Design of Cu(II)-MOFs Containing Triangular Hydroxo Clusters Based On 1,2,4-Triazolyl Carboxylate Derivatives

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

Introduction

Metal organic frameworks (MOFs) incorporating trinuclear hydroclusters [$Cu_3(\mu_3\text{-OH})$] have been subject to extensive exploration motivated by multiple possible applications, like gas storage and sorption, catalysis (like peroxidative oxidation of alkanes) and magnetism (*e.g.* to test magnetic exchange models for spin-frustrated systems, or for spin-canted ferro- and antiferromagnetism). Fascinating structure and redox properties make them very attractive models for the active sites of many biomolecules, like the multicopper oxidases. After a successful study on a linear trinuclear complex [1], we now report on a related triangular system (**Figure 1**, inset), which appears to be spin-frustrated.

Experimental

High-field EPR spectra were recorded on the transmission instrument of the EMR facility. Magnetic measurements as well as the X and Q Band EPR experiments were performed at the Wroclaw University.

Results and Discussion

The magnetic susceptibility data are consistent with the antiferromagnetic interactions in the triangular trimer. Anomalously low magnetic moment values (lower than for a single electron, see **Figure 2**) at the lowest temperatures, at which only the S = 1/2 states are occupied are characteristic of a spin-frustrated trimer [2].

Conclusions

The anomalously low magnetic moment and very low $g_{effective}$ value observed in EPR are caused by the spin frustration and by the antisymmetric exchange (Dzialoshinskii-Moriya) interactions [2]. Further research on the present system is in progress.

Acknowledgements

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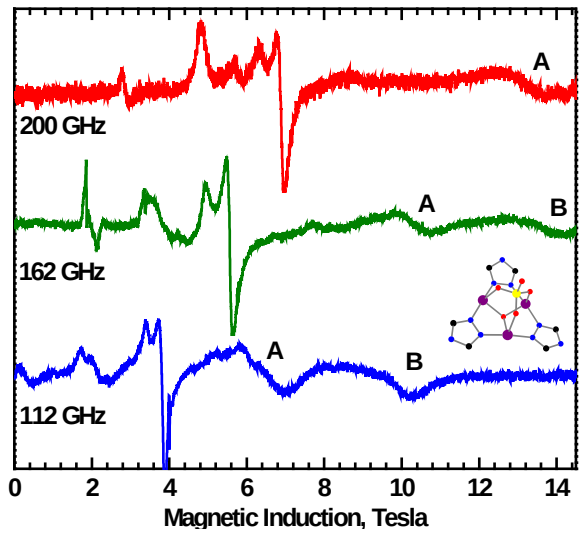

Figure 1. EPR spectra at 3 K of the triangular system [$Cu_3(\mu_3\text{-OH})(\mu_3\text{-SO}_4)$]. The frequency dependence of the resonances marked with A and B indicate $g_{effective}$ values of 1.1 and 0.9, respectively, a result of the spin frustration. The skeleton of the molecule is shown in the inset.

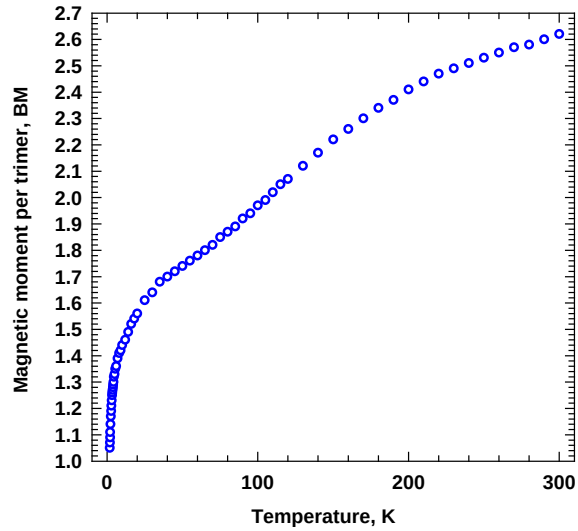

Figure 2. Magnetic moment of the trinuclear system.

References

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[2] Yoon, J., *et al.,* J. Am. Chem. Soc., **126**, 12586-12595 (2004).