Studies of Magnetic Properties of 1-D Polymeric Cu(II)-fatty Acid-azacrown Ether Complex

K. Wojciechowski (Warsaw University of Technology, Poland); M. Brynda (UC Davis, Chemistry); A. Ozarowski (NHMFL)

Introduction

We have investigated a newly synthesized adduct of dimeric copper(II)-hexanoate (CuHxt) and 1,10-diaza-18-crown-6 ether (A). This adduct was obtained as one of two products from reaction of CuHxt with A, and its solid-state structure could not be fully resolved by X-ray methods. The second product of the reaction could be easily crystallized and characterized as a copper(II)-diaazacrown ether complex with hexanoate counterions (CuAHxt). Our interest in studying this adduct arises from the mechanistic studies of copper(II) transport through Permeation Liquid Membranes (PLM). A PLM device consists of two aqueous compartments (source and strip) separated by an organic solvent. The latter contains a carrier, which selectively transports metal species from the source to the strip solution. The membranes containing a mixture of N,N-didecyl-diaza-18-crown-6 ether (22DD) and a carboxylic acid, both dissolved in an organic solvent, can transport Cu(II) ions and are very useful for studying the chemical speciation of this metal in natural waters.

Experimental

The X-ray diffraction studies of the adduct were performed at the University of Geneva. X-band and Q-band EPR powder spectra were recorded at the UC Davis. High field EPR experiments were performed at the NHMFL using the multi-frequency transmission instrument of the EMR facility.

Results and Discussion

Figure 1 shows a typical EPR spectrum of the CuAHxt-CuHxt adduct, recorded at 220.8 GHz at room temperature. The spectrum contains two groups of signals: one associated with paramagnetic CuAHxt complex, and the second associated with the dimeric CuHxt units. The spectrum can be fitted with the following parameters: D = 0.348 cm^{-1}, E = 0 cm^{-1}; $g_x = g_y$ = 2.072, g_z = 2.375 for the CuHxt part, and g_x = 2.055, g_y = 2.066, g_z = 2.288 for the CuAHxt part. The fitting parameters are in satisfactory agreement with the EPR parameters computed using DFT. In all spectra, additional signals were present which could not be simulated with above parameters, suggesting the existence of the second product with slightly different geometrical arrangement, as also suggested by the X-ray results.

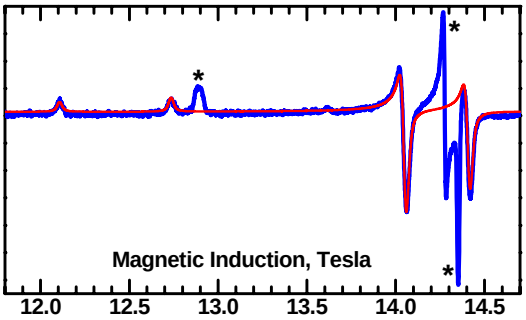

Figure 1. Blue: Experimental EPR spectrum of the CuAHxt-CuHxt adduct at 412.8 GHz, 287 K. Signals marked with * are due to the CuAHxt monomer. Red line is the simulated triplet state spectrum of the dimeric CuHxt.

Conclusions

The high-field EPR results obtained at NHMFL confirmed the structure of the studied adduct of copper(II) hexanoate with the azacrown ether, proposed on the basis of previous spectroscopic (IR, NMR, UV/Vis) results [1]. The adduct consists of the alternating units of dimeric CuHxt and CuAHxt, forming infinite polymeric 1D chains. In addition, the current HF EPR results suggest that the symmetry of dimeric CuHxt unit in the adduct is higher than that of the isolated CuHxt dimer.

Acknowledgements

M.B. thanks Manno Switzerland supercomputer center for computer time.

References

[1] K. Wojciechowski, M. Brynda, G. Bernardinelli., *in preparation.*