EPR Studies of a Covalently Bonded Dimer of Triangular Mn_3 Single-Molecule Magnets

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Introduction

A supramolecular aggregate of triangular Mn_3 single-molecule magnets (SMMs), $[Mn_6O_2(O_2CMe)_6(dpd)_3)](I_3)_2$ (**1**), has recently been synthesized. Complex **1** consists of two $[Mn^{III}{}_3O]^{7+}$ triangular units which are covalently linked through a dioximate bridging ligand [1]. The ability to engineer robust couplings between magnetic molecules is of interest from the point-of-view of quantum information processing. Previous studies focused on dimers in which the coupling was crystallographically imposed, resulting in weak intra-dimer hydrogen bonding interactions. The covalent linkage employed here offers the prospect of maintaining the coupling between molecules in solution, enabling their deposition onto surfaces or into field-effect devices.

Experimental

High-field/frequency EPR measurements on a single-crystal of **1** were performed using a cavity perturbation technique and a spectrometer that employs a Millimeter-wave Vector Network Analyzer (MVNA). EPR data were also obtained for a constrained-powder and a solution sample using a homodyne EPR spectrometer, employing a phase-locked Virginia Diodes solid-state source and a bolometer detector.

Results and Discussion

Fig. 1 shows the EPR spectra for a single-crystal of **1** recorded at 137.63 GHz, with the easy-axis of magnetization approximately parallel to the applied field. The pattern of peaks, with one strong low-field peak followed by multiple weaker peaks at elevated temperatures, is typical for a SMM. The shoulder **(x)** originates from a weak exchange coupling between the two Mn_3 units within the dimer [2]. Fig. 2 shows powder and solution spectra of **1**, which are essentially identical, indicating that the supramolecular dimers appear to remain intact in solution and thus their unique properties survive outside of a crystal. We are currently repeating the solution measurements with a more concentrated sample to see if we can confirm the shoulder (**x**) indicative of the exchange coupling within the dimer.

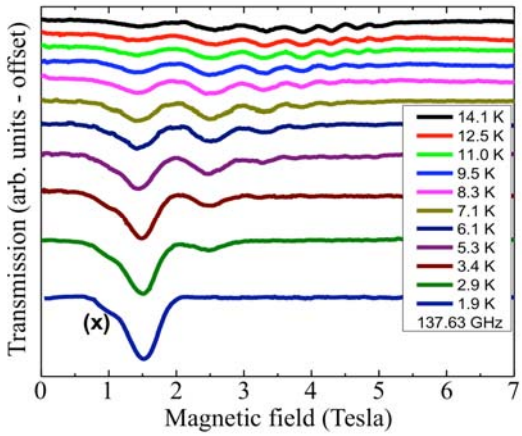

Figure 1. Temperature dependence spectra of **1** recorded for a single-crystal at 137.63 GHz, with the field aligned close to the easy-axis.

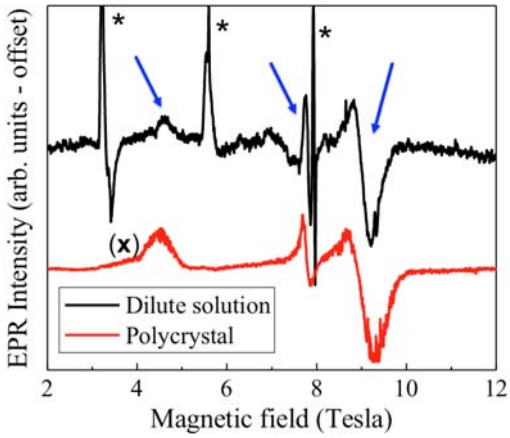

Figure 2. Comparison of the EPR spectra for a polycrystal and a dilute solution of **1** at T = 2.5 K and ~218 GHz. The arrows denote features that are attributed to the dimers; asterisks denote known impurities in the sample holder.

Conclusions

Single-crystal EPR studies of the $[Mn_3]_2$ dimer **1** reveal a weak exchange coupling between the Mn_3 clusters. Moreover, powder and solution spectra are essentially identical, indicating that the supramolecular dimers appears to remain intact in solution so that their unique properties survive outside of a crystal.

Acknowledgements

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References

[1] Nguyen, T.N., *et al.*, J. Am. Chem. Soc., **133**, 20688-20691 (2011).
[2] Hill, S., *et al.*, Science, **302**, 1015-1018 (2003).