EPR Studies of a Mn(III)–Cu(II) Dimer Containing a Jahn–Teller Compressed Mn Ion

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Introduction

The heterobimetallic complex $[Cu(II)Mn(III)(L)_2(py)_4](ClO_4)\cdot EtOH$ (**1**), where L is 2,2′-biphenol, is a rare example of a dimeric [Cu(II)Mn(III)] compound, and the first example to exhibit a Jahn-Teller compressed Mn(III) center [1]. Analysis of high-field and high-frequency EPR, magnetic susceptibility and DFT studies reveal that this interesting complex exhibits antiferromagnetic interactions between the Cu and Mn centers (J = −33.4 cm^{-1}) resulting in an S = 3/2 ground state.

Experimental

Powder EPR data were collected in a transmission-type spectrometer employing a 17 T superconducting magnet. A phase-locked oscillator, in conjunction with a series of multipliers and amplifiers, was employed as a microwave source covering the frequency range from 50 to 600 GHz.

Results and Discussion

At frequencies below 200 GHz (**Figure1** bottom), the spectra exhibit three strong resonance branches that pass through the origin, which represent the x, y and z-transitions within the ground-state Kramers doublet (open red, blue and black circles, respectively). Above 200 GHz, additional resonance branches are evident at low fields (solid black squares and circles). These resonances meet at a finite frequency at zero field, which corresponds to the zero-field splitting between the two lowest Kramers doublets (381±5 GHz). The frequency-dependent EPR data were simulated employing the spin Hamiltonian (1) with S = 3/2, yielding the parameters: D_S = +6.27 cm^{-1}, E_S = ±0.57 cm^{-1}, $g_{S,x}$ = $g_{S,y}$ = 1.97 and $g_{S,z}$ = 1.98.

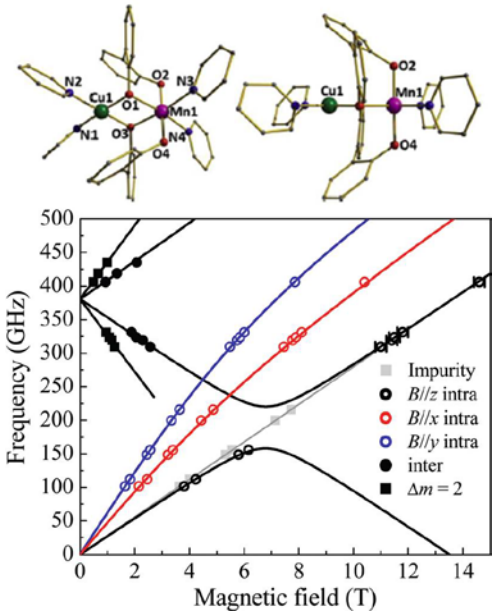

Figure 1. (top) Ortep drawings of complex **1**. (bottom) Frequency versus field powder EPR data for **1** showing intra- (open circles) and inter-Kramers transitions (solid circles); the solid curves represent simulations.

$$\hat{H}_s = \mu_B \vec{B}\cdot\vec{g}_s\cdot\hat{S} + D_s\hat{S}_z^2 + E_s(\hat{S}_x^2 - \hat{S}_y^2) \qquad (1)$$

In these simulations, the magnitude of D_S (axial cluster anisotropy) is well constrained by the zero-field intercept, while the rhombic term, E_S, is constrained by the sizable splitting exhibited by the x (red circles) and y (blue circles) intra-Kramers branches. Projection of the single-ion $D_{Mn(III)}$ value onto the S = 3/2 ground state of the coupled dimer leads to the prediction $D_{Mn(III)} = 0.71D_S$ = +4.45 cm^{-1}, which agrees with magnetic measurements [1].

Conclusions

Spectroscopic studies have been carried out on an interesting antiferromagnetically coupled Cu-Mn dimer that reveals an S = 3/2 ground state experiencing significant easy-plane type magnetic anisotropy, which is consistent with a Jahn-Teller compressed Mn(III) ion.

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References

[1] Berg, N., *et al.*, Dalton Transactions, **42**, 207-216 (2013).