High-Field EPR Investigation of the Zero-Field Splitting in a Series of Vanadium(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^+ and $^nBu_4N^+$ 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 of 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 [1,2]. Reduced magnetization studies on the A[Tp*VX_3] family revealed very large 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 zero field splitting (zfs) parameter which is responsible for Ising (or easy axis) anisotropy.

Experimental

Multi-frequency EPR measurements based on a cavity perturbation technique were performed in 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 the temperature of 1.6 K.

Results and Discussion

High-field EPR studies were performed on one of the members of the S=1 V(III) family, i.e., PPN[Tp*VCl_3], with the magnet field oriented close to the hard plane of this anisotropic crystal. The transmission spectra for selected measured frequencies up to about 302 GHz are shown in **Figure 1**. We observe three main resonances that shift rapidly to magnetic fields above 25 T within the measured frequency range. The preliminary analysis of the frequency dependence of these peaks yields a significant easy axis anisotropy (*D*) of about -40 cm^{-1}, and a transverse anisotropy (*E*) of ~1.1 cm^{-1}. A plausible origin of three resonance could be the presence of inequivalent V(III) sites, requiring a more detailed analysis.

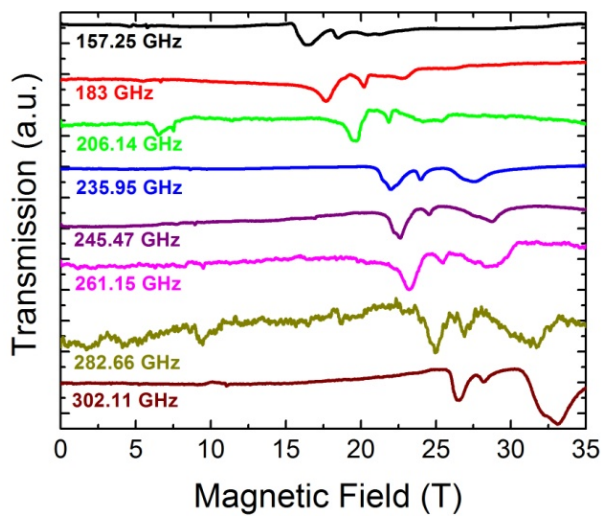

Figure 1: EPR spectra of PPN[Tp*VCl_3] for selected frequencies from 157 GHz to 303 GHz are shown with vertical offset.

Conclusions

The high-frequency EPR studies on PPN[Tp*VCl_3] clearly provide a better understanding of the magnetic anisotropy in these strongly anisotropic SI-SMMs by allowing a reliable estimation of the various spin-Hamiltonian parameters. For a comprehensive understanding of this new family of compounds, the role of the different ligand types in tuning the magnitude of the zfs parameters requires a systematic investigation.

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