was recorded. The frequency dependence of the resonance in PPN[TpVCl_3] is shown in Fig. 1 as an example. The inset shows the EPR spectra for selected frequencies up to ~320 GHz. The resonances for all three compounds shift rapidly to higher magnetic fields with increasing frequency. The preliminary analysis of the frequency dependence of these peaks yields significant axial anisotropy (*D*) values in the range from -40 cm^{-1} to -55 cm^{-1} and transverse anisotropy (*E*) between 1.0 cm^{-1} and 2.0 cm^{-1}.

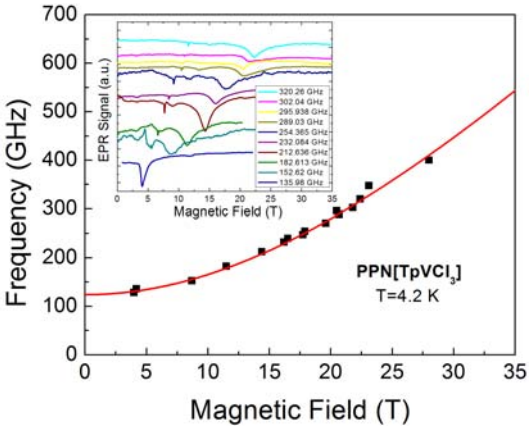

Figure 1: Frequency vs magnetic field plot of the EPR resonances in PPN[TpVCl_3]. Inset shows the EPR spectra for selected frequencies from 135 GHz to 320 GHz with vertical offset.

Conclusions

The high-frequency EPR studies on the A[Tp*VX_3] family clearly provide a more reliable determination of the magnetic anisotropy in these strongly anisotropic SI-SMMs. A detailed analysis will offer more insight into the effect of ligand-field and spin-orbit effects on the measured magnetic anisotropy of the V(III) ions.

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References

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