

Frustrated Zig-Zag Spin Chains Formed by Hydrogen Bonds in $[\text{Cu}(\text{H}_2\text{O})(\text{OH})(\text{tmen})]_2[\text{Pd}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$

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The magnetic properties of the novel dimeric compound $[\text{Cu}(\text{H}_2\text{O})(\text{OH})(\text{tmen})]_2[\text{Pd}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (tmen=N,N,N',N'-tetramethylethylenediamine) with modulated crystal structure were studied in the temperature range from 95 mK to 300 K. Magnetic measurements revealed a presence of weak antiferromagnetic exchange coupling in the compound. The temperature dependence of specific heat is characterized by the presence of a Schottky-like maximum at 0.47 K and a λ -anomaly at 0.28 K, indicating the formation of long-range order in the system. The comparison of the experimental data with theoretical predictions revealed the presence of antiferromagnetic intradimer exchange coupling $J/k_B = -1.2$ K and interdimer coupling of a similar strength mediated via hydrogen bonds between dimeric units forming a frustrated magnetic zig-zag chain structure.

DOI: [10.12693/APhysPolA.131.940](https://doi.org/10.12693/APhysPolA.131.940)

PACS/topics: 75.30.Et, 76.30.-v, 75.40.-s

1. Introduction

Magnetic interactions in low-dimensional magnets are mediated by superexchange paths built of covalent bonds, but may be mediated by weak intermolecular interactions, e.g. π - π stacking interactions or by hydrogen bonds (HBs). The presence of HBs in supramolecular materials is also important for crystal packing due to the ability to control and direct the assembly of structural building blocks. Consequently, the presence of additional exchange paths through the HBs leads to the creation of complex motifs with alternating or frustrating exchange interactions. Among the different magnetic systems, frustrated spin chains can display interesting properties such as the appearance of spontaneous dimerization, chiral order, and the presence of field-induced spin-density waves depending on the ratio between frustrating and interchain exchange interaction [1–3]. Here we report thermodynamic and magnetic properties of a novel dimeric compound $[\text{Cu}(\text{H}_2\text{O})(\text{OH})(\text{tmen})]_2[\text{Pd}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (abbreviated as CTPC, see crystal structure in Fig. 1), where covalent-bond and HB mediated exchange coexist to form a frustrated spin-chain system.

2. Magnetic and thermodynamic properties

The local symmetry of Cu(II) ions in CTPC has been studied at 2 K by EPR measurements using a Bruker

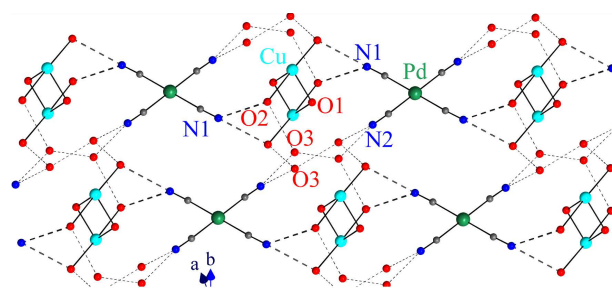


Fig. 1. The mean crystal structure of CTPC. The crystal structure of CTPC is ionic and is composed of dimeric $[\text{Cu}(\text{H}_2\text{O})(\mu\text{-OH})(\text{tmen})_2]^{2+}$ cations, $[\text{Pd}(\text{CN})_4]^{2-}$ anions, and two water molecules of crystallization per formula unit. Due to a unique modulated structure of CTPC, the co-ordination number of the Cu(II) ions varies between 5 (square-pyramidal) and 6 (deformed octahedral) in every 7th dimeric unit due to the occupancy of the water molecules coordinated to Cu(II). This modulation also affects the bond lengths, which vary depending on the coordination number of Cu(II) atom. The HBs network interconnects Cu(OH)₂-Cu dimeric units within the *ac*-plane [4]. The tmen ligands are omitted for the sake of clarity.

ELEXSYS-II E500 X-band spectrometer. The powder spectra are characterized by a typical shape arising from randomly oriented crystallites possessing an axially symmetric *g*-tensor, two contributions with slightly different *g*-factors can be identified. The data have been analyzed using the EasySpin simulation package [5] and the best fit to the data yielded two sets of *g*-factors. Specifically, $g_{\parallel} = 2.197$, $g_{\perp} = 2.089$, and $g_{\parallel} = 2.191$, $g_{\perp} = 2.094$,

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were obtained with abundance ratio of 1:5. This is very close to expected ratio 1:6 taking into account alternation of the square-pyramidal and octahedral coordination in the modulated structure of CTPC. Anisotropic g -factors ($g_{\parallel} > g_{\perp}$) typical for both Cu(II) coordinations indicate that an unpaired electron resides in the $d_{x^2-y^2}$ orbitals along intramolecular bonds. Consequently, exchange paths via the oxygen atoms in the hydroxo groups can be expected, so in the first approximation, CTPC might be considered as an assembly of isolated magnetic dimers ($\text{Cu}-(\text{OH})_2-\text{Cu}$).

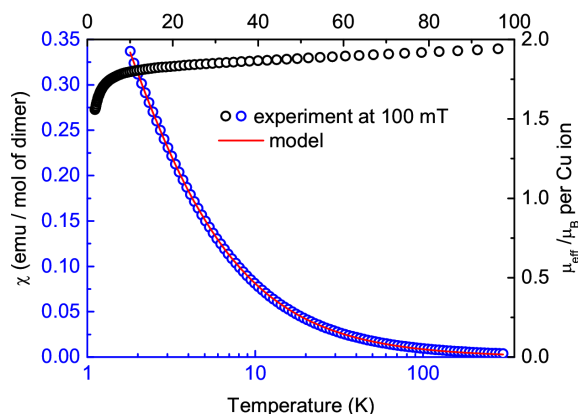


Fig. 2. Temperature dependence of susceptibility (left-bottom axis) and effective magnetic moment (right-top axis) of CTPC (open symbols). The solid line represents fit of interacting dimers model [6].

The temperature dependence of the susceptibility of a nascent polycrystalline sample (determined as the ratio of the magnetic moment and the applied field of 100 mT, measured using a Quantum Design SQUID magnetometer) is characterized by the Curie-like behaviour, but the rapid decrease of effective magnetic moment below 10 K suggests the influence of an antiferromagnetic (AFM) exchange coupling (Fig. 2). Consequently, an estimate of the effective strength of the exchange coupling was obtained by fitting the data ($5 \text{ K} \leq T \leq 100 \text{ K}$) to a Curie-Weiss equation, yielding $\Theta = -1.89 \text{ K}$. Using mean-field approximation for spin 1/2, the effective exchange coupling is calculated as $zJ/k_B = 4\Theta = -7.5 \text{ K}$, where z is the number of the nearest neighbours [7]. Hereafter, the data have been analyzed using a modified Bleaney-Bowers equation, which incorporates weak interdimer interaction J' in the mean-field approximation and the presence of a monomeric impurity [6] with resulting values $J/k_B = -1.19 \text{ K}$, $zJ'/k_B = -0.51 \text{ K}$, $g = 2.15$ and $\rho = 0.07$ (mole fraction of the non-coupled Cu(II) impurity) (see Fig. 2). Despite the good agreement with experimental data, the relatively strong zJ' value (when the condition for the application of mean-field approximation is $zJ' \ll J$) suggests the presence of a more complicated magnetic structure.

With the aim to resolve the magnetic structure, the specific heat of the pellet CTPC powder was investi-

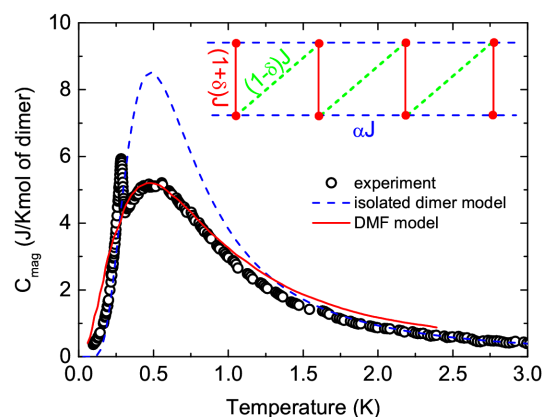


Fig. 3. Temperature dependence of magnetic specific heat of CTPC (open symbols). The solid line represents DMF model [8] sketched in the inset with $J/k_B = -1.2 \text{ K}$, $\alpha = 0.24$, and $\delta = 0$ (for comparison an isolated dimer model is shown by dashed line). The uncertainty of C_{mag} is $\pm 3\%$.

gated in zero magnetic field in the temperature range for $0.095 \text{ K} \leq T \leq 3 \text{ K}$ by using an Oxford Instruments TLE 200 dilution refrigerator. The temperature dependence of the magnetic specific heat of CTPC (Fig. 3) displays a round maximum at $T_{max} = 0.48 \text{ K}$ and a λ -like anomaly, associated with long-range ordering, at 0.28 K . The lattice contribution to the total specific heat was subtracted after fitting the temperature region from 1.5 K to 3 K to the dependence $a/T^2 + bT^3$, where a/T^2 describes the high-temperature expansion of magnetic specific heat and bT^3 represents the low-temperature Debye approximation of the lattice contribution [9]. The best fit was obtained for $a = 1.75 \text{ J mol}^{-1} \text{ K}$ and $b = 0.011 \text{ J mol}^{-1} \text{ K}^{-4}$. Exchange coupling can be estimated from parameter a using De Klerk formula for a Heisenberg magnet [10] within an approximation of non-interacting dimers ($z = 1$) as $|J/k_B| = 1.5 \text{ K}$, which is consistent with the estimates from the magnetic data. The magnetic entropy $S_{mag} = 5.22 \text{ J mol}^{-1} \text{ K}^{-1}$ calculated from the data after subtraction of the lattice contribution represents 91% of the predicted value for a magnetic system with a spin 1/2. The magnetic entropy removed above the ordering temperature represents 75% of the total magnetic entropy suggesting the low-dimensional character of the studied system.

The height of the round maximum $C_{max} = 2.58 \text{ J mol}^{-1} \text{ K}^{-1}$ in the specific heat is only about half of the value theoretically predicted for isolated AFM dimers (see Fig. 3). According to various series expansions for dimerized systems [11, 12], a C_{max} value close to our experimental one is obtained for zJ' values comparable with J , which is also consistent with our susceptibility analysis using the model of interacting dimers. Considering the topology of the covalent and hydrogen bonds, a few different models might be used to describe the experimental results for the specific heat, and a dimerized

frustrated chain (DFC) model [8] was chosen for further analysis. The dimerization (δ) and frustration (α) parameters of the DFC model are defined in the inset sketch of Fig. 3. For $\alpha = 0$, the $\delta = 1$ limit yields the isolated dimer model, with intradimer exchange coupling J , whereas $\delta = 0$ gives the frustrated zig-zag chain. The best agreement with the experimental data was obtained for $J/k_B = -1.2$ K, $\alpha=0.24$, and $\delta=0$, and these parameters suggest the presence of a zig-zag chain presumably formed between dimeric units through cations along the c -axis. Nevertheless, this model may be only approximate when taking into account the modulated structure of CTPC.

For planar dinuclear bis-hydroxo-bridged Cu(II) compounds, an empirical correlation formula is known [13], suggesting strong AFM coupling in CTPC mediated by the Cu–O–Cu exchange bridge. However, as already reported in the literature [14–17], observed exchange couplings may vary considerably due to the presence of even minor structural effects. In the structure of CTPC, one finds the deviation from the planarity of the double Cu–O–Cu bond up to angles of 12° and also the out-of-plane orientation of hydrogen atom from hydroxo group is expected. The influence of an out-of-plane shift of hydrogen atoms in combination with a hinge distortion of double Cu–O–Cu bond may lead to the significant reduction of AFM coupling [16, 17] as observed in our experiments. The presence of relatively strong superexchange mediated by HBs has been also observed in other systems [18, 19]. The origin of the long-range order below 0.28 K can be explained by the presence of dipole–dipole interactions or the existence of additional exchange couplings. Using a simple approach [20], the upper limit of the dipolar coupling between the copper atoms from neighboring zig-zag chains is estimated to be $|J_{dip}/k_B| \approx 3.3$ mK and an ordering temperature of 0.13 K for $J/k_B = -1.2$ K can be calculated [21]. This value is much lower than the experimentally observed position of the λ -like anomaly and suggests the presence of additional weak exchange pathways between zig-zag chains.

3. Conclusions

The analysis of experimental data suggests the presence of a magnetic zig-zag chain structure, where HBs also participate in the exchange pathways with an exchange coupling strength comparable to those mediated by the covalent bonds. The transition to the long-range order observed in the specific heat at 0.28 K can be explained by the interplay of dipolar interaction and the presence of additional weak HBs, suggesting the significant influence of HBs on the magnetic structure of CTPC at sufficiently low temperatures.

Acknowledgments

This work was supported by ERDF EU via ITMS26220120005, VEGA 1/0145/13 and the NSF via DMR-1202033 (MWM), DMR-1157490 (NHMFL), and the State of Florida.

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