High-Field EPR Studies on Dimeric and Tetrameric Copper Trifluoroacetates

I. B. Szymanska, T. Muziol (Nicolaus Copernicus U., Chemistry); A. Ozarowski (NHMFL, EMR)

Introduction

While copper complexes of unsubstituted carboxylic acids readily form dimeric systems, copper perfluorocarboxylates are very different in that respect and often tend to form more complicated polynuclear compounds.\(^1\)\(^-\)\(^3\) In the course of this work, two previously unknown quinoline adducts of copper trifluoroacetate were synthesised. One of them was a dimeric species while the other one exhibited high-field EPR spectra characteristic of the S=2 spin state and was therefore identified as a tetramer. X-Ray structure, unrefined yet, confirmed the tetrameric structure of \(\text{Cu}_4\text{O(CF}_3\text{COO})_6(\text{quinoline})_4\) (1). Single-crystal EPR spectra of two known dimers, \([\text{Cu(CF}_3\text{COO})_2(\text{quinoline})]_2\) (2)\(^1\) and \([\text{Cu(CF}_3\text{COO})_2(\text{CH}_3\text{CN})]_2\) (3)\(^1\) were also investigated.

Experimental

High-field and frequency EPR spectra were recorded on the transmission device of the NHMFL EMR facility at frequencies 96 - 432 GHz and at temperatures 4 - 280 K.

Results and Discussion

Least-squares fitting of the frequency - field dependencies in the high-field EPR spectra of 1 allowed the spin Hamiltonian parameter determination for the quintet spin state (S=2): \(g_x=2.115\), \(g_y=2.146\), \(g_z=2.065\), \(D=-0.827\) cm\(^{-1}\), \(E=-0.127\) cm\(^{-1}\). The intensity patterns in single-crystal triplet-state spectra of 2 and 3 are consistent with negative D parameter in both compounds. For 2 we found \(g_x=g_y=2.085\), \(g_z=2.390\), \(D=-0.435\) cm\(^{-1}\), \(E=0\), and for 3 \(g_x=g_y=2.072\), \(g_z=2.390\), \(D=-0.410\) cm\(^{-1}\), \(E=-0.0056\) cm\(^{-1}\). The EPR parameters for 2 published previously\(^1\) appear to bear substantial errors.

Conclusions

Detailed interpretation of the EPR parameters for the tetrameric complex 1 requires refinement of the X-Ray structure (in progress). The determination of the negative sign of D in the dimers 2 and 3 was accomplished by analysis of the intensity patterns in the high-field single-crystal EPR spectra. This result is in agreement with a recent study on copper acetate\(^5\) (where \(|D|\) is significantly smaller) and suggests that D is negative in all dimeric copper(II) carboxylates, which has important implications for the theory of anisotropic exchange interactions in polynuclear transition metal complexes.

Acknowledgements

This work was supported by the NHMFL. The NHMFL is funded by the NSF through the Cooperative Agreement No. DMR-0654118, by the State of Florida and by the DOE.

References