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COPPER(II) MALONATE COORDINATION FRAMEWORKS WITH AMINO-1,2,4-TRIAZOLE: CRYSTAL STRUCTURES AND MAGNETIC PROPERTIES OF $[\text{Cu}_2(\text{mal})_2(\text{datz})_2(\text{H}_2\text{O})] \cdot 5\text{H}_2\text{O}$ AND $[\text{Cu}_2(\text{mal})_2(\text{atz})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ **E.N. Nfor¹, E.A. Eno², J.N. Foba-Tendo¹, G.E. Iniama², E.O. Duke², O.E. Offiong²**¹*Department of Chemistry, University of Buea, Buea, SWR, Cameroon, e-mail: nforemman@gmail.com*²*Department of Pure and Applied Chemistry, University of Calabar, Calabar, CRS, Nigeria*

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Two new malonato-bridged copper(II) complexes of the composition $[\text{Cu}_2(\text{mal})_2(\text{datz})_2(\text{H}_2\text{O})] \cdot 5\text{H}_2\text{O}$ (**1**) and $[\text{Cu}_2(\text{mal})_2(\text{atz})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (**2**) (mal = malonate, atz = 4-amino-1,2,4-triazole, datz = 3,5-diamino-1,2,4-triazole) are prepared and characterized by X-ray crystal structure determination and magnetic studies. The environment of each copper atom in **1** and **2** has distorted square pyramidal and octahedral geometries. The intrachain copper-copper separation is 6.305 Å and 3.640 Å across the carboxylates and triazoles bridges respectively for complexes **1** and **2**. The magnetic properties of **1** and **2** are investigated in the temperature range 2–300 K. The overall antiferromagnetic behavior is observed in both cases.

Keywords: malonate, 1,2,4-triazole, carboxylate, crystal structures, magnetic properties.**INTRODUCTION**

Multidimensional coordination polymers have recently gained great attention due to their fascinating magnetic [1], electronic [2], optical [3], and catalytic [4] properties as well as their structurally aesthetic motifs. The investigation of novel inorganic-organic hybrid framework assemblies represents one of the most active areas of materials science and chemical research [5]. In particular, the metal-carboxylate chemistry represents a potential source for the synthesis of multidimensional frameworks due to the versatility of the carboxylate group(s) to act as both linker(s) and spacer(s) between metal ions [6]. The pore size and performance of these frameworks depends on the combination of metal and linker, as well as the structure in which they are connected. In some cases, the pores are stable to elimination of guest molecules (often solvents) and can be used for the storage of gases such as hydrogen and carbon dioxide. Consequently, metal-organic frameworks are promising materials in areas such as gas purification, gas separation, gas storage (other than hydrogen), and heterogeneous catalysis because of their shape, size selectivity, and accessible bulk volume.

The most commonly used strategy to obtain the extended structures is to employ appropriate bridging ligands that are capable of binding to several metal centers through direct bond formation. Much of the current effort on such extended hybrid metal organic complexes is directed towards synthesizing interesting frameworks using polycarboxylates [7–12] due to thermal stability. These polycarboxylates may exhibit versatile coupling to mediate magnetic interactions owing to their different coordination modes, i.e., *syn*–*syn*, *anti*–*syn*, *anti*–*anti*, etc., accomplishing the transmission of magnetic coupling to different degrees [9].

1,2,4-Triazole and its derivatives are very interesting bridging ligands, and these ligands could provide a 1,2 bridging form; in addition, 4-unsubstituted 1,2,4-triazole also has a 2,4-bridging fashion that is similar to the 1,3-imidazolate bridging found in enzyme [13]. In this paper, we report the syn-

thesis, single crystal X-ray diffraction analysis, and variable temperature (300—2 K) magnetic behavior of two new mixed-ligand copper(II) malonate complexes with 4-amino-1,2,4-triazole (**1**) and 3,5-diamino-1,2,4-triazole (**2**).

EXPERIMENTAL

Materials and physical measurements. All reagents were of analytical grade and were used without purification. Elemental analysis for C, H, and N was performed on a Perkin-Elmer 240C analyzer. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 400—4000 cm^{-1} region. Variable-temperature magnetic susceptibility and field dependence of magnetization were measured on a Quantum Design MPMSXL-5 SQUID system. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables) [1].

Synthesis of $[\text{Cu}_2(\text{mal})_2(\text{atz})_2(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (1**).** A methanol solution (10 ml) of 4-amino 1,2,4-triazole (210 mg; 2.5 mmol) was added to a warm aqueous solution (20 ml) of copper sulfate pentahydrate (625 mg; 2.5 mmol). Potassium malonate (generated *in situ* by the reaction of stoichiometric amounts of malonic acid and potassium carbonate) dissolved in water (2.5 mmol; 10 ml) was added to the previously warm purple-blue solution under continuous stirring for four hours and then filtered. The filtrate was left to evaporate slowly at room temperature and a week later blue there formed crystals of the complex suitable for the X-ray analysis. Yield 80 %. Anal. Calcd.: C, 19.20; H, 3.69; N, 17.92. Found; C, 19.20; H, 3.69; N, 17.92 %. Main IR absorption bands (KBr, cm^{-1}): 3444, 3313, 1524, 1201.

Synthesis of $[\text{Cu}_2(\text{mal})_2(\text{datz})_2(\text{H}_2\text{O})] \cdot 5\text{H}_2\text{O}$ (2**).** Solid copper(II) basic carbonate (221 mg; 1 mmol) was added to an aqueous solution (20 ml) of malonic acid (280 mg; 2 mmol) with constant stirring. This solution was filtered and mixed with an aqueous (30 ml) solution of 3,5-diamino-1,2,4-triazole (991 mg; 1 mmol) under stirring. The resulting solution was filtered and the filtrate was allowed to crystallize at room temperature. Single crystals of the complex suitable for the X-ray diffraction measurement were obtained within a week. Yield 80 %. Anal. Calcd.: C, 19.97; H, 3.69; N, 23.29. Found; C, 19.97; H, 3.69; N, 23.29 %. Main IR absorption bands (KBr, cm^{-1}): 3402, 3319, 3115, 1639, 1496, 1405.

X-ray crystallography. The crystal structure determination by X-ray diffraction was performed on a Bruker Nonius Kappa CCD diffractometer equipped with a normal focus of 24 KW sealed tube X-ray source [MoK_α radiation, $\lambda = 0.7103 \text{ \AA}$] operating at 50 kV and 40 mA. A hemisphere of intensity data was collected in 2202 frames with ω scans (width of 0.30 and exposure time of 10 sec per frame) in the θ range from 1.00° to 27.48° . The total data collected were reduced using the SCALEPACK program and the orientation matrix along with the detector and the cell parameters were refined for every 50 frames on all measured reflections. The structures were solved by SIR92, which readily revealed the positions of heavy atoms [Cu, O] and enabled the location of other non-hydrogen positions from the difference Fourier maps. All the hydrogen positions were found in the difference Fourier maps. For the final refinement, hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of the refinement included atomic positions, anisotropic thermal parameters for non-hydrogen atoms, and isotropic parameters for all hydrogen atoms. Full matrix least-squares on $[F^2]$ was done using the SHELXL-97 program included in the WINGX package of programs. All crystallographic data are summarized in Table 1. The final geometrical calculations and graphical manipulations were carried out with PARST-97 and PLATON programs. Selected bond lengths and bond angles are given in Table 2. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC No 802201 for **1** and CCDC No 802200 for **2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK.(fax:+44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Magnetic susceptibility measurements. The measurements of magnetic susceptibilities on powder samples were carried out with a Quantum Design MPMS-XL SQUID magnetometer in the 1.8—300 K range. The applied magnetic field was 2 kG, and the data were corrected for diamagnetism using

Table 1

Crystal data and structure refinement for complexes **1** and **2**

Compound	1	2
Empirical formula	C ₁₀ H ₂₀ Cu ₂ N ₁₀ O ₁₂	C ₂₀ H ₅₂ Cu ₄ N ₁₆ O ₃₀
<i>FW</i>	599.44	1250.94
<i>T</i> , K	293(2)	293(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
Wavelength, Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Unit cell dimensions: <i>a</i> , <i>b</i> , <i>c</i> , Å;	11.596(2), 11.263(2), 16.742(3);	8.0706(16), 10.475(2), 13.687(3);
α, β, γ, deg.	—, 96.53(3), —	91.85(3), 90.37(3), 101.29(3)
<i>V</i> , Å ³	2172.3(8)	1134.1(4)
<i>Z</i>	4	1
<i>d</i> _x , g/cm ⁻³	1.833	1.832
μ, mm ⁻¹	2.039	1.964
<i>F</i> (000)	1216.0	640.0
Crystal size, mm	0.18×0.20×0.15	0.15×0.15×0.30
θ range, deg.	27.480	27.440
Index range (<i>h</i> , <i>k</i> , <i>l</i>)	15, 14, 21	10, 13, 17
Reflection collected / Independent reflections (<i>R</i> _{int})	21174 / 4080(0.0568)	21943 / 3181(0.0445)
Absorption correction	None	None
Data / restraints / parameter	4080 / 0 / 292	3181 / 0 / 502
Goodness-of-fit on <i>F</i> ²	1.110	1.199
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0374, <i>wR</i> 2 = 0.1098	<i>R</i> 1 = 0.0455, <i>wR</i> 2 = 0.1533

Table 2

Selected bond lengths *d* (Å) and bond angles ω (deg.) for complexes **1** and **2**

Bond lengths	<i>d</i>	Bond angles	ω	Bond lengths	<i>d</i>	Bond angles	ω
1				2			
Cu(1)—O(4)	1.940(2)	O(4)—Cu(1)—O(1)	88.36(9)	Cu(1)—O(4)	1.928(5)	O(4)—Cu(1)—O(1)	90.55(10)
Cu(1)—O(1)	1.959(2)	O(4)—Cu(1)—N(1)	87.50(10)	Cu(1)—O(1)	1.942(6)	O(4)—Cu(1)—N(1)	86.19(10)
Cu(1)—N(1)	1.984(2)	O(7)—Cu(1)—N(1)	36.15(8)	Cu(1)—N(6)	2.006(6)	O(4)—Cu(1)—N(6)	87.42(13)
Cu(1)—N(7)	1.989(2)	O(1)—Cu(1)—N(7)	93.04(9)	Cu(1)—N(2)	2.006(5)	N(1)—Cu(1)—N(6)	95.53(10)
Cu(2)—O(9)	2.426(3)	N(1)—Cu(1)—N(7)	94.68(9)	Cu(1)—O(5)	2.402(7)	O(4)—Cu(1)—O(5)	90.26(10)
		O(7)—Cu(1)—O(4)#1	83.61(9)	Cu(1)—O(8)	2.582(8)	O(1)—Cu(1)—O(5)	94.51(10)
Cu(2)—O(2)	2.491(2)	O(8)—Cu(2)—O(5)	55.29(8)	Cu(2)—O(6)	1.922(6)	N(1)—Cu(1)—O(8)	103.45(10)
Cu(2)—O(8)	1.970(2)	O(9)—Cu(2)—N(6)	88.47(8)	Cu(2)—O(9)	1.951(6)	N(6)—Cu(1)—O(8)	82.32(10)
Cu(2)—N(2)	2.001(2)	N(2)—Cu(2)—N(6)	92.57(8)	Cu(2)—N(1)	1.994(6)	O(9)—Cu(2)—N(2)	87.29(10)
Cu(2)—N(6)	1.998(2)	O(9)—Cu(2)—O(5)	86.52(10)	Cu(2)—N(5)	2.026(6)	O(6)—Cu(2)—N(5)	85.87(10)
Cu(2)—O(5)	1.952(3)	O(2)—Cu(2)—O(5)	84.68(9)	Cu(2)—O(10)	2.364(7)	N(2)—Cu(2)—N(5)	95.98(10)
		N(2)—Cu(2)—O(9)	88.47(9)			N(2)—Cu(2)—O(10)	94.39(10)
						N(5)—Cu(2)—O(10)	91.00(10)

Symmetry transformations used to generate equivalent atoms: #1 *x*, $-y+1/2$, $z+1/2$; #2 *x*, $-y+1/2$, $z-1/2$.

Pascal's constants and the temperature-independent paramagnetism estimated at 60×10^{-6} emu/mol per Cu(II) ion.

RESULTS AND DISCUSSION

The coordination environment of the Cu(II) ion with the atom numbering scheme of **1** is shown in Fig. 1.

The structure of **1** consists of a tetranuclear core with a centre of inversion. There are two independent copper atoms: Cu1 and Cu2. The two Cu(II) ions are crystallographically independent with Cu1 exhibiting a five-coordinate, distorted square-pyramidal geometry. The basal plane is occupied by two nitrogen atoms from two 3,5-diamino-1,2,4-triazole ligands, two carboxylate oxygen with the apical position occupied by an O2A oxygen atom from malonate of another tetranuclear unit. The Cu1 atom is shifted by 0.104(3) Å above the mean square plane defined by the O1, O4, N1, N7 set towards the apical position. The Cu2 exhibits a six coordinate, distorted (4+2) octahedral geometry with the equatorial plane built by two nitrogen atoms from two 3,5-diamino-1,2,4-triazole at Cu2—N2 = 2.001(2) Å, Cu2—N6 = 1.998(2) Å and two malonate oxygen atoms Cu2—O5 = 1.952(2) Å, Cu2—O8 = 1.970(2) Å. The apical positions are occupied by malonate oxygen from a symmetrically equivalent dimer O2, and oxygen of a water molecule [Cu2—O2 = 2.491(2) Å, Cu2—O9 = 2.426(3) Å respectively]. The dihedral angle between the N₂O₂ equatorial planes is 73.28(6)°. The structural framework can be viewed as a dimer of the dinuclear unit of Cu1 and Cu2 and its symmetrical equivalence connected by the axial carboxylate oxygen bond [Cu2—O2].

The 3,5-diamino-1,2,4-triazole ligand behaves as a bidentate ligand, linking the Cu(II) ions through the N1 and N7 nitrogen atoms which subtend the angles of 94.68(9), 92.57(8)° [for N1—Cu1—N7 and N2—Cu2—N6] for Cu1 and Cu2 respectively. Triazoles are significantly folded, with a dihedral angle of 58.04(1)° between the triazolate ring planes. The two malonate ligands exhibit an *envelope* conformation and simultaneously adopt a bidentate orientation within the dinuclear unit and *bis-monodentate* coordination mode that links two dinuclear units into a tetramer and through O2 to Cu1 in the chain. In addition, the carboxylate bridges exhibit *anti—anti* conformation; they connect an equatorial site of one copper atom with an apical site of the adjacent copper atom, i.e (i) (Cu(1)—O7d—C(10d)—O(8d)—Cu(2d) along the chain and (ii) Cu1—O4—C5—O2—Cu2 within a tetranuclear unit.

The Cu...Cu separation is 3.640 Å across the triazolate bridge, while a distance of 6.305 Å is observed across the carboxylate bridges. The angles subtended at the metal centers by the chelating malonate groups are 46.12(9)° for Cu1 and 94.56° for Cu2. The average C—O bond distance and the O—C—O bond angle are 1.251(3) Å and 121.48(3)° respectively. These values have been reported for other Cu(II) malonate chelates [7b, 14, 15]. Both intra- and intermolecular hydrogen bonds are operative in this complex, thus increasing the dimensionality.

The temperature dependence of the magnetic susceptibility of **1** in the form of $\chi_M T$ versus T plots is shown in Fig. 2. At 300 K $\chi_M T$ is 0.77 cm³·mol⁻¹·K, a value that is as expected for two magnetically isolated spin doublets [10]. This value gradually decreases upon cooling from room temperature to attain a value of 0.0105 cm³·mol⁻¹·K at 3.6 K. This curve reveals the occurrence of an overall anti-ferromagnetic coupling in this complex [16].

The structure of this compound reveals that the main superexchange pathway, by which the Cu(II) atoms are antiferromagnetically coupled, is through the double bridging triazole ligand. Furthermore, there exists an additional superexchange pathway; the Cu(II) centers are bridged by carboxylate groups exhibiting *anti—anti* co-

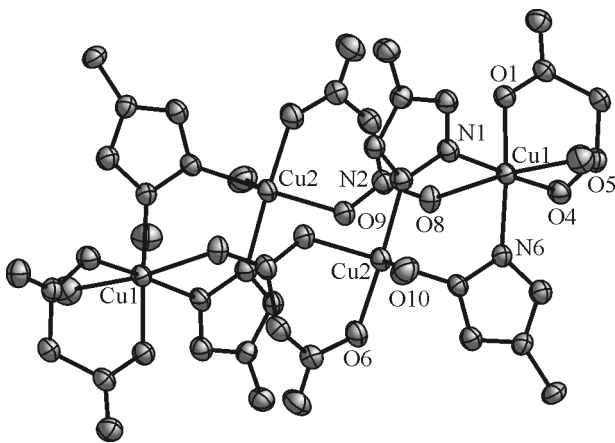


Fig. 1. ORTEP drawing of aqua bis(μ -3,5-diamino-1,2,4-triazole-malonato)copper(II) trihydrate [Cu₂ × (C₃H₂O₄)₂(C₂N₃H₃)₂(H₂O)] · 3H₂O showing the atom labeling scheme. The lattice water molecules and hydrogen atoms are omitted for clarity

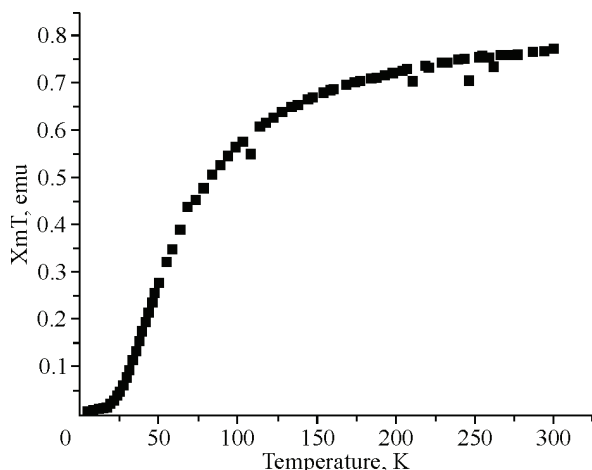


Fig. 2. Magnetic susceptibility curve for aqua bis(μ -3,5-diamino-1,2,4-triazole-malonato)copper(II) trihydrate $[\text{Cu}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{C}_2\text{N}_5\text{H}_5)_2 \times (\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$

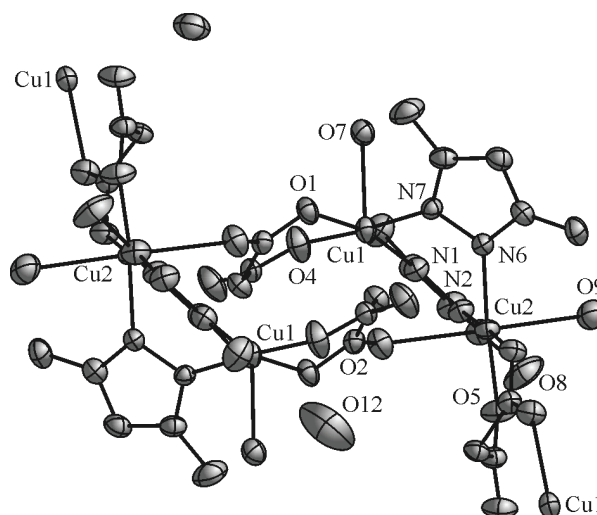


Fig. 3. Tetranuclear unit of bis(aqua)[μ -4-amino-1,2,4-triazole-valonato]copper(II) pentahydrate $[\text{Cu}_2 \times (\text{C}_3\text{H}_2\text{O}_4)_2(\text{C}_2\text{N}_4\text{H}_4)(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$ showing atom labeling. The hydrogen atoms are omitted for clarity

ordination modes at distances 6.228 Å and 6.305 Å. Although both conformations are able to mediate a significant magnetic coupling among paramagnetic centers, the latter pathway gives much weaker interactions than the former. In view of the above, the bis(μ -3,5-diamino-1,2,4-triazole-malonato)copper(II) trihydrate complex can be described as triazole-bridged Cu(II) chains linked through *anti*–*anti* carboxylate groups.

The structure of **2** with the atom numbering scheme is shown in Fig. 3. The asymmetric unit of the complex contains two crystallographically independent Cu(II) cations, as in Fig. 3 below. The Cu...Cu separations across the double triazole bridge is 3.938 Å, which is slightly longer than the Cu...Cu separation of 3.640 Å in bis-(μ -3,5-diamino-1,2,4-triazole-malonato)copper(II) trihydrate above and 3.564 Å in $\text{Cu}^{\text{I}}(\text{admtrz})\text{SCN}$ [17], but comparable to 3.937(1) Å in bis(μ -1,2,4-triazole- $\kappa^2\text{N}^1:\text{N}^2$)bis[*diaqua*-(oxalato- $\kappa^2\text{O},\text{O}'$)copper(II)] [18] that also features the dinuclear $\text{N}',\text{N}^1,\text{N}^2,\text{N}$ double bridging coordination mode with an additional bridging oxalato co-ligand.

The Cu1 atom has a six coordinate, distorted (4+2) octahedral geometry with the equatorial plane built by two nitrogen atoms from two 4-amino-1,2,4-triazole at Cu1—N1 = 2.023(6) Å and Cu1—N6 = 2.006(6) Å with two chelating malonate oxygen atoms (Cu1—O1 = 1.942(6) Å, Cu—O4 = 1.928(5) Å). The apical positions are filled by monodentate malonate oxygen from a symmetrically equivalent dimer O8, and oxygen from a water molecule [Cu1—O8 = 2.582(8) Å, Cu1—O5 = 2.402(7) Å respectively]. The Cu2 atom exhibits a five coordinate, distorted square pyramidal geometry with the basal plane occupied by two nitrogen atoms from two 4-amino-1,2,4-triazole ligands (Cu2—N2 = 1.994(6) Å, Cu2—N5 = 2.020(6) Å), and two chelating carboxylate oxygen atoms (Cu2—O6 = 1.922(6) Å, Cu2—O9 = 1.951(6) Å). The apical position is occupied by an oxygen atom from a water molecule (Cu2—O10 = 2.364(7) Å). The Cu1 atom is shifted by 0.104(3) Å above the mean square plane defined by the O1, O4, N1, N6 set towards the apical position. The dihedral angle between the N_2O_2 equatorial planes is 73.28(6)°. As in bis(μ -3,5-diamino-1,2,4-triazole-malonato)copper(II) trihydrate above, the structural framework can be viewed as dimers of the dinuclear unit of Cu1 and Cu2 and its symmetrical equivalence connected by the axial carboxylate oxygen bond [Cu1—O8].

The 4-amino-1,2,4-triazole ligand acts as bidentate ligands linking the Cu(II) ions through N1, N2 and N5, N6 nitrogen atoms and subtends the angles of 95.53(2)° and 95.98(2)° [for N1—Cu1—N6 and N2—Cu2—N5] for Cu1 and Cu2 respectively. Triazoles are significantly folded, with a dihedral angle of 58.04(1)° between the triazolate ring planes.

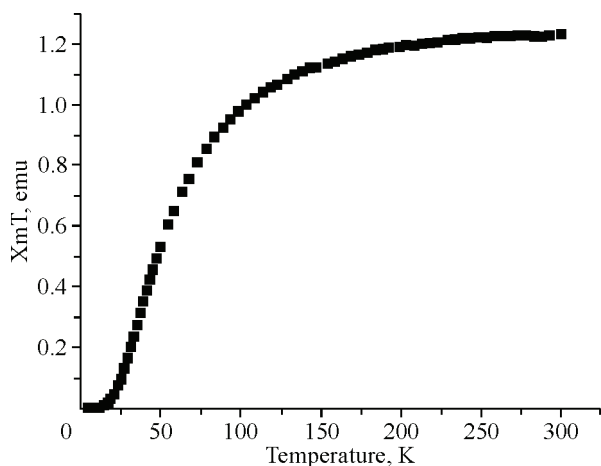


Fig. 4. Magnetic susceptibility curve for bis(aqua)[μ -4-amino-1,2,4-triazole-malonato]copper(II) pentahydrate [$\text{Cu}_2(\text{C}_3\text{H}_2\text{O}_4)_2(\text{C}_2\text{N}_4\text{H}_4)(\text{H}_2\text{O})_2$] $\cdot 5\text{H}_2\text{O}$

The two malonate ligands exhibit an *envelope* conformation, simultaneously adopting a bidentate orientation within the dinuclear unit and monodentate coordination modes [through O6 to Cu1], that links two dinuclear units into a tetramer. In addition, the carboxylate bridges exhibit *anti-anti* conformation; they connect an equatorial site of one copper atom with an apical site of the adjacent copper atom [Cu(1)—O(8)—C(10)—O(9)—Cu(2) = 5.771 Å] within a tetranuclear unit.

The magnetic properties of bis(aqua)[μ -4-amino-1,2,4-triazole-malonato]copper(II) pentahydrate in the form of $\chi_{\text{M}}T$ versus T plots (χ_{M} being the magnetic susceptibility per four Cu(II) ions) is shown in Fig. 4. The product $\chi_{\text{M}}T$ at 300 K is $1.232 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, a value which is somewhat below that expected for four magnetically isolated spin doublets ($1.65 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ with $g \sim 2.10$) [19]. Upon cooling, the $\chi_{\text{M}}T$ value for the complex decreased continuously to $0.009 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at a temperature of 3.0 K. This curve reveals the occurrence of an overall antiferromagnetic coupling in this complex [20]. The structure of this compound reveals that the main superexchange pathway, by which the Cu(II) atoms are antiferromagnetically coupled, is through the double bridging triazole ligand. Furthermore, there exists an additional superexchange pathway; the Cu(II) centers are bridged by carboxylate groups exhibiting *anti-anti* coordination modes at distances of 6.228 Å and 6.305 Å. Although both conformations are able to mediate a significant magnetic coupling among the paramagnetic centers, the latter pathway gives much weaker interactions than the former. As observed above, for bis(μ -3,5-diamino-1,2,4-triazole-malonato) copper(II) trihydrate, the present complex can also be described as triazole-bridged Cu(II) chains linked through *anti-anti* carboxylate groups. Previous magnetostructural studies have shown that the magnetic coupling between copper(II) ions through this type of bridges usually favors a weak antiferromagnetic coupling [21–24].

CONCLUSIONS

In the present paper, we have discussed the syntheses, crystal structures, and magnetic behavior in the temperature range 2–300 K of two metal-organic based polymers of Cu(II) with similar bridging ligands. In complexes **1** and **2**, 1,2,4-triazole behaves as a bidentate bridging ligand. A variable-temperature magnetic study for the two complexes shows the existence of the dominant antiferromagnetic interaction.

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