Halide and Hydroxide Linearly Bridged Bimetallic Metal(II) Complexes: Trends in Strong Antiferromagnetic Superexchange Interactions

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Introduction

One of the dominant themes in transition metal chemistry, for more than 50 years, are the magnetic superexchange interactions [1]. Extensive work has shown that magnetic exchange between two metals bridged by small ligands such as carboxylate, hydroxide, alkoxide, halide, etc., correlates with the type and geometry of the metal centers and the bridging ligands. The study of magnetic exchange interactions is fundamentally important as it impacts on materials science (molecular magnets) and the active sites of many metalloenzymes.

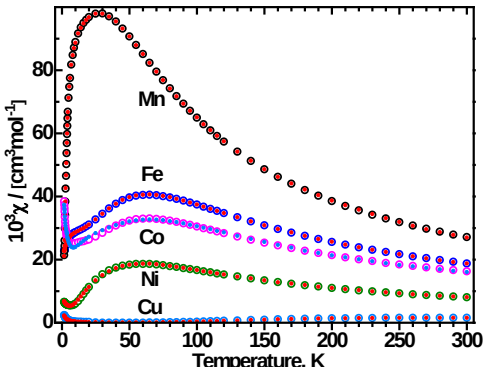

Figure 1. Magnetic susceptibility data. Circles: experimental; dots: calculated.

Experimental

Complexes of general formula $[M_2(\mu\text{-}F)(\mu\text{-}\mathbf{L}_m\mathbf{*})_2]A_3$ were prepared, where M is Mn(II), Fe(II), Co(II), Ni(II), Cu(II), $\mathbf{L}_m$* is the new ditopic ligand *m*–bis[bis(3,5–dimethyl–1–pyrazolyl)methyl]benzene)], and the anion A^- is ClO_4^- or BF_4^- [1,2]. 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

Exchange integrals were determined from the magnetic susceptibility data (**Figure 1**) and were successfully reproduced by theoretical calculations using the Density Functional Theory (DFT). Zero-field splitting (zfs) parameters were found from the EPR spectra. Interpretation of the experimental data for complexes of metals other than Cu required usage of a spin Hamiltonian expressed in spin operators of individual metal ions [2].

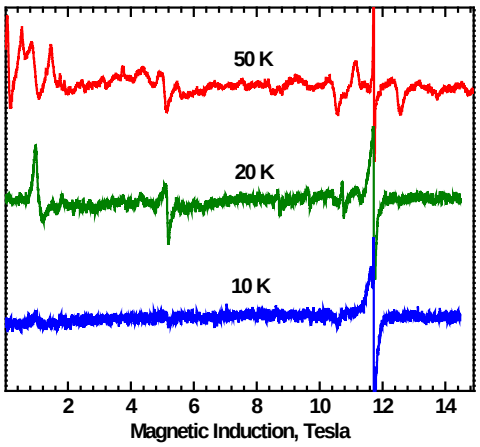

Figure 2. EPR spectra (328.8 GHz) of $[Fe_2(\mu\text{-}F)(\mu\text{-}\mathbf{L}_m\mathbf{*})_2](BF_4)_3$.

Conclusions

In the series of the Cu^{2+} complexes a very strong dependence of the exchange interactions on the bridging atom was seen, which increased from 340 cm^{-1} for F^- to 950 cm^{-1} for the Br^- bridge [1]. Rarely encountered d_{z^2} ground state of Cu^{2+} was observed. Detection of an EPR spectrum of a dinuclear Fe^{2+} complex may be the first of a kind (**Figure 2**) [2]. The zero-field splitting in the latter system is dominated by the zfs on individual Fe^{2+} ions. DFT calculations in this work reproduced the experimental *J* values semi-quantitatively and allowed identification of the orbital interactions which contribute to the exchange interactions. In particular, the trend observed in the Cu complexes with F^-, Cl^-, OH^- and Br^- bridges could be well explained [1].

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References

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