Structure and Magnetism of Triangular Copper(II) Hydroxo-Bridged Clusters

A.B. Lysenko, S.I. Vasylevs'kyy, G.A. Senchyk, K.V. Domasevitch, E.B. Rusanov, A.N. Chernega (Kiev U., Ukraine, Chemistry); J. Jezierska (Wroclaw U., Poland, Chemistry); H. Krautscheid (Leipzig U., Germany, Chemistry); A. Ozarowski (NHMFL)

Introduction

Growing interest is observed in recent literature in the "spin frustration" in antiferromagnetic triangular transition metal complexes and in the underlying antisymmetric exchange interactions, also called the Dzialoshinskii-Moriya interaction. Possible applications of the Metal Organic Frameworks (MOFs) containing triangular trinuclear clusters [$Cu_3(\mu_3$-OH)] (Fig. 1) in the areas of gas storage and sorption as well as catalysis are being explored [1]. Such clusters are also part of some biomolecules. Research on three compounds of that class was performed in 2013.

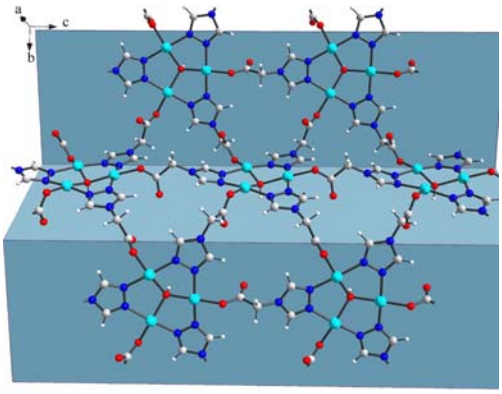

Figure 1. Extended MOF structure consisting of triangular $Cu_3(\mu_3$-OH) motifs.

Experimental

High-field EPR spectra were recorded on the 15/17 T transmission instrument of the EMR facility. Magnetic measurements and the EPR experiments in X and Q frequency bands were performed at the Wroclaw University.

Results and Discussion

Although the ground state of a trinuclear copper(II) complex is S = 1/2, the low-temperature magnetic moment drops below the value expected for one unpaired electron as a result of spin frustration and the antisymmetric exchange interactions [2]. The same phenomena cause reduced Zeeman splitting when the magnetic field is in the triangle plane, which is reflected in the low $g_{effective}$ values found from the EPR spectra. The steep branches marked in red in Fig. 2 correspond to $g_{effective}$ values of 0.9 and 1.0, instead of normally encountered g > 2 for Cu^{2+}.

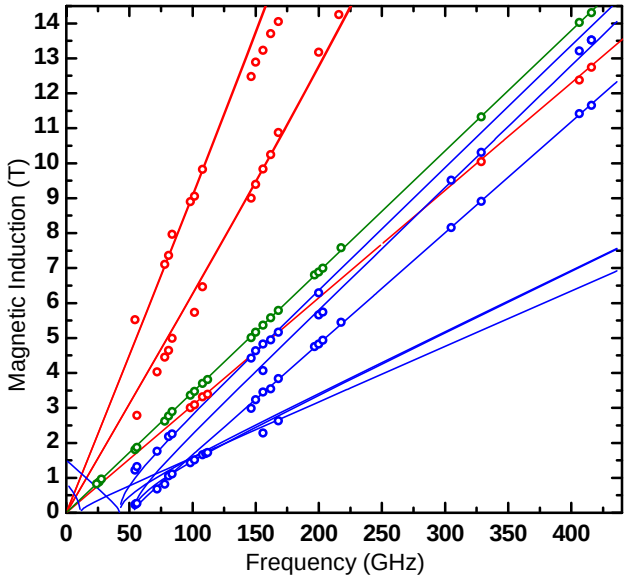

Figure 2. Frequency dependencies of the EPR resonance fields observed for the triangular Cu^{2+} complex [$Cu_3(\mu_3$-OH)(trgly)$_3$(SO_4)]·2H_2O (trgly=1,2,4-triazol-4-yl-acetic acid).

Conclusions

The magnetic susceptibility data and the high-field EPR spectra could be successfully interpreted and the isotropic as well antisymmetric exchange parameters were determined. The Density Functional Theory calculations were also performed to get insight into the isotropic part of the metal-metal interactions. Presence of dinuclear and mononuclear defects in the extended MOF structure was inferred from the high-field EPR spectra [3].

Acknowledgements

Financial support by Deutsche Forschungsgemeinschaft is gratefully acknowledged. We are also grateful to the Ministry of Science and Higher Education of Poland for financial support.

References

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