High-Field EPR and Magnetic Susceptibility Studies on Tetranuclear Ferromagnetic Quinoline Adducts of Copper(II) Trifluoroacetate

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Introduction

While dimeric ‘paddlewheel’ structures are very conspicuous among copper(II) complexes of formic acid and its homologues, such arrangements are much less numerous in the case of the perfluorinated carboxylic acids, which tend to form either monomeric copper complexes or extended chains. Copper(I) and copper(II) perfluorocarboxylates are volatile which makes them potentially useful in the chemical vapor deposition technique to produce thin metallic copper layers, and from that viewpoint the determination of nuclearity of such complexes is very important. In this work, magnetic properties and high-field EPR spectra of three previously unknown tetranuclear quinoline adducts of copper(II) trifluoroacetate were studied and their X-Ray structures were determined.

Experimental

High-field and frequency EPR spectra were recorded on the 15/17 T transmission instrument at the NHMFL EMR facility at microwave frequencies 52-432 GHz and magnetic fields up to 15 T. Magnetic susceptibility data of powdered samples were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8–300 K.

Results and Discussion

Very well resolved EPR spectra due to a quintet (\(S = 2\)) spin state were observed for the tetrameric complexes (Fig. 1). The magnetic properties (Fig. 2) were interpreted by using the Heisenberg-Dirac-Van Vleck Hamiltonian

\[
H = J_1(S_1S_2 + S_3S_4) + J_2(S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4) \]  \[1\]

\(J_1 = -102 \text{ cm}^{-1}, J_2 = -39 \text{ cm}^{-1}\) were found.

Conclusions

Terms describing the Zeeman and zero-field splitting, which were derived from the High-field EPR spectra (Fig. 1), had to be added to properly reproduce the magnetic susceptibility at the lowest temperatures. ‘Broken symmetry’ Density Functional Theory (DFT) calculations\(^3\) were performed to estimate the exchange integrals resulting in \(J_1 = -115 \text{ cm}^{-1}\) and \(J_2 = -56 \text{ cm}^{-1}\), in a surprisingly good agreement with experimental results. The results of this work were published in\(^4\).

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References