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$Cu_3(tmen)_3(tma)_2(H_2O)_2 \cdot 6.5H_2O$ — New $S = 1/2$ "Sawtooth" Chain?

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The results of the investigation of magnetic susceptibility, magnetization and specific heat of $Cu_3(tmen)_3(tma)_2(H_2O)_2 \cdot 6.5H_2O$ (tmen = N,N,N',N'-tetramethylethane-1,2 diamine; H_3tma = 1,3,5--benzenetricarboxylic acid) are reported. The spatial arrangement of magnetic Cu(II) ions and network of covalent bonds suggest that the studied material might be a representative of $S = 1/2$ sawtooth chain with moderate exchange coupling J/k_B. The investigation of the temperature dependence of susceptibility and magnetic field dependence of magnetization yielding $J/k_B \approx -0.63$ K is consistent with the structural features. In addition, specific heat data reveal short-range correlations in milikelvin temperature range and indicate long-range ordering below 150 mK.

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1. Introduction

Nowadays low dimensional frustrated magnets are of great interest. In these systems strong quantum fluctuations arising from combined effect of restricted dimensionality and geometrical frustration can induce novel ground states and excited modes [1]. Quantum chains, in which spins are arranged in a chain consisting of a corner sharing triangles and antiferromagnetic exchange coupling, represent one of prominent examples of the lattice in which frustration and quantum fluctuation lead to the variety of new properties [2]. For example, anomalous magnetocaloric effect at low temperatures ($T \ll J/k_B$) and in the vicinity of the saturation field B_{sat} has been predicted in sawtooth chains [3] and the behavior was attributed to the condensation of localized magnons [4]. Experimental investigation of the predicted phenomenon requires a frustrated system with a moderate exchange interaction so that saturation field can be conveniently achievable. On the other hand, for a system with a low value of exchange coupling constant, experimental investigation of the predicted magnetocaloric behavior may require very low temperatures.

The present work was motivated by the possibility of experimental verifying the aforementioned theoretical prediction using compound $Cu_3(tmen)_3(tma)_2(H_2O)_2 \cdot 6.5H_2O$ (hereafter abbreviated as Cutmen). As the first step of the investigation, the thermodynamic properties of the Cutmen were studied to estimate the values of characteristic parameters J/k_B and subsequently B_{sat}.

2. Crystal structure and experimental

The title compound contains three crystallographically non-equivalent $[Cu(tmen)]^{2+}$ moieties which are bridged by tma(3–) anions (Fig. 1). Two perpendicularly running chains formed of $\{Cu(1)(tmen)\}_3$ triangles with one common $\{Cu(2)(tmen)\}$ unit result in embedded layered structure. Chain-like cavities filled by H_2O molecules of crystallization are present between the resulting sheets [5]. Coupled sawtooth chains are formed within the layers [6].

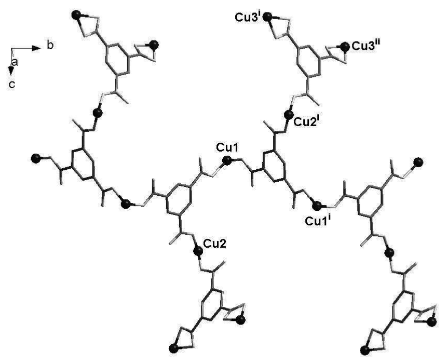

Fig. 1. Schematic view of the crystal structure of Cutmen with triangular arrangement of Cu(II) atoms. Water molecules and tmen ligands are omitted for the sake of clarity. Symmetry codes: (i) $0.5 - x$, $0.5 + y$, $2 - z$; (ii) $1 - x$, $1 - y$, $2 - y$. The figure was drawn using Diamond program [6].

Cutmen was synthesized following well established procedure [5]. Its phase identity was confirmed using powder X-ray diffraction and the experimental diffraction pattern is in a very good agreement with the calculated one based on X-ray data reported in Ref. [5]. The susceptibility and magnetization of the powder sample were studied in a commercial SQUID magnetometer. Specific heat was investigated in a commercial dilution refrigerator TLE200 using a dual-slope technique [7].

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3. Results and discussions

Magnetic susceptibility studied in magnetic field 1 kOe from 2 K to 300 K is characterized by monotonic decrease with increasing temperature, see Fig. 2. The analysis of

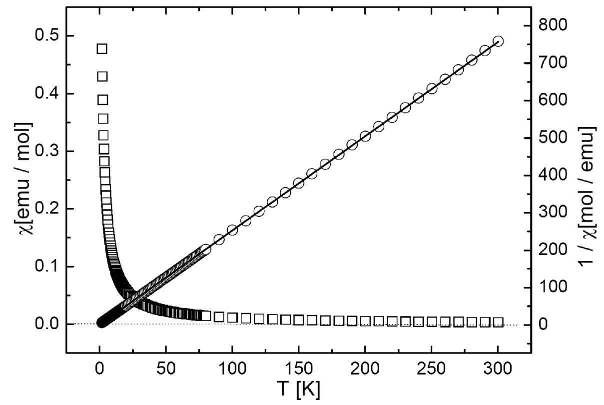

Fig. 2. Temperature dependence of magnetic susceptibility (left) and inverse susceptibility (right) of Cutmen. The solid line represents a fit using the Curie–Weiss law.

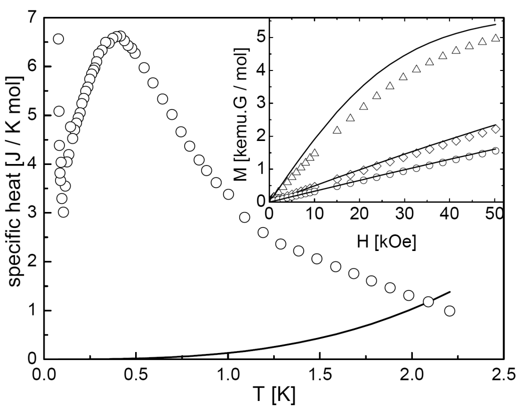

Fig. 3. Temperature dependence of specific heat of Cutmen. Magnetic specific heat is denoted by empty circles, solid line represents a lattice contribution. Inset: Field dependence of magnetization of Cutmen studied at 2 K (empty triangles), 8 K (empty diamonds), and 12 K (empty circles). Solid line represents the prediction for $S = 1/2$ paramagnet with $g = 2.06$.

inverse susceptibility using the Curie–Weiss law yielded $g = 2.06$ and $\Theta = -2.5$ K suggesting weak antiferromagnetic coupling. Exchange interaction constant was estimated from Θ using mean-field approximation $\Theta \approx zJ$, where z denotes the number of nearest neighbors. Considering the number of the nearest neighbors within the chain ($z = 4$), the estimation yielded $J/k_B = -0.63$ K. The value of B_{sat} can be obtained using the relation [8], $B_{sat} = 2zJ/g\mu_B$, yielding $B_{sat} = 36.4$ kOe. Weak exchange interactions are also revealed by the comparison of the field dependence of magnetization experimentally studied in magnetic fields up to 50 kOe at temperatures 2 K, 8 K and 12 K and the behavior of $S = 1/2$ paramagnet, see inset in Fig. 3. The observed behavior supports weak interactions among magnetic Cu(II) ions, which may be ascribed to rather complicated exchange bridges mediating by tmen units. The investigation of specific heat was performed from nominally 150 mK up to 2.2 K. Since the studied compound represents a magnetic insulator, only magnetic and lattice subsystems contribute to the total specific heat. The lattice contribution was estimated using the Debye approximation, specifically by fitting the specific heat data using the relation $C(T) = aT^{-2} + bT^3$, where aT^{-2} represents high-temperature part of a magnetic specific heat and bT^3 describes the lattice contribution. This analysis, adopted in the temperature range 1.5–2.2 K, yielded $a = 5.01$ J K/mol, $b = 0.128$ J/(K^4 mol). Broad maximum in magnetic specific heat confirmed the formation of short-range correlations in the millikelvin temperature range, see Fig. 3. In addition, sharp increase of magnetic specific heat with decreasing temperatures indicates magnetic phase transition below 150 mK. Given that critical temperature $T_c < 150$ mK, using the estimation $T_c = zJ'$ enables to estimate interchain interaction J', yielding $J'/k_B = 37.5$ mK, which represents the upper limit for the interchain coupling. The resultant ratio $J'/J = 0.06$ suggests low-dimensional character of magnetic interactions in Cutmen.

4. Conclusion

In summary, the investigation of thermodynamic quantities of Cutmen enabled the identification of the studied compound as a representative of $S = 1/2$ low--dimensional system with $J/k_B \approx -0.63$ K and $B_{sat} \approx 36.4$ kOe. The conjecture that Cutmen may serve as an example of an $S = 1/2$ sawtooth chain, will be verified by systematic study of specific heat in magnetic field and subsequent investigation of magnetocaloric effect. The effort in preparing an appropriate single crystal is in progress.

Acknowledgments

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References

[1] T. Yavors'kii, T. Fennel, M.J.P. Gingras, S.T. Bramwell, *Phys. Rev. Lett.* **101**, 037204 (2008).

[2] S. Chen, Y. Wang, W.Q. Ning, C. Wu, H.Q. Lin, *Phys. Rev. B* **74**, 174424 (2006).

[3] M.E. Zhitomirsky, A. Honecker, *J. Statist. Mech., Theor. Exp.*, P07012 (2004).

[4] M.E. Zhitomirsky, *Phys. Rev. B* **67**, 104421 (2003).

[5] S. Konar, P.S. Mukherjee, E. Zangrando, M.G.B. Drew, C. Diaz, J. Ribas, N.R. Chaudhuri, *Inorg. Chim. Acta* **358**, 29 (2005).

[6] *Diamond.* Crystal Impact, Bonn, 2007.

[7] S. Riegel, G. Weber, *J. Phys. E., Sci. Instrum.* **19**, 790 (1986).

[8] F.M. Woodward, A.S. Albrecht, C.M. Wynn, C.P. Landee, M.M. Turnbull, *Phys. Rev. B* **65**, 144412 (2002).