High-Field EPR Studies on a Novel Ferromagnetic Nickel(II) Cubane Complex

D.L. Reger, A. Pascui (U. of South Carolina, Chemistry); J. Jezierska (U. of Wrocław, Poland, Chemistry); A. Ozarowski (NHMFL)

Introduction

Our previous syntheses of metal complexes of *m*-bis[bis(1-pyrazolyl)-methyl]benzene ($\mathbf{L_m}$) resulted in dinuclear systems in which metal atoms are bridged by single-atom anions – halogenides [1] or OH^- [2]. The same ligand produced with Ni^{2+} a tetrameric "cubane" complex $[Ni_4(\mu\text{-}OH)_4(\mu\text{-}\mathbf{L}_{\boldsymbol{m}})_2(DMF)_4](ClO_4)_4$, shown in Fig. 1 (DMF = dimethylformamide), in which ferromagnetic exchange interactions are transmitted *via* the hydroxo bridges [3].

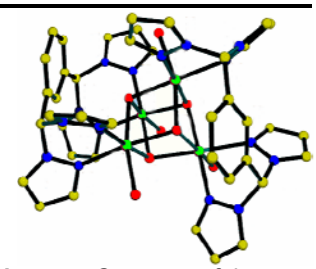

Figure 1. Structure of the complex. Green: Ni, red: O, blue: N, yellow: C.

Experimental

The compound has been characterized by X-ray crystallography (USC) and magnetic susceptibility measurements (UW). High-field and frequency EPR spectra were recorded on the transmission EPR instrument of the NHMFL EMR facility at frequencies ca. 100-432 GHz.

Results and Discussion

The magnetic properties (Fig. 2) were interpreted using a Heisenberg-Dirac-VanVleck Hamiltonian (HDVV) in the form appropriate to the molecular pseudosymmetry,

$$\hat{H}_{HDVV} = -J_1(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_4 + \hat{S}_3\hat{S}_4) - J_2(\hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_3) \quad [1]$$

to which terms expressing the zero-field splitting on the Ni^{2+} ions as well as the Zeeman splitting had to be added to explain the maximum of the effective magnetic moment (Fig. 2). J_1 and J_2 of quite different magnitudes were found, *ca*. 9 cm^{-1} and *ca*. 2 cm^{-1}, respectively. S = 4 is the ground state of the tetranuclear molecule. High-Field EPR spectra due to that state (Fig. 3), which were interpreted in terms of the standard "giant spin" Hamiltonian [2],

$$\hat{H}_{S=4} = \mu_B B(\{\boldsymbol{g}\}\hat{S} + D\,[\hat{S}_z^2 - S(S_i+1)/3] + E(\hat{S}_x^2 - \hat{S}_y^2) \quad [2]$$

allowed determination of the magnitude and sign of the zero-field splitting (zfs) parameters , D = -0.299 cm^{-1}, E = -0.036 cm^{-1}.

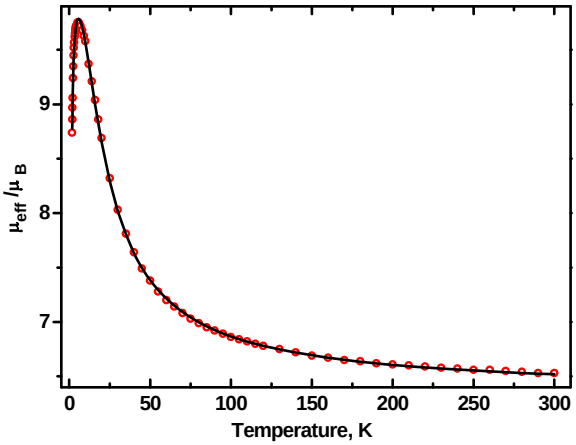

Figure 2. The effective magnetic moment as a function of temperature.
Circles: experimental, solid line: calculated.

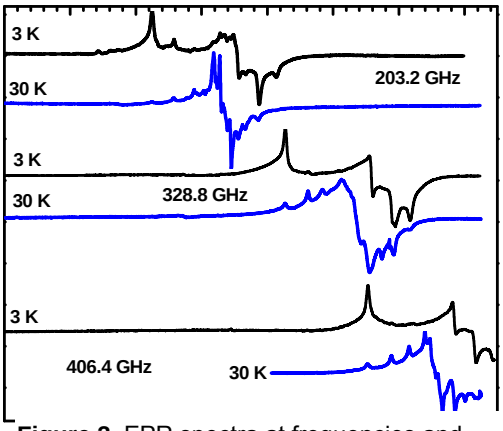

Figure 3. EPR spectra at frequencies and temperatures indicated.

Conclusions

Because of the different geometry of various Ni-O-Ni units, the 6 possible exchange interactions in the tetrameric molecule were divided into 2 groups of 3 equal interactions (see equation [1]). "Broken symmetry" Density Functional Theory calculations were performed which confirmed the inequivalence of the exchange pathways in the system.

Acknowledgements

This work was supported by the NSF through grant CHE-1011736 (DLR).

References

[1] Reger, D.L., *et al*., Inorg. Chem., **51**, 11820-11836 (2012).
[2] Reger, D.L., *et al*., Inorg. Chem., submitted.
[3] Reger, D.L., *et al*., Inorg. Chem., submitted.