CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF POLYNUCLEAR HETEROMETALLIC Cu/Mn CARBOXYLATE COMPLEXES

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Introduction

A number of novel heterometallic Cu/Mn complexes have been synthesized in a one-pot reaction of copper powder and potassium permanganate with non-aqueous solutions of dicarboxylic acids and ethylenediamine dihydrochloride. In the crystal structure of $[Cu(en)_2][Mn_2(succ)_2Cl_2]$ (determined in this work, Fig. 1), where succ is the di-anion of succinic acid, the anion chains of $[Mn_2(succ)_2Cl_2]_n^{2n-}$ are joined by $[Cu(en)_2]^{2+}$ cations to form a two-dimensional network.

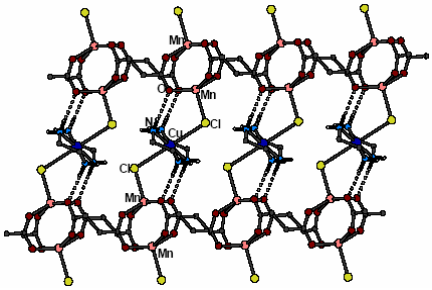

Fig. 1. The two-dimensional structure of $[Cu(en)_2][Mn_2(succ)_2Cl_2]$.

Experimental

High-frequency EPR spectra up to 413 GHz were recorded on the transmission spectrometer at the EMR facility of the NHMFL. Magnetic susceptibility data of a powdered sample were measured with a SQUID magnetometer (Quantum Design MPMSXL-5) over the temperature range 1.8–300 K at the magnetic induction of 0.5 T.

Results and Discussion

Very well defined triplet state spectrum was observed in high-field, high-frequency EPR at temperatures above 4K, in addition to a typical axially-symmetric spectrum of uncoupled Cu^{2+} ion with $g_{x,y} = 2.042$, $g_z = 2.200$. The triplet spectrum was interpreted using the spin Hamiltonian

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

The g tensor was found to be isotropic with $g_{xx}=g_{yy}=g_{zz}=2.00$. The values of D and E were -3.038 cm^{-1} and 0, respectively.

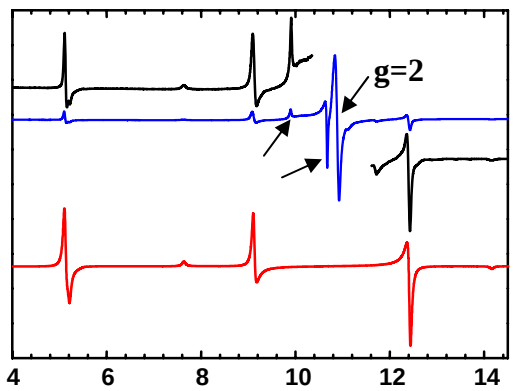

Fig. 2. EPR spectrum of $[Cu(en)_2][Mn_2(succ)_2Cl_2]$ at 304.8 GHz, 30K. Blue: experimental, black: magnified experimental, red: simulated triplet spectrum. Arrows indicate the signals of Cu^{2+} and the position of g=2. Magnetic induction is in Tesla.

Conclusions

The triplet spectrum comes from the S=1 state of the exchange-coupled Mn-Mn pair. The g=2 value is characteristic for Mn^{2+} and indicates that copper is not coupled to the Mn-Mn 'dimer'. This is also confirmed by the presence of a single-copper ion spectrum with the g components consistent with $Cu(en)_2^{2+}$. The triplet spectrum described here could not be observed in X- or Q-Band EPR owing to the very large D magnitude. There are also signals present in the spectrum whose nature is not clear yet. They may be due to higher excited states (S=2,3…) of the Mn-Mn system, or to a contamination.

Acknowledgements

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