High Field EPR Study of a New Cu(II) Acetate Chain Complex

V. Ramachandran, J. Wang (FSU, Chemistry); J. van Tol, A. Ozarowski (NHMFL); N.S. Dalal (NHMFL & FSU, Chemistry); L. Zhu (FSU, Chemistry)

Introduction

A new polymeric chain complex containing the unique binuclear Cu(II) acetate paddlewheel units linked by a 1,4-functionalized 1,2,3-triazole ligand [Fig. 1 Inset: 1,1'-(pyridine-2,6-diylbis(methylene))bis (1,2,3-triazole-4,1-diyl))dimethanol], [1] is studied using variable frequency (9 – 306 GHz) EPR. The two Cu^{2+} ions are bridged by four acetate groups in each Cu(II) acetate unit. The ligand bridges two neighboring Cu(II) acetate dimer units (each Cu^{2+} center coordinates with a triazole nitrogen atom, see Fig. 1) resulting in a linked chain that runs through the crystal structure in a spiral-like fashion. An exchange coupling of ~ -350 cm^{-1} between the two Cu^{2+} centers of each dimer was determined from magnetic susceptibility data. The sign of the zero-field splitting parameter D in this complex is determined using HF-EPR.

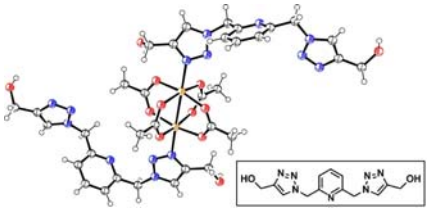

Figure 1: Molecular structure of the Cu(II) acetate chain; only one link is shown. (Atom color code: Cu-Yellow; O-Red; N-Blue; C-Empty circles; H-Not shown). Inset: Ligand molecule used.

Experimental

X band (9.4 GHz) and Q band (34 GHz) EPR spectra were measured using a Bruker Elexsys 500 spectrometer available at FSU Chemistry Department. Variable temperature, high frequency (101 – 305 GHz) EPR spectra were measured on powder and single crystal samples using the home-built spectrometers at the NHMFL.

Results and Discussion

Powder HF-EPR spectra showed four well-resolved lines (labeled as 1, 1', 2, 2' in Fig. 2a) corresponding to the allowed transitions of an S = 1 system with axial symmetry, and a forbidden line ($\Delta M_S = \pm 2$; not shown) due to the transition between the triplet sublevels |-1> and |+1>. Low temperature, 34 GHz powder spectra revealed a 7-line hyperfine structure, which is a signature of the Cu-Cu coupling (No. of hyperfine lines: 2nI+1 = 7; nuclear spin I = 3/2; caused by two equivalent Cu nuclei). The powder spectrum disappeared at temperatures below 70 K, confirming the ground state to be diamagnetic. Orientation dependent, high field, single crystal spectra showed that there are two different sites occupied by the Cu-Cu dimer units (splitting of lines 2 and 2' in Fig. 2b). Analysis of the EPR signal intensities of the spectra at low temperatures revealed that the sign of the zfs parameter D to be negative (~ -0.34 cm^{-1}). Further work is in progress.

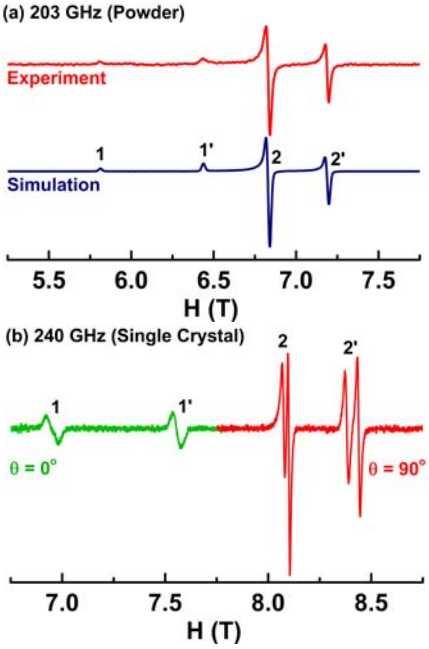

Figure 2: HFEPR: (a) 203 GHz, experimental and simulated powder spectra at 210 K; (b) 240 GHz, experimental single crystal spectra at 200 K, at two principal orientations aligned with the field (See text).

Conclusions

The two Cu^{2+} centers of each Cu(II) acetate unit are coupled antiferromagnetically. EPR spectra disappeared below 70 K, indicating a diamagnetic ground state. Low temperature and high field EPR was vital in the determination of the sign of D to be negative, as common to most Cu(II) carboxylate dimers. The spin Hamiltonian parameters are extracted using computer simulation of the spectra as: $g_x = g_y = 2.0678$; $g_z = 2.3685$; D = -0.34 cm^{-1}; E = 0.

Acknowledgements

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References

[1] Brotherton, W.S., *et al*., Dalton Trans., **40**, 3655 (2011).
[2] Ramachandran, V., *et al*., unpublished results (2013).