High-Field EPR and Magnetic Studies on a Ferromagnetic Copper Nitrobenzoate Dimer

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Introduction

In recent years, crystal engineering of supramolecular architectures based on organic and/or inorganic molecular building blocks has been rapidly expanding owing to potential applications of the novel and diverse topologies in host-guest chemistry, catalysis, electrical conductivity and magnetism. In one such complex, $[Cu_2(H_2tea)_2(2\text{-nitrobenzoate})_2]\cdot 2H_2O$ (H_3tea = triethanolamine), the dimeric units are joined by hydrogen bonds and arranged in molecular ribbons.

Experimental

Magnetic susceptibility measurements (Fig. 1) were performed at the Wroclaw University using a Quantum Design SQUID MPMSXL-5 magnetometer. High-field EPR spectra (Fig. 2) were recorded on the 17 T instrument of the EMR facility.

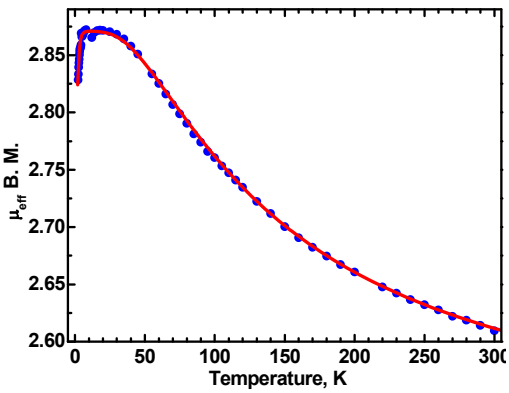

Fig. 1. Effective magnetic moment of the dimer: dots: experimental; line: calculated with J = -100 cm^{-1} and the EPR parameters of Fig. 2.

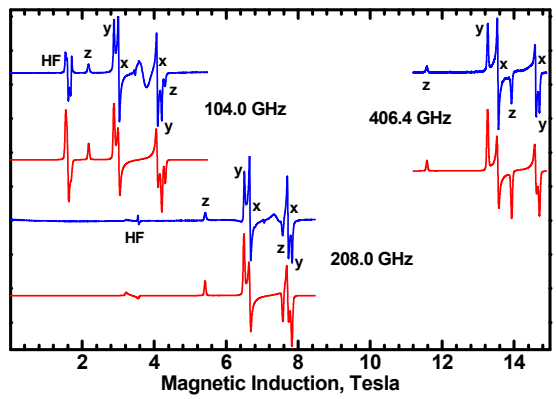

Fig. 2. High-Field EPR spectra: blue: experimental; red: simulated with g_x = 2.060, g_y = 2.060, g_z = 2.303, D = -1.135 cm^{-1}, E= - 0.0430 cm^{-1}.

Results and Discussion

The dimeric complex exhibits relatively strong ferromagnetic exchange with J = -100 cm^{-1} (corresponding to $\hat{\mathbf{H}} = J\hat{\mathbf{S}}_1\hat{\mathbf{S}}_2$). EPR spectra coming from the ground spin-triplet state were interpreted in terms of the spin Hamiltonian

$$\hat{H} = \mu_B \mathbf{B}\cdot\hat{\mathbf{g}}\cdot\hat{\mathbf{S}} + D\,[\hat{\mathbf{S}}_z^2 - 1/3\cdot S(S+1)] + E\,(\hat{\mathbf{S}}_x^2 - \hat{\mathbf{S}}_y^2) \qquad [1]$$

with the parameters given in Fig. 2 caption. High-field EPR allowed determination of the sign of the zero-field splitting (zfs) parameters D and E, which in turn made possible evaluation of the exchange-related contribution to the zfs.

Conclusions

The exchange-related part of zfs was found to be axial (E/D = 0.006) which could be rationalized [1]. The J value calculated by using the Density Functional Theory (DFT) was in a reasonable agreement with the experiment. The results of this work were published [1].

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References

[1] Sharma, R.P., *et al*., New Journal of Chemistry, in print, DOI: 10.1039/C3NJ00736G (2014).