Determination of the Sign of the Zero-Field Splitting in Binuclear Copper Carboxylates from High-Field EPR

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Introduction

Copper acetate monohydrate was the first binuclear transition metal complex ever studied by EPR in the famous paper by Bleaney and Bowers.[1] The wide group of antiferromagnetic binuclear complexes in which copper atoms are bridged by four carboxylato bridges in a 'paddlewheel' arrangenment[2] has played an important role in the history and theory of the molecular magnetism. The sign of the zero-field splitting parameter D has far-reaching implications to the theory of anisotropic exchange interactions,[3] but could not be experimentally determined from traditional EPR spectra. Reports of positive D exist in the literature.[3]

Experimental

High-field and frequency EPR spectra of copper acetate monohydrate (**1**) and its pyrazinate analogue (**2**) were recorded on the transmission EPR instrument of the NHMFL EMR facility at frequencies 406-432 GHz and at temperatures 50-80K.

Results and Discussion

At very high fields and at low temperatures the Zeeman interaction is comparable to the thermal energy *kT* and different intensity patterns in EPR spectra of S>1/2 states are observed depending on the sign of zero-field splitting parameters. In the high-field EPR spectra of single-crystals of **1** and **2**, the low-field line due to transitions within the triplet spin state was found to be stronger than the high-field line at the molecular orientation '**Z**', while it was less intense at the molecular orientations '**X, Y**'. Such intensity pattern is consistent with the negative sign of D.

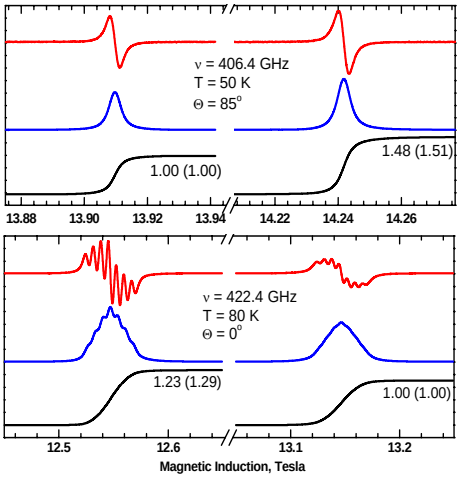

Fig. 1. Single-crystal EPR spectra of **2**. Molecular orientations are designated by the angle Θ. The red, blue and black traces are the original EPR spectra, their first and second integrals, respectively. The measured and calculated (in parentheses) relative intensity is shown.

Conclusions

The determination of the sign of D was possible thanks to the high-field EPR technique and allowed extract the exchange-related contribution to D from the experimental D values. That contribution was found, contrary to literature reports, to be comparable in sign and magnitude to the dipole-dipole interaction. This result is important for the theory of anisotropic metal-metal exchange interactions in polynuclear transition metal complexes.[4]

Acknowledgements

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References

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