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**Cu3(tmen)3(tma)2(H2O)2·6.5H2O**

— New $S = 1/2$ “Sawtooth” Chain?

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The title compound contains three crystallographically non-equivalent $[\text{Cu}(\text{tmen})]^{2+}$ moieties which are bridged by tma(3−) anions (Fig. 1). Two perpendicularly running chains formed of $\{\text{Cu}(1)(\text{tmen})\}_3$ triangles with one common $\{\text{Cu}(2)(\text{tmen})\}_3$ unit result in embedded layered structure. Chain-like cavities filled by H2O 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].
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 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 $\Theta$ 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 $B_{\text{sat}}$ can be obtained using the relation [8], $B_{\text{sat}} = 2zJ/g\mu_B$, yielding $B_{\text{sat}} = 36.4$ 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 $B_{\text{sat}} \approx 36.4$ 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.

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References