Ligand Design for Molecular and Supramolecular Control of the Structures of Metal Complexes: Investigations of Unusual Magnetic and EPR Properties

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Introduction

Dinuclear exchange-coupled metal complexes are important in many fields of science, including inorganic chemistry, materials and biochemistry. We have been able to synthesize the first series of such complexes with linear or nearly linear bridges consisting of a single-atom anion. These complexes show unique EPR and magnetic properties. They also hold the dinuclear structure in solution [1].

Experimental

All new complexes have been fully characterized, including in the solid state by X-ray crystallography and magnetic properties [2] and in many cases by NMR [1]. 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 first extensive series of metal complexes containing single hydroxide bridges with large M-O-M angles, ranging from 141° to exactly 180°, of the formula $[M_2(\mu\text{-OH})(\mu\text{-}\mathbf{L})_2](ClO_4)_3$, **L** = *m*-$[CHpz_2]_2C_6H_4$, [M = Cu(II) (complexes 3, 6 in Fig. 1), Fe(II), Co(II) (complexes 2, 4 in Fig. 2),] have been prepared. The cobalt(II) complexes show moderate antiferromagnetic coupling, $-J$ = 48-56 cm^{-1}. The copper(II) complexes show strong antiferromagnetic coupling, $-J$ = 555-808 cm^{-1}. The exchange interactions were found to increase with the linearity of the Cu-O-Cu bridge and the d_{z^2} character of the copper(II) ground state, a conclusion supported by the Density Functional Theory (DFT) calculations. These complexes show interesting variable temperature NMR spectra that also yield $-J$ values [1].

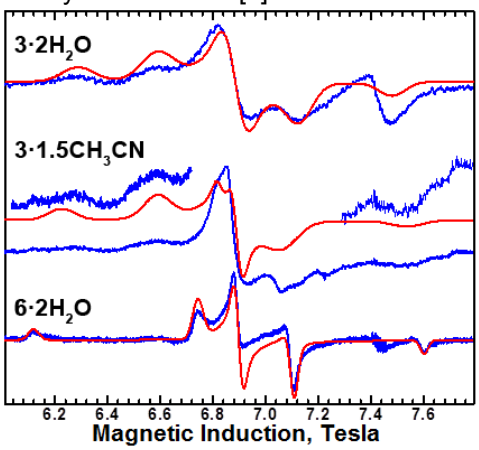

Figure 1. EPR spectra of the copper complexes

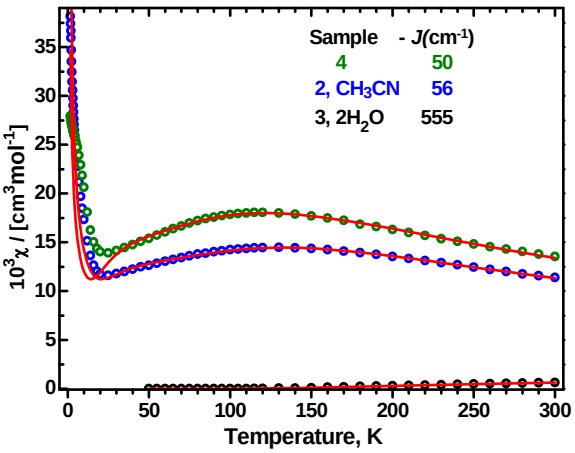

Figure 2. Magnetic susceptibility of the cobalt complexes (**2** and **4**) compared to the copper complex (**3**).

Conclusions

The EPR parameters of the copper(II) complexes show strong "rhombicity," which could be qualitatively understood by considering the interactions between the ground state of one copper(II) ion with the excited states of the other [2].

Acknowledgements

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References

[1] Reger, D.L., *et al.*, Inorg. Chem., **52**, 12741-12748 (2013).
[2] Reger, D.L., *et al.*, Inorg. Chem., submitted.