Magneto-Structural Correlations in $Cu(en)_2SO_4$ — a new Magnet with Two-Dimensional Triangular Arrangement of Cu(II) ions

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$Cu(en)_2SO_4$ (en = 1,2-diaminoethane) was synthesized and its crystal structure determined. From a crystallographic point of view, the compound might represent an example for the realization of a $S = 1/2$ Heisenberg magnet on a two-dimensional spatially anisotropic triangular lattice. Magnetic susceptibility and magnetization studies were performed to analyze the magneto-structural correlations and to characterize the magnetic subsystem of the present compound. The results indicate the presence of antiferromagnetic interactions between magnetic ions with $zJ/k_B \approx -14.6$ K and short-range order near 7 K.

1. Introduction

The physics of the frustrated quantum spin $S = 1/2$ two-dimensional (2D) Heisenberg antiferromagnets with spatially anisotropic triangular lattice (HAFTM) and interactions J_1 and J_2 has been of a great interest in recent years [1, 2]. The ground state properties of HAFTM depend on the value of the ratio J_2/J_1 [3]. Until now, only a few experimental examples of the $S = 1/2$ HAFTM have been identified, so the main goal of the present work is the study and analysis of the magneto-structural correlations in a polymeric complex of $Cu(en)_2SO_4$ (en = 1,2-diaminoethane = $C_2H_8N_2$) that might represent an example for the realization of HAFTM.

2. Experimental

The title compound has been prepared by the reaction of anhydrous copper(II) sulphate with en in a molar ratio of 1:1 in D_2O. Dark blue prismatic

crystals were obtained after two months by slow evaporation of the solvent used (at 5°C). Data collection was performed on an Xcalibur2 diffractometer equipped with a CCD detector Sapphire2 (Oxford Diffraction) at 105(2) K. The CrysAlis software package [4] was used for data collection and reduction. The structures were solved by the SIR97 program [5] incorporated in the WinGX program package [6]. All non-hydrogen atoms have been refined anisotropically by the full-matrix least-squares procedure [SHELXL-97] [7] on F^2 with weight: $w = 1/[\sigma^2(F_0)^2 + (0.034P)^2 + 5.321P]$, where $P = (F_0^2 + 2F_c^2)/3$. Hydrogen atoms have been located from difference Fourier maps and refined using a "riding" model*.

The magnetic properties of $Cu(en)_2SO_4$ were measured by a Quantum Design MPMS system. The magnetic susceptibility studies were performed in a magnetic field of 0.1 kGs, in "zero field cooling" and "field cooling" regimes, while the temperature was varied from 2 to 300 K. The magnetization was measured at 2, 3, 5, 10 and 100 K, while varying the magnetic field from 0 to 50 kGs. The data was corrected for the holder background and the diamagnetic contribution of the core electrons.

3. Results and discussion

$Cu(en)_2SO_4$ crystallizes in the orthorhombic system, the space group *Cmca* with the unit cell parameters: $a = 14.5058(7)$ Å, $b = 9.6379(5)$ Å, $c = 13.8945(7)$ Å, $Z = 8$. The Cu(II) magnetic ions are octahedrally coordinated by four N atoms of two en ligands and two O atoms of $(SO_4)^{2-}$ anions placed in the *trans* position. The central atoms are connected via covalent bonds of the $(SO_4)^{2-}$ anions into 1D-polymeric chains running along the crystallographic *c*-axis (Fig. 1). A similar one-dimensional structure was found for $[Cu(en)_2(S_2O_6)]_n$ and $\{[Cu(en)(NO_3)][SeCN]\}_n$ [8, 9]. The crystal structure is further stabilized by N–H$\cdots$O hydrogen bonds connecting the neighbouring chains in the *ac* plane. The N$\cdots$O distances are 2.964(2) and 3.069(3) Å. The Cu$\cdots$Cu separation in the chain is 6.962(2) Å, while the shortest interchain distance is 6.1154(2) Å. It is known that they may also serve as exchange paths [10, 11].

Apart from intrachain interactions (J_1), hydrogen bonds present in the structure can potentially mediate an additional exchange path (J_2) among the chains in the *b*-direction. Thus, on the basis of structural considerations, the magnetic system formed by both sorts of exchange paths might represent a planar system with triangular spatially anisotropic exchange coupling within *bc*-layers.

The experimental data of the temperature dependence of magnetic susceptibility below 30 K is characterized by a round maximum observed at 7 K (Fig. 2a).

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*Crystallographic data for $Cu(en)_2SO_4$ has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 648304. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).
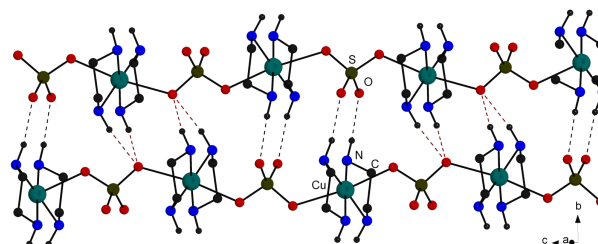
Fig. 1.   A view of fragment of the crystal structure of Cu(en)$_2$SO$_4$ in the *bc*-plane. The covalent chains are running along the *c* axis. The hydrogen bonds connecting the chains are denoted by dashed lines. Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.
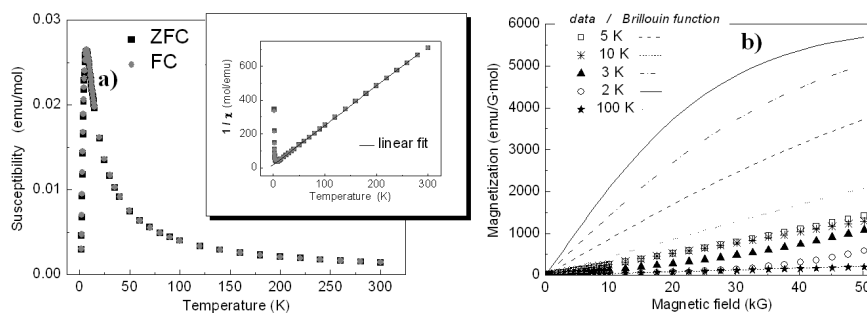

Fig. 2.   (a) Temperature dependence of magnetic susceptibility of Cu(en)$_2$SO$_4$. The inset shows the temperature dependence of the inverse molar magnetic susceptibility, analysed using the Curie–Weiss law (solid line). (b) The magnetic field dependence of the molar magnetization at given temperatures. The lines represent the Brillouin functions for $S = 1/2$, $g = 2.28$ at corresponding temperatures.

This round maximum can be attributed to short-range correlations. The susceptibility data above 20 K was fitted by the Curie–Weiss law (Fig. 2a — inset). The fit yielded $\theta = -7.3 \pm 0.1$ K and $g = 2.28 \pm 0.02$. The negative value of θ indicates the antiferromagnetic character of exchange coupling $zJ/k_B \approx -14.6$ K. The experimental data of magnetization vs. magnetic field are characterized by upward curvature (Fig. 2b). This behaviour exists at temperatures below 100 K, which suggests that interactions in the material might be relatively strong. The magnetization data was compared with the Brillouin function describing an $S = 1/2$ paramagnet with the value $g = 2.28$ as obtained from susceptibility analysis. The comparison confirms the presence of antiferromagnetic coupling since the total magnetization at a given magnetic field is significantly smaller when compared with the prediction for paramagnetic system. The temperature dependence of the magnetization at constant field is corresponding with an assumption of existence of a gap, closing near 4 T.

4. Conclusion

The study of magneto-structural correlations of $Cu(en)_2SO_4$ reveals that the magnetic ions Cu(II) are connected with two types of links. Consequently, magnetic system of the studied material is probably formed by two types of exchange paths: J_1 via the covalent chains and J_2 through the hydrogen bonds connecting the chains into the plane.

The conjecture is supported by the analysis of magnetic susceptibility which manifests the existence of short-range order in the system, with the effective strength of the exchange coupling $zJ/k_B \approx -14.6$ K. $Cu(en)_2SO_4$ might represent $S = 1/2$ 2D antiferromagnetic system with triangular spatially anisotropic exchange coupling in layers.

Further experimental and theoretical studies will be performed to specify the measure of the spatial anisotropy of exchange coupling in the system including the experimental study of temperature and magnetic field dependence of heat capacity, electron-spin resonance, and the calculation of exchange interaction directly from the crystal structure.

Acknowledgments

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