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# One Trinuclear Copper(II) Polymer Based on Pyridine-2,4,6-Tricarboxylic Acid: Synthesis, Structure, and Magnetic Analysis[1]

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**Abstract**—The reaction of $CuCl_2 \cdot 2H_2O$ with pyridine-2,4,6-tricarboxylic acid ($H_3Pyta$) in ethanol and water under hydrothermal synthesis conditions leads to the formation of a trinuclear copper polymer $\{[Cu_3(Pyta^{3-})_2(H_2O)_8] \cdot 4H_2O\}n$ (**I**) ($C_{16}H_{28}N_2O_{24}Cu_3$, $Mr = 823.05$, $\rho_{calcd} = 1.955$ g cm$^{-3}$). The polymer was characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis, and X-ray single-crystal diffraction (CIF file CCDC no. 1525203). The result showed that **I** belongs to the monoclinic system, $P2_1/c$ space group. TGA curve shows that polymer **I** first removes water molecules, and then the ligand split for polymer **I**, and the remained residue is CuO. The magnetic measurement reveals the pyridine-2,4,6-tricarboxylic acid as bridge ligand can mediate the antiferromagnetic coupling interaction between magnetic centers.

*Keywords*: pyridine-2,4,6-tricarboxylic acid, polymer, structure, magnetic

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## INTRODUCTION

In recent years, design and synthesis of the paramagnetic transition polymetallic cluster since the discovery of "single-molecule magnets" (SMMs) are attractive to researchers [1–5], and the field of SMMs is developing fast. How to design and synthesize SMMs is the key to magnetic materials. In our previous work [6, 7], we have been reported and studied antiferromagnetic (AF) coupling interaction between magnetic centers.we found that *N*-[(3-pyridine)-sulfonyl]aspartate can act as excellent building blocks with charge and multi-connecting ability in the construction of functional coordination polymers with porosity, photolumineseent or magnetic properties [8, 9]. Generally, there are many factors that affect self-assembly of coordination assemblies: such as chemical structure of the ligands chosen, the coordination geometry preferred by the metals ions, the reaction temperature and the solvent system, the counterions and the methods of crystallization [10–14]. Compared with the previously investigated *N*-[(3-pyridine)-sulfonyl]aspartate ligands, herein, we choosing pyridine-2,4,6-tricarboxylic acid ($H_3Pyta$) as reagent, obtained one trinuclear copper(II) polymer: $\{[Cu_3(Pyta^{3-})_2(H_2O)_8] \cdot 4H_2O\}_n$ (**I**). This polymer was characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis, and X-ray single-crystal diffraction.

## EXPERIMENTAL

**Physical measurements.** All solvents, chemicals and ligand L were commercial reagents and used without further purification. Ligand $H_3Pyta$ was synthesized according to references [15]. Elemental analyses (C, H, and N) were performed with a Perkin-Elmer 240 elemental analyzer. The crystal structure was determined by Agilent supernova diffractometer. The thermal stability of complexes was studied in the range of 45–1000°C under a nitrogen atmosphere with 5°C min$^{-1}$ heating rate on Pyris Daimond TG-DTG Analyzer.

**Synthesis of I.** A mixture of $CuCl_2 \cdot 2H_2O$ (0.0511 g, 3 mmol), $H_3Ptc$ (0.0211 g, 1 mmol), in 7 mL distilled $H_2O$ water and 3 mL ethanol, and adjusted the pH to 7 with 1 mol/L NaOH, and then sealed in a 23 mL Teflon-lined stainless-steel autoclave. The mixture was heated in an oven at 100°C for two days, and cooled to room temperature at a rate of 10°C/h. Blue

[1] The article is published in the original.

**Table 1.** Crystallographic data and refinements of polymer **I**

| Parameter | Value |
|---|---|
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$, Å | 7.100(4) |
| $b$, Å | 18.777(10) |
| $c$, Å | 10.797(6) |
| β, deg | 101.396(9) |
| $V$, Å$^3$; $Z$ | 1397.9(44); 4 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.955 |
| Crystal size, mm | 0.30 × 0.15 × 0.08 |
| μ, mm$^{-1}$ | 2.37 |
| Limiting indices | $-9 \le h \le 8$, $-20 \le k \le 24$, $-11 \le l \le 14$ |
| $F$(000) | 836 |
| θ Range for data collection, deg | 2.9–28 |
| Reflections collected/unique | 8691/2848 |
| $R_{int}$ | 0.023 |
| $R$ ($F^2 > 2\sigma(F^2)$) | 0.028 |
| $wR$ ($F^2$) | 0.084 |
| $S$ | 1.07 |
| $(\Delta/\sigma)_{max}$ | 0.001 |
| $\Delta\rho_{max}/\Delta\rho_{min}$, $e$ Å$^{-3}$ | 0.48/–0.62 |

massive crystal **I** were obtained. The yield was 91% (based on $H_3Ptc$).

| For $C_{16}H_{28}N_2O_{24}Cu_3$ | | | |
|---|---|---|---|
| anal. calcd., % | C, 23.33 | H, 3.40 | N, 3.40 |
| Found, % | C, 23.77 | H, 3.40 | N, 3.48 |

**X-ray crystallography.** Blue massive single crystals of polymer **I** having approximate dimensions of 0.30 × 0.15 × 0.08 mm was mounted on the top of a glass fiber. The diffraction data for polymer **I** were measured on a Bruker APEX-II CCD diffractometer equipped with a graphite-monochromatized Mo$K_\alpha$ radiation (λ = 0.71073 Å) at 293(2) K. A total of 8691 reflections were collected in the range of ($-9 \le h \le 8$; $-20 \le k \le 24$; $-11 \le l \le 14$), of which 2848 are unique ($R_{int}$ = 0.023), and with $I > 2\sigma(I)$ were used in the refinement of the structure of polymer **I**. The anisotropic displacement parameters were applied to all non-hydrogen atoms in full-matrix least-squares refinements based on $F^2$ were performed SHELXL-2013. The structure was solved by direct methods using Olex2 program [16] and refined with Olex2 program [17]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic crystal data and structure processing parameters for polymer **I** are summarized in Table 1. Selected bond lengths and bond angles for polymer **I** are listed in Table 2, hydrogen bonds for polymer **I** are listed in Table 3.

Supplementary material for **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1525203; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

X-ray single-crystal diffraction analysis reveals that the asymmetric unit consists of three $Cu^{2+}$ ions (Fig. 1a), two deprotonated $Pyta^{3-}$ ligand, eight coordinated water molecules, and four free water molecules. There are three separate $Cu^{2+}$ ions and two coordination modes in polymers **I**. The first $Cu^{2+}$ ion coordination mode is that the $Cu^{2+}$ ion is coordinated

**Table 2.** Selected bond lengths (Å) and bond angles (deg) of polymer **I***

| Bond | *d*, Å | Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|---|---|
| Cu(2)—O(2) | 1.958(2) | Cu(1)—O(1) | 2.313(2) | Cu(1)—O(7) | 2.008(2) |
| Cu(2)—O(9) | 2.040(3) | Cu(1)—O(5*B*) | 1.9534(2) | Cu(1)—O(8) | 1.986(2) |
| Cu(2)—O(10) | 2.419(5) | Cu(1)—O(6) | 2.425(2) | Cu(1)—N(1) | 2.038(2) |
| Angle | ω, deg | Angle | ω, deg | Angle | ω, deg |
| O(9)Cu(2)O(2) | 88.77(10) | O(10)Cu(2)O(2) | 83.89(10) | O(5*A*)Cu(1)O(1) | 107.97(7) |
| O(10)Cu(2)O(9) | 84.56(14) | O(10*A*)Cu(2)O(9) | 95.44(14) | O(6)Cu(1)O(1) | 148.62(6) |
| N(1)Cu(1)O(6) | 73.56(7) | O(8)Cu(1)O(7) | 177.56(8) | O(6)Cu(1)O(5*A*) | 103.01(7) |
| N(1)Cu(1)O(7) | 92.31(8) | N(1)Cu(1)O(1) | 75.42(7) | O(7)Cu(1)O(1) | 88.95(9) |
| N(1)Cu(1)O(8) | 89.85(8) | N(1)Cu(1)O(5*B*) | 176.55(7) | O(7)Cu(1)O(5*A*) | 87.15(8) |
| | | | | O(7)Cu(1)O(6) | 87.69(8) |
| | | | | O(8)Cu(1)O(1) | 90.49(9) |
| | | | | O(8)Cu(1)O(5*A*) | 90.76(8) |
| | | | | O(8)Cu(1)O(6) | 94.01(8) |

* Symmetry codes: (*A*) $x, -y + 1/2, z - 1/2$.

**Table 3.** Geometric parameters of hydrogen bonds of structure **I**

| D—H···A | Distance, Å | | | Angle D—H···A, deg |
|---|---|---|---|---|
| | D—H | H···A | D···A | |
| O(7)—H(7*B*)···O(11*D*) | 0.85(1) | 1.94(2) | 2.737(3) | 157(3) |
| O(8)—H(8*A*)···O(11*E*) | 0.84(1) | 1.91(1) | 2.749(3) | 175(3) |
| O(8)—H(8*B*)···O(4*F*) | 0.85(1) | 1.88(1) | 2.719(3) | 171(3) |
| O(9)—H(9*A*)···O(4*G*) | 0.85(1) | 1.89(2) | 2.691(3) | 157(4) |
| O(9)—H(9*B*)···O(12) | 0.85(1) | 1.99(2) | 2.817(4) | 163(5) |
| O(10)—H(10*A*)···O(1*A*) | 0.85(1) | 1.89(4) | 2.662(4) | 150(6) |
| O(11)—H(11*A*)···O(3) | 0.85(1) | 1.91(1) | 2.757(3) | 175(3) |
| O(11)—H(11*B*)···O(12*H*) | 0.85(1) | 2.00(1) | 2.830(4) | 169(4) |

* Symmetry codes: (*A*) $-x + 1, -y + 1, -z$; (*B*) $x, -y + 1/2, z - 1/2$; (*D*) $-x + 1, y - 1/2, -z + 1/2$; (*E*) $-x, y - 1/2, -z + 1/2$; (*F*) $-x, -y + 1, -z + 1$; (*G*) $x, y, z - 1$; (*H*) $-x, -y + 1, -z$.

by one nitrogen atom (N(1)) and three oxygen atoms (O(1), O(6),O(5*B*)) (symmetry code: (*B*) $x, -y + 1/2, z - 1/2$) from deprotonated $Pyta^{3-}$ ligand and two coordinated water molecules (O(7), O(8)). The another $Cu^{2+}$ ion coordination mode is that the $Cu^{2+}$ ion in **I** is coordinated by six oxygen atoms (O(2), O(2*B*)) are from two different deprotonated $Pyta^{3-}$ ligand and O(9), O(9*A*), O(10), O(10*A*) (symmetry code: (*A*) $-x + 1, -y + 1, -z$) are from four coordinated water molecules). The center $Cu^{2+}$ ions in **I** are six-coordinated. For polymer **I**, the Cu—O distances fall in the range of 1.9536(19) to 2.425(2) Å (the distances of Cu(1)—O(1) 2.313(2), Cu(1)—O(5) 1.9536(19), Cu(1)—O(6) 2.425(2), Cu(1)—O(7) 2.008(2), Cu(1)—O(8) 1.986(2), Cu(2)—O(2) 1.958(2), Cu(2)—O(9) 0.2040(3), Cu(2)—O(10) 2.419(5) Å). The Co—N distance is 2.038(2) Å. These bond distances all fall in the normal ranges [18, 19].

In polymer **I** , the five coordination sites on the ligand all are involved in the coordination. So, the $H_3Pyta$ ligand adopts a $\mu_5$-$\eta^1$:$\eta^2$:$\eta^2$ bridging style to participate in coordination. Two O atoms from carboxyl of ligand are coordinated with two $Cu^{2+}$ ions, so

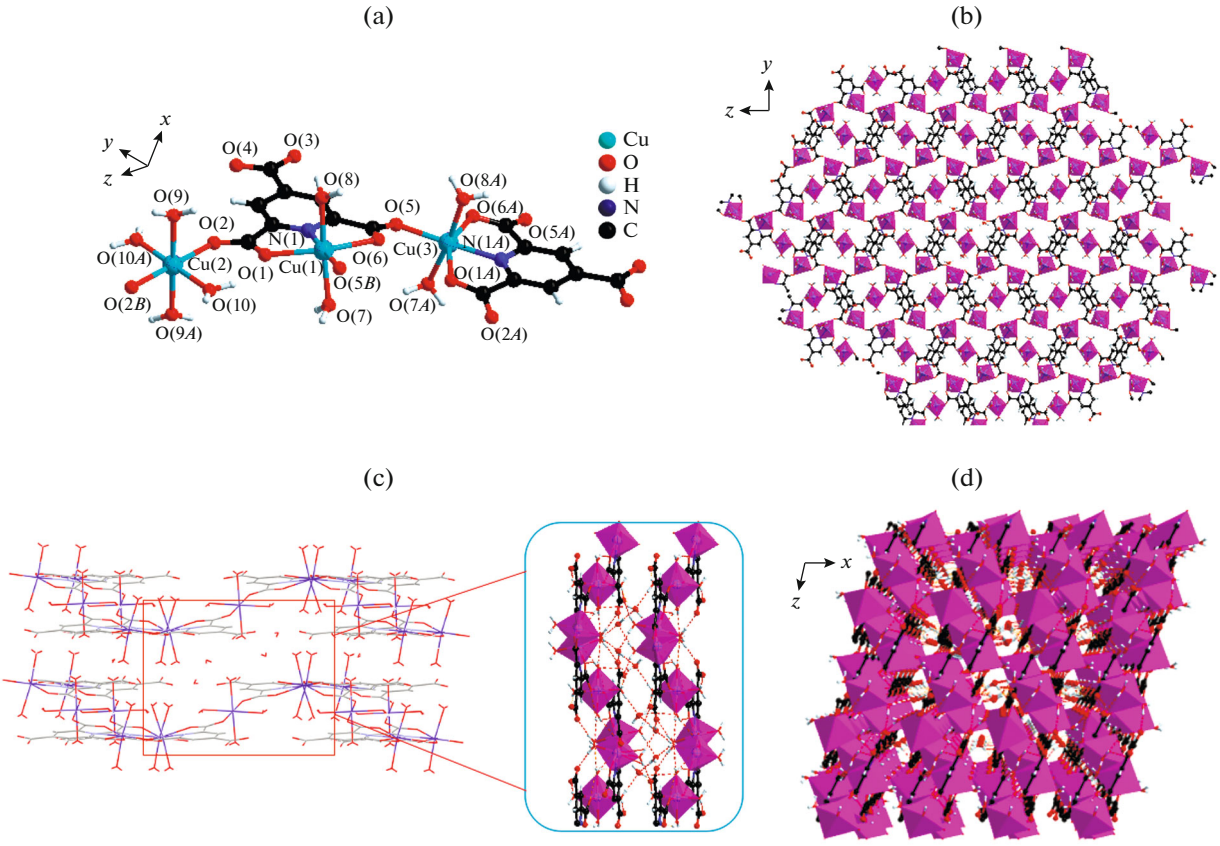


**Fig. 1.** The coordination environment of $Cu^{2+}$ ions in **I** with thermal ellipsoids at 50% level (a); 2D network structure of polymer **I** along *x* axis (b); hydrogen bonds in **I** (c); by hydrogen bonds formed 3D structure (*y* axis) (d).

carboxyl adopts a $\mu_2$-$\eta^1$:$\eta^1$ bridging style to participate in the coordination. As the ligand adopts a $\mu_5$-$\eta^1$:$\eta^2$:$\eta^2$ bridging style and carboxyl takes a $\mu_2$-$\eta^1$:$\eta^1$ bridging style, the polymers **I** exhibits a very special two-dimensional network structure along a axis (Fig. 1b). Owing to the introduction of water molecules, polymer **I** had a large number of hydrogen bonds. It not only has intramolecular hydrogen bonds, but also have intermolecular hydrogen bonds. The O atom in carbonyl group on the ligand formed O–H···O intramolecular hydrogen bonds with coordinated water molecules and between coordinated water molecules. These four free water molecules in polymer **I** formed O–H···O intermolecular hydrogen bonds with coordinated water molecules (Fig. 1c). These hydrogen bonds finally generating a three-dimensional network structure along *y* axis by intermolecular hydrogen bonds Bridge two two-dimensional planes (Fig. 1d).

The IR spectral data of the polymer **I** and the ligand are shown in Fig. 2. There are indications that broad bands in the range of 3442 $cm^{-1}$ can be assigned to the stretching frequency of the intermolecule hydrogen bond between atom O and H of the free ligand and polymer **I**. The ν(C=O) carbonyl group of the free ligand at 1747 $cm^{-1}$ was shifted to lower frequency (1630 $cm^{-1}$) in the polymer **I**, also indicating the O atom of the carbonyl group participation coordination [20]. The polymer **I** showed two new strong bands at 1272 and 1036 $cm^{-1}$ which may be assigned to the ν(C–N) stretching frequencies. The peaks observed at 453 $cm^{-1}$ can be assigned to ν(Cu–O), probably originating from the coordination of the ligand [21].

In order to check the purity of polymer **I**, powder X-ray diffraction of the as-synthesized sample was measured at room temperature. The peak positions of experimental patterns are in good agreement with the simulated ones, which clearly indicates good purity of the polymer **I** (Fig. 3).

The thermal stability of polymer **I** was tested in the range of 45–1000°C under a nitrogen atmosphere at a heating rate of 5°C $min^{-1}$ for Pyris Daimond TG-

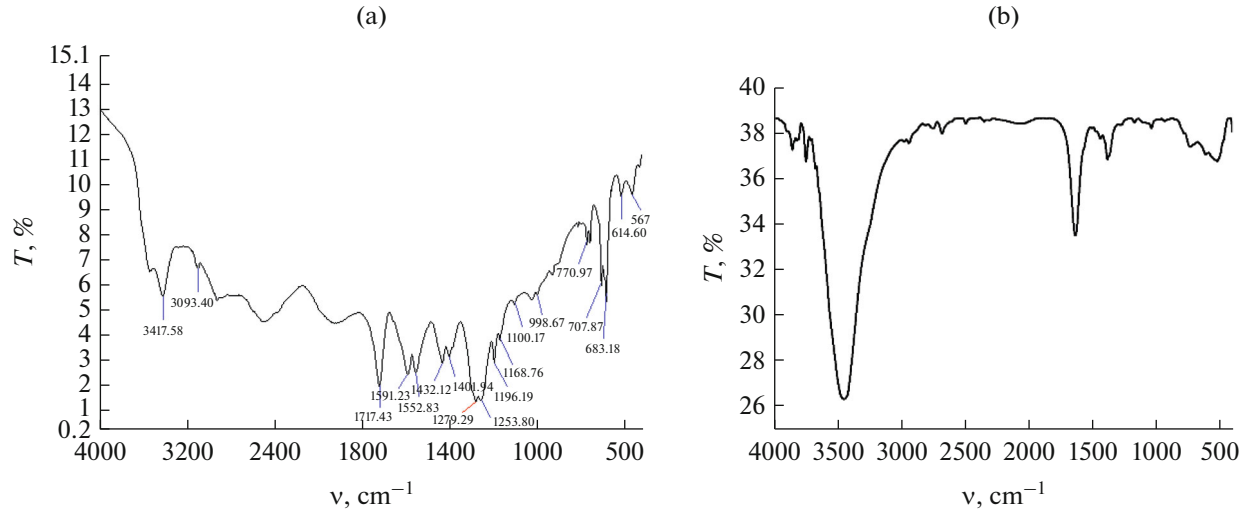


**Fig. 2.** IR spectra of free ligand (a) and **I** (b).

DTG Analyzer. The thermal gravimetric analysis curve for polymer **I** was shown in Fig. 4. The TGA curve show that the **I** first loses twelve water molecules (obsd. 23.52%, calcd. 23.75%) in the range of 45° to 123°; further weight loss, responsible for all organic components in the range of 123° to 503°; the last remaining amount of 28.79% CuO.

Polymer **I** is a $Cu^{2+}$ ($d^9$) polymer having unpaired electrons, so its magnetic properties are studied. The molar magnetic susceptibilities ($\chi_m$) of **I** were measured in the 2–300 K temperature range, and shown as $\chi_m$ and $\chi_m T$ versus $T$ plots. As seen in Fig. 5, the molar magnetic susceptibility $\chi_m$ of polymer **I** increases gradually as the temperature lowers, and more rapidly increases below 25 K, then reaches a maximum value of 0.67 $cm^3\ mol^{-1}$ at 2 K. It can be seen from the $\chi_m T$ curve that the $\chi_m T$ value is 2.04 $cm^3\ mol^{-1}$ K at 300 K, which is significantly higher than the theoretical value 1.88 $cm^3\ mol^{-1}$ K of the high-spin triplet $Cu^{2+}$ ($J$ = 4.92 $cm^{-1}$, $g$ = 2.02), indicating a great spin-orbit coupling contribution. As the decrease of temperature, the $\chi_m T$ began to decrease slowly, and the decrease in the range of 300–25 K could be attributed to the single ion behavior of $Cu^{2+}$, but more rapidly reduction below 25 K, then reaches a minimum value of 1.34 $cm^3\ mol^{-1}$ K at 2 K. Combined with the decrease in the $\chi_m T$ value when cooling, this result indicates the presence of weak AF interactions in polymer **I** [22]. At 300 K, $\chi_m T$ = 2.04 $cm^3\ mol^{-1}$ K, the magnetic moment ($\mu_{eff}$) of copper(II), which is determined by

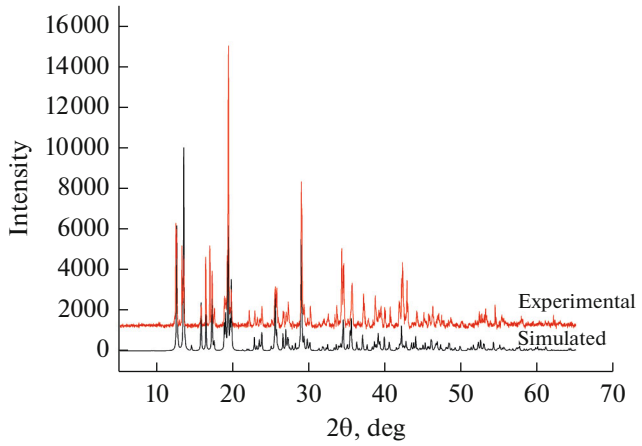


**Fig. 3.** The powder diffraction of polymer **I**.

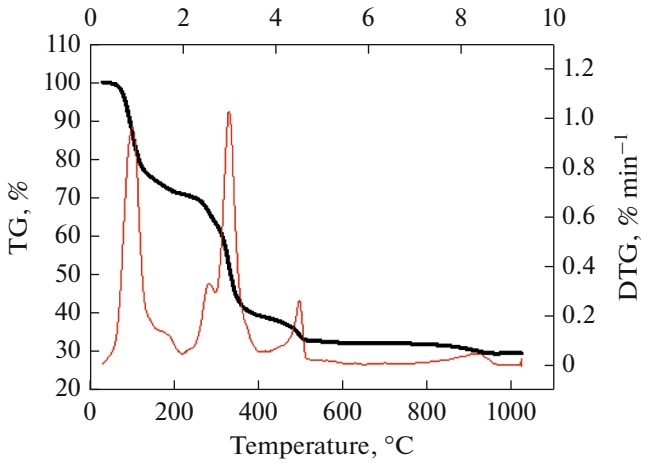


**Fig. 4.** The TGA for **I**.

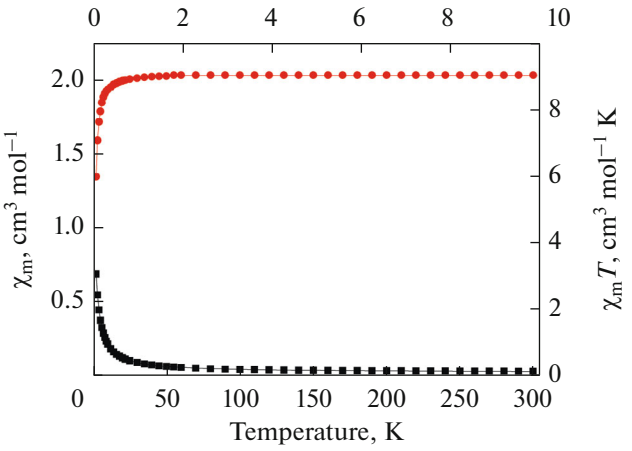


**Fig. 5.** $\chi_m$, $\chi_m T$ vs. $T$ of polymer **I**.

the equation $\mu_{eff} = 2.828\ (\chi_m T)^{1/2}$, reaches the peak value of 4.04 $\mu_B$. This value is slightly higher than that expected for an isolated divalent high-spin Cu(II) system with $\mu_{eff} = 1.88\ \mu_B$.

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