

Experimental Study of Magneto-Structural Correlations in Low-Dimensional Quantum Magnets $\text{Cu}(en)\text{Cl}_2$ and $\text{Cu}(tn)\text{Cl}_2$

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The present work is focused on the investigation of magneto-structural correlations in $\text{Cu}(en)\text{Cl}_2$ and $\text{Cu}(tn)\text{Cl}_2$. A comparative study of powder susceptibility and magnetization of both compounds revealed that the replacement of tn by en ligand did not affect single-ion properties. On the other hand, the structure modification led to significant reduction of magnetic interactions as well as lowering the crystal symmetry. The impact of the high pressure on magnetic properties of the compounds is discussed.

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1. Introduction

In the last decades, two-dimensional (2D) quantum antiferromagnets have received a significant amount of theoretical and experimental interest [1,2]. Mermin and Wagner [3] demonstrated that thermal fluctuations prevent 2D Heisenberg magnets to spontaneously break their continuous spin-rotation symmetry at finite temperatures. However, the low lattice dimensionality and a low spin value enhance the effect of quantum fluctuations affecting also ground-state properties. Theoretical studies of the spin 1/2 Heisenberg antiferromagnet (HAF) on the square lattice (Fig. 1a) which represents an important paradigm of a low-dimensional magnetism, indicate a strong suppression of the ordered moment, about 60 %, relative to the full moment [1]. The 2D-1D crossover in the lattice dimensionality further increases the effect of the quantum fluctuations, leading to the spin liquid ground state in the limit of HAF chain [1].

In comparison with the limit models, the intermediate state interpolating between the 1D and 2D, a spatially anisotropic square lattice (SASL) depicted in Fig. 1b, has not received so much attention. The absence of corresponding theoretical predictions and difficulties with preparation of such materials did not allow finding proper experimental realizations. A few realizations of SASL with spin 1/2 appeared only recently [4,5].

The organo-metallic compound $\text{Cu}(tn)\text{Cl}_2$ ($tn = \text{C}_3\text{H}_{10}\text{N}_2$) belongs to quasi-2D magnetic systems with high measure of the spatial anisotropy of exchange coupling. Previous specific heat studies of powder sample performed in zero magnetic field did not observe magnetic phase transition down to 50 mK [6]. Application of magnetic field induced a response characteristic for the

Berezinskii-Kosterlitz-Thouless transition [7]. A comparative analysis with other low-dimensional compound $\text{Cu}(en)(\text{H}_2\text{O})_2\text{SO}_4$ ($en = \text{C}_2\text{H}_7\text{N}_2$) found nearly identical manifestation of two-dimensional magnetic correlations in zero magnetic field [8]. Recent first-principle studies of magnetic interactions in $\text{Cu}(en)(\text{H}_2\text{O})_2\text{SO}_4$ revealed that the compound is a representative of a spatially anisotropic zig-zag square lattice [9]. Accordingly, a similar 2D lattice model can be expected also in $\text{Cu}(tn)\text{Cl}_2$.

Present work is motivated by the effort to modify exchange interactions in the studied crystal structure of $\text{Cu}(tn)\text{Cl}_2$ via replacement of the organic ligand tn by en . The latter has smaller volume, thus the enhancement of the inter-layer coupling could be expected, accompanied with a potential observation of a magnetic phase transition at temperatures higher than 50 mK.

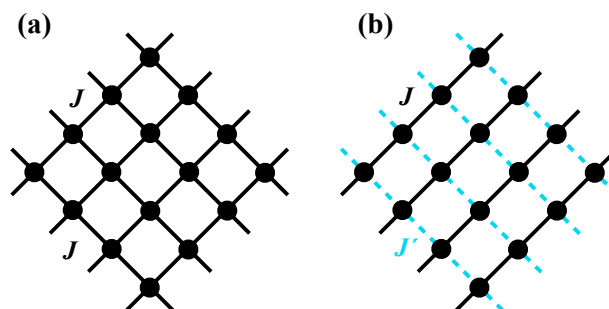


Fig. 1. (a) Spatially isotropic square lattice. (b) Spatially anisotropic square lattice. J and J' denote intra-chain and inter-chain coupling, respectively.

2. Crystal structures and experimental details

The crystal structure of $\text{Cu}(tn)\text{Cl}_2$, established at 150 K, is orthorhombic (space group $\text{Pna}2_1$) with the unit cell parameters $a = 17.956 \text{ \AA}$, $b = 6.759 \text{ \AA}$, $c = 5.710 \text{ \AA}$. The structure consists of $\text{Cu}(\text{II})$ covalent ladders, running along the c -axis. Adjacent ladders are coupled through

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a system of hydrogen bonds [6]. A local surrounding of Cu(II) ion comprises of four Cl and two N ions, forming a distorted octahedron (Fig. 2a) which has nearly the same parameters as that in the compound $\text{Cu}(en)\text{Cl}_2$ (Table I). $\text{Cu}(en)\text{Cl}_2$ crystallizes in the monoclinic space group $P2_1/m$ with unit cell parameters $a = 6.775 \text{ \AA}$, $b = 5.760 \text{ \AA}$, $c = 7.224 \text{ \AA}$ and $\beta = 93.75^\circ$. Alike $\text{Cu}(tn)\text{Cl}_2$, the structure is built of covalent ladders parallel with the b -axis, which are connected by hydrogen bonds [10]. As can be seen in Table I, the local surrounding of Cu(II) ion is nearly identical in both compounds, thus very similar single-ion properties as g -factors can be expected. On the other hand, the differences in the spatial packing of ladders could project into the differences in the magnetic correlations.

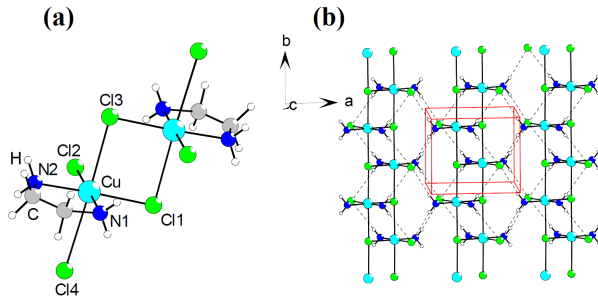


Fig. 2. (a) Local surrounding of Cu(II) ion in $\text{Cu}(en)\text{Cl}_2$ and $\text{Cu}(tn)\text{Cl}_2$. (b) The crystal structure of $\text{Cu}(en)\text{Cl}_2$, dashed lines represent hydrogen bonds. The unit cell is depicted by red lines.

Following modified method published in ref. [10], polycrystalline sample of $\text{Cu}(en)\text{Cl}_2$ was synthesized in the form of dark blue plates. To prevent the effect of texture, the material was powdered. The amount of the material with the mass of 190 mg was placed in a gel capsule and used for magnetization and susceptibility measurements performed in a commercial Quantum Design SQUID magnetometer. Magnetic susceptibilities were measured in the temperature range from 1.7 to 300 K in the magnetic field 100 mT. The measurements in field cooling (FC) and zero-field cooling (ZFC) regimes yielded the same experimental results. The data were corrected for the diamagnetic contribution of the background as well as for the core diamagnetism. The latter was estimated by using the Pascal constants. Isothermal magnetization curves were measured at the temperature 1.7 K in magnetic field up to 5 T.

3. Results and discussion

Temperature dependence of magnetic susceptibility of $\text{Cu}(en)\text{Cl}_2$ and $\text{Cu}(tn)\text{Cl}_2$ is depicted in Fig. 3. A closer look at the data reveals identical behavior at temperatures above 20 K which is a demonstration of very similar single-ion properties resulting from nearly identical local surrounding of Cu(II) ion in both compounds (Table I). The deviations caused by magnetic correlations

TABLE I

Bond lengths [\AA] in the local octahedron in $\text{Cu}(en)\text{Cl}_2$ and $\text{Cu}(tn)\text{Cl}_2$. Labels of the ligands correspond to those in the Fig. 2a.

bond	$\text{Cu}(tn)\text{Cl}_2$	$\text{Cu}(en)\text{Cl}_2$	bond	$\text{Cu}(tn)\text{Cl}_2$	$\text{Cu}(en)\text{Cl}_2$
Cu-N1	2.014	2.016	Cu-Cl2	2.31	2.279
Cu-N2	2.006	2.014	Cu-Cl3	2.773	2.793
Cu-Cl1	2.327	2.305	Cu-Cl4	2.764	2.793

in $\text{Cu}(tn)\text{Cl}_2$ appear at lower temperatures. This simple comparison of the susceptibility data indicates nearly the same single-ion properties and rather weaker magnetic coupling in $\text{Cu}(en)\text{Cl}_2$. The latter manifests in higher values of a low-temperature susceptibility of $\text{Cu}(en)\text{Cl}_2$. A temperature dependence of the effective magnetic moment, μ_{eff} , derived from the susceptibility of $\text{Cu}(en)\text{Cl}_2$ is represented in Fig. 4. A rapid decrease observed below 10 K can be related to the formation of a short-range antiferromagnetic (AF) order. At the highest temperatures, μ_{eff} saturates towards the value, $1.73 \pm 0.02 \mu_B$, corresponding to a g -factor, $g = 2.003 \pm 0.010$, which is consistent with that obtained from Curie-Weiss law.

As expected, the fitting of the inverse susceptibility of $\text{Cu}(en)\text{Cl}_2$ by Curie-Weiss law in the temperature range from 10 K to 300 K (Fig. 3 inset) provided a value of g -factor, $g = 2.005 \pm 0.050$, which is close to $g = 2.07 \pm 0.05$ reported for the powder sample of $\text{Cu}(tn)\text{Cl}_2$ [6].

On the other hand, Curie temperature, $\Theta = -0.75 \text{ K}$ is much lower than $\Theta = -4.17 \text{ K}$ for $\text{Cu}(tn)\text{Cl}_2$, which indicates weakening of short-range correlations in $\text{Cu}(en)\text{Cl}_2$.

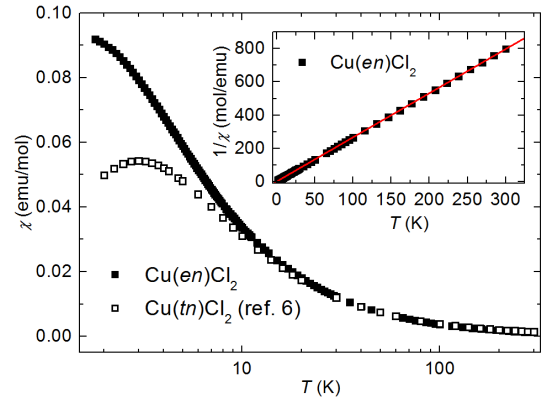


Fig. 3. Temperature dependence of powder magnetic susceptibility of $\text{Cu}(en)\text{Cl}_2$ and $\text{Cu}(tn)\text{Cl}_2$ (ref. [6]) measured in magnetic field 100 mT. Inset: Temperature dependence of inverse susceptibility of $\text{Cu}(en)\text{Cl}_2$. The solid line represents fit by Curie-Weiss law with $g = 2.005$ and $\Theta = -0.75 \text{ K}$.

Weaker magnetic correlations are also apparent from the comparison of isothermal magnetization curves of both compounds at the temperature 2 K with the theoretical prediction for a free spin system represented by

Brillouin function with spin 1/2 and $g = 2.005$ (inset of Fig. 4). The interplay of AF magnetic correlations and applied magnetic field results in lower magnetization values than those of Brillouin function; the stronger AF interactions, the lower increase of magnetization with growing magnetic field. Correspondingly, much stronger correlations manifest in $\text{Cu}(tn)\text{Cl}_2$. Rather significant change of exchange interactions in $\text{Cu}(en)\text{Cl}_2$ reflects high sensitivity of exchange pathways to the change in the distribution of hydrogen bonds in the structure. While omitting one C-H₂ group did not affect the spatial geometry of the local surrounding of Cu(II) ions, it had considerable influence on the global packing leading to lowering the global crystal symmetry from orthorhombic in $\text{Cu}(tn)\text{Cl}_2$ to monoclinic space group in $\text{Cu}(en)\text{Cl}_2$.

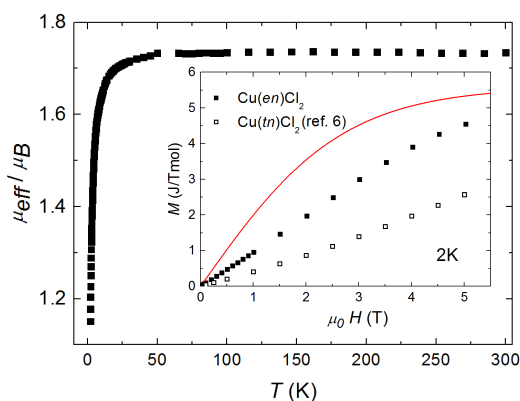


Fig. 4. Temperature dependence of the effective magnetic moment of $\text{Cu}(en)\text{Cl}_2$. Inset: Magnetic field dependence of isothermal magnetization of powder samples of $\text{Cu}(en)\text{Cl}_2$ (full squares) and $\text{Cu}(tn)\text{Cl}_2$ (empty squares) [6]. The solid line represents Brillouin function with spin 1/2, $g = 2.005$ and $T = 2$ K.

4. Conclusions

Experimental study of magneto-structural correlations in $\text{Cu}(en)\text{Cl}_2$ was performed. A comparative analysis of powder susceptibility and isothermal magnetization curves of $\text{Cu}(tn)\text{Cl}_2$ and $\text{Cu}(en)\text{Cl}_2$ revealed nearly identical single-ion properties manifesting by identical high-temperature susceptibility data and similar g -factors. The close similarity results from the fact that the replacement of tn ligand by en ligand did not introduce significant changes to local coordination of Cu(II) ion. On the other hand, it affected packing to 3D structure

causing lowering crystal symmetry. Besides that, it had surprisingly strong impact on the exchange pathways mediating much weaker exchange coupling in $\text{Cu}(en)\text{Cl}_2$.

In the future, a comparative study will be performed using monocrystalline samples. Besides that, ab-initio studies of exchange interactions in both compounds is desirable to elucidate the origin of the high sensitivity of the exchange pathways. In this respect, both compounds can be proper candidates for the studies under the high pressure, a way how to modify physical properties of both materials.

Acknowledgments

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