# High-Field EPR Studies of a Family of Mononuclear Single-Molecule Magnets Based on V(III)-dicyanide Building Blocks

Saber, M. (Texas A&M U., Chemistry); Thirunavukkuarasu, K. (NHMFL); Dunbar, K. (Texas A&M U., Chemistry); Hill, S. (NHMFL and FSU, Physics)

## Introduction

During the past decade, considerable effort has been directed towards synthesizing single-molecule magnets (SMMs) by increasing the magnetic anisotropy associated with single magnetic ions. In 3d transitional metal complexes, the magnetic anisotropy may be increased by tuning the ligand field and spin-orbit interactions. The vanadium(III) ion is known to participate in strong ferromagnetic super-exchange interactions in dinuclear species and often exhibits very large zero-field splitting parameters with negative axial components $D_z$ of up to -20 $cm^{-1}$ [1-3]. These attributes render V(III) building blocks excellent prospects for bistable systems such as SMMs and single chain magnets, and for molecular magnets in general. Molecules that contain cyanovanadate building blocks are quite rare. Therefore, we recently synthesized and investigated new anisotropic vanadium dicyanide building blocks with acetylacetone (acac) and the salen ligands, N,N'-Ethylenebis(salicylimine) (salen), N,N'-Ethylenebis(methoxysalicylimine) (MeOsalen), and N,N'-Phenylenebis(salicyl-imine)(salphen).

## Experimental

Multi-frequency EPR measurements were performed using a quasi-optical homodyne broadband EPR spectrometer for powdered samples, and a cavity perturbation-based microwave spectrometer for single crystal measurements at magnetic fields up to 15 T. The experiments were performed over the temperature range from 2-10 K, and in the frequency range from 50 to 432 GHz.

## Results and Discussion

The magnetic anisotropies of four compounds of the family of V(III)-cyanide building blocks were estimated using high-field EPR. A spectrum for PPN[(acac)2V(CN)2]•PPNCl•2MeCN (**1**) is shown in Fig. 1 as an example. Fits of the resonance field positions as a function of frequency yield the magnetic anisotropy parameters. The axial zero-field splitting parameter, *D*, was found to lie in the range of +3-6 $cm^{-1}$, and is consistent with the strength of the ligand field of the capping ligands in the VCN building blocks.

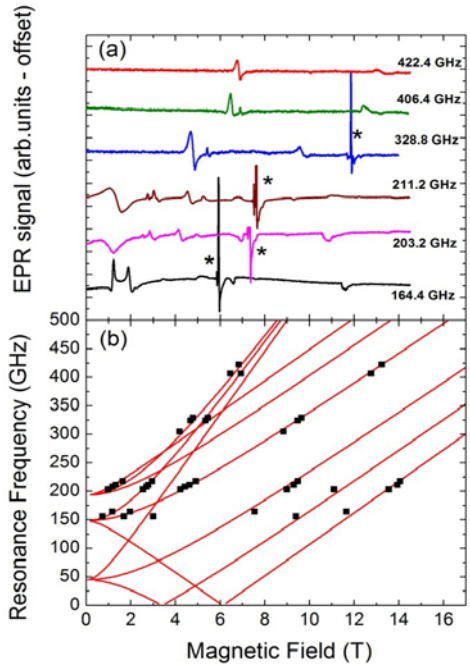


Fig. 1. (a) EPR spectra of a powdered sample of compound **1** for selected frequencies in the range from 164 GHz to 423 GHz. The peaks marked by asterisks (*) are due to impurities in the sample holder. (b) Plot of frequency as a function of the resonance positions for compound **1**. The solid data points are the measured positions while the red lines are the fit using the effective spin Hamiltonian.

## Conclusions

High-field EPR studies were successfully performed for a family of V(III)-dicyanide complexes to accurately determine their magnetic anisotropy parameters. The compounds exhibit moderate easy-plane anisotropies, the strengths of which are consistent with the ligand field strengths associated with the capping cyanide ligands.

## Acknowledgements

A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490, the State of Florida, and the U.S. Department of Energy. Additional NSF grant DMR-1309463 is acknowledged. Work in the KRD group was funded by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. DoE through Grant DE-FG02-02ER45999. KRD also thanks the Robert A. Welch Foundation (Grant A-1449) for summer salary for MS. KT acknowledges financial support from the German Alexander von Humboldt foundation.

[1] Knopp, P., *et al*., Inorg. Chem., **29**, 363-371 (1990).
[2] Tidmarsh, I. S., *et al*., Dalton Trans., 9402-9409 (2009).
[3] Krzystek, J., *et al*., Inorg. Chem., **43**, 5645-5658 (2004).