High-Field EPR Studies on Trinuclear and Binuclear Copper(II) Compounds

Sharma, R.P. (Panjab U., Chandigarh, India, Chemistry); Ferretti, V. (U. of Ferrara, Italy, Center for Structural Diffractometry); Jezierska, J. (Wroclaw U., Poland, Chemistry); Ozarowski, A. (NHMFL)

Introduction

Multinuclear copper(II) complexes are of considerable interest in many modern research areas such as catalysis [1], magnetism and theory [2]. As a continuation of our studies on polymeric Cu(II) complexes [3], we report new magnetic and High-Field EPR data for a series of centrosymmetric binuclear and trinuclear copper complexes, bridged by carboxylate groups and triethanolamine (TEA). The general formulas for the trimeric and dimeric species are $[Cu_3(RCOO)_4(TEA)_2]$ and $[Cu(H_2TEA)(RCOO)]_2$, respectively.

Experimental

High-field EPR spectra were recorded on the transmission instrument of the EMR facility and the 15/17 T SC magnet. Magnetic measurements were performed and crystal structures determined at Wroclaw U. and U. of Ferrara, respectively.

Results and Discussion

The magnetic susceptibility of the trimers (an example shown in Fig. 1) was fitted using the Hamiltonian

$$\hat{H} = J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) + D_{12}\{\hat{S}_{1z}\hat{S}_{2z} - \hat{S}_1\hat{S}_2/3\} + E_{12}(\hat{S}_{1x}\hat{S}_{2x} - \hat{S}_{1y}\hat{S}_{2y}) + D_{12}\{\hat{S}_{2z}\hat{S}_{3z} - \hat{S}_2\hat{S}_3/3\} + E_{12}(\hat{S}_{2x}\hat{S}_{3x} - \hat{S}_{2y}\hat{S}_{3y}) + \mu_B B\{g_1\}\hat{S}_1 + \mu_B B\{g_2\}\hat{S}_2 + \mu_B B\{g_1\}\hat{S}_3 \quad [1]$$

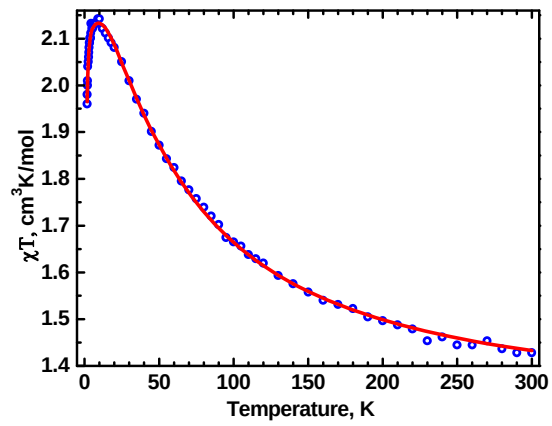

Fig.1. Product of the magnetic susceptibility and temperature for one of the trimers.

The zero-field splitting (zfs) parameters D_{12} and E_{12} were determined from EPR (Fig. 2) and were fixed in magnetic fitting. All trimeric complexes were found to be ferromagnetic with J of about 80 cm^{-1}. Two of the three dimeric compounds were ferromagnetic.

The HF EPR spectra of the S = 3/2 state for trimers and S = 1 for dimers, were simulated in terms of the "giant spin" Hamiltonian [2]:

$$\hat{H} = \mu_B \boldsymbol{B}\cdot\{g\}\cdot\hat{S} + D\{\hat{S}_z^2 - S(S+1)/3\} + E(\hat{S}_x^2 - \hat{S}_y^2) \quad [2]$$

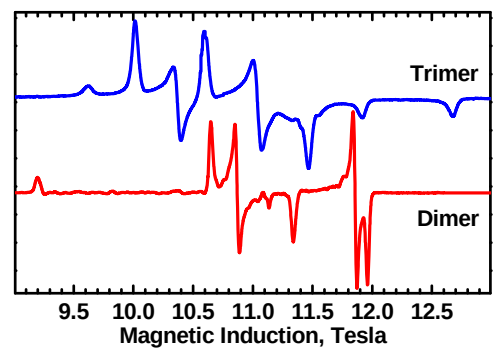

Fig. 2. Comparison of the HF EPR spectra of one of the trimers and the corresponding dimer, recorded with 328.8 GHz at 30 K.

Conclusions

The $\{g\}$ and zero-field splitting tensors were found to be non-coaxial. Agreement between the parameters of equations [1] and [2] was achieved. Density Functional Theory (DFT) calculations are being performed to understand the exchange interactions in the trimeric complexes. This work is in progress.

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References

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