Syntheses, crystal structure and properties of two novel coordination polymers with the flexible tetrazole-1-acetic acid (Htza)

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ABSTRACT

Two new coordination polymers, $[Ag(tza)]_\infty$ (**1**) (Htza = tetrazole-1-acetic acid) and $[Cu(tza)_2]_\infty$ (**2**) have been prepared at room temperature and characterized by X-ray crystallography, IR, UV–vis, fluorescence spectra and magnetism analysis. Compound **1** exhibits extended helical chains through bridging ligand tza. The Ag•••Ag interactions between the adjacent chains form a 3-D framework featuring the extended tza-connected Ag chains that obviously affect the photoluminescent property. Compound **2** features undulated layered structure with hourglass-shaped $[Cu_4(tza)_4]$ as subunits with the weak ferromagnetic interactions between Cu(II) ions, which are further stabilized by inter-lamellar C–H•••O hydrogen bonds in the resulting 3-D supramolecular framework.

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1. Introduction

The design and synthesis of functional coordination polymers have been attracting considerable attention owing to their potential application [1–3] and intriguing topologies [4,5]. Suitable organic linkers employed play an important role in the construction of extended solid structures. Tetrazoles and its derivatives have been widely used as polyfunctional ligands [6–8] due to the aromaticity and multiple coordinating modes, some of which such as 5-substituted tetrazolate ligands [9–14] have been made an intensive study yet. Very recently, 1-substituted tetrazolate ligand has received increasing interest because of the low-temperature ferromagnetism and thermal spin-state transition of their metal complexes [15–18]. A series of Cu(II) or Fe(II) complexes of 1-substituted tetrazoles (1-*R*-tetrazoles), *R* = alkyl [19–21], phenyl [22,23], chloroethyl [16,17,24] and methoxyethyl [15] have been reported. Unfortunately, these complexes have low-dimensional structures due to the fact that unfunctionalized 1-substituents show no coordination ability and thus disfavor the formation of highly extended structures [15–24]. Taken this concern in mind, 1-carboxylated derivative, tetrazole-1-acetic acid (Htza), was selected for the following several considerations: (i) the additional strong coordinating ability of carboxylate arms is expected to exhibit more varied coordinating patterns in the construction of multidimen-

sional coordination frameworks; (ii) the –CH_2– spacer between the tetrazole ring and CO_2 donor group offers the flexible orientations the carboxylate arm favoring the formation of varied framework structures. Although it is expected to be a powerful ligand in the construction of coordination polymer, only Cu(II)–Ln(III) heterometallic derivatives have been documented [25]. In the present work, the parallel double-stranded helical Ag(I) complex **1** and 2-D layered Cu(II) complex **2** will be reported in aspects of synthesis, crystal structure, luminescent and magnetic property.

2. Experimental

2.1. General

Htza was synthesized in accordance with a published procedure [26]. All other chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Fluorescent spectra were measured with an Edinburgh FLS920 analytical instrument. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the 4000–400 cm^{-1}. The UV–vis spectral measurements were carried out on a Perkin Elmer Lambda 900. Variable-temperature (2.0–300.0 K) magnetic susceptibility measurements were carried out on a Quantum Design PPMS60000 in a magnetic field of 10 kOe, and the diamagnetic corrections were evaluated by using Pascal's constants [27].

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2.2. Synthesis of [Ag(tza)]$_\infty$ (1)

An aqueous solution of AgNO$_3$ (0.025 g, 0.15 mmol) in distilled water (2 mL) was added to an aqueous solution (3 mL) of Htza (0.02 g, 0.15 mmol). The resultant solution became cloudy immediately and was stirred for 0.5 h at 80 °C The resulting solution was allowed to stand in air at room temperature for about 1 day, yielding colourless crystals of 1. Yield: 80%. Calc. for C$_3$H$_3$N$_4$O$_2$Ag: C, 15.34; H, 1.29; N, 23.85%. Found: C, 15.32; H, 1.33; N, 23.84%. IR (KBr; cm^{-1}): 3154.1m, 3097.8w, 2958.5w, 3008.4w, 1615.2s, 1384.9s, 1318.8m, 1178.5m, 1108.8m, 886.4m, 789.7m, 693.9s.

2.3. Synthesis of [Cu(tza)$_2$]$_\infty$ (2)

A mixture of Htza (0.04 g, 0.3 mmol) and CuCl$_2$ · 2H$_2$O (0.026 g, 0.15 mmol) was dissolved in water (5 mL) at room temperature. The reaction mixture was stirred for 0.5 h. The resulting solution was allowed to stand in air at room temperature for about 1 week, yielding blue single crystals of 2. Yield: 60%. Calc. for C$_6$H$_6$CuN$_8$O$_4$: C, 22.68; H, 1.90; N, 35.27%. Found: C, 22.65; H, 1.97; N, 35.33%. IR (KBr; cm^{-1}): 3081.7m, 2993.7w, 2959.3w, 1658.7s, 1417.1w, 1386.7s, 1296.1s, 1185.0m, 1098.5s, 1019.7m, 703.6s.

2.4. X-ray single-crystal determination

Crystal data collection were performed at 273 K on a Rigaku Mercury-CCD with a graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). All absorption corrections were performed using the CrystalClear programs [28]. All structures were solved by the direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXTL-97 [29]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at geometrically calculated positions. Crystallographic data and structural refinements for compounds 1 and 2 are summarized in Table 1. The selected bond distances and bond angles are summarized in Table 2.

Table 1
Crystallographic data for compounds 1 and 2

	1	2
Formula	C$_3$H$_3$Ag N$_4$O$_2$	C$_6$H$_6$CuN$_8$O$_4$
M	234.96	317.73
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/c
a (Å)	5.0200(16)	4.806(2)
b (Å)	13.717(4)	11.806(5)
c (Å)	8.430(3)	9.478(5)
α (°)	90.000	90.000
β (°)	99.798(6)	103.682(5)
γ (°)	90.000	90.000
Volume (Å^3)	572.0(3)	522.5(4)
Z	4	2
d_{calc} (g/cm^3)	2.728	2.019
μ (mm^{-1})	3.454	2.120
F (000)	448	318
Crystal size	0.26 × 0.17 × 0.17	0.20 × 0.12 × 0.09
Data/restraint/parameters	1278/0/91	1189/0/88
Reflections collected	4238	3984
Independent reflections	1278	1189
Goodness of fit	1.061	1.004
$R_1[I > 2\sigma(I)]$	0.0179	0.0235
$\omega R_2[I > 2\sigma(I)]$	0.0438	0.0632
R_1 (all data)	0.0205	0.0277
ωR_2 (all data)	0.0447	0.0658
Residuals (e/Å^3)	0.382, −0.460	0.422, −0.283

Table 2
Selected bond lengths (Å) and angles (°) for 1 and 2

Complex 1			
Ag(1)–N(4)	2.1842(16)	N(4)–C(1)	1.314(2)
Ag(1)–O(1)♯1	2.1896(15)	N(4)–N(3)	1.352(2)
Ag(1)–Ag(1)♯2	2.9996(8)	N(3)–N(2)	1.292(3)
Ag(1)–Ag(1)♯3	3.3595(8)	N(2)–N(1)	1.341(2)
N(1)–C(1)	1.323(2)		
N(4)–Ag(1)–O(1)♯1	163.44(6)	C(3)–O(1)–Ag(1)♯4	107.00(12)
N(4)–Ag(1)–Ag(1)♯2	76.35(5)	N(2)–N(3)–N(4)	109.87(16)
O(1)♯1–Ag(1)–Ag(1)♯2	110.38(4)	C(1)–N(4)–N(3)	106.24(15)
N(4)–Ag(1)–Ag(1)♯3	117.16(4)	N(3)–N(2)–N(1)	106.96(15)
O(1)♯1–Ag(1)–Ag(1)♯3	76.69(5)	N(4)–C(1)–N(1)	108.70(16)
Ag(1)♯2–Ag(1)–Ag(1)♯3	104.12(3)	C(1)–N(1)–N(2)	108.23(16)
C(1)–N(4)–Ag(1)	126.00(12)	N(2)–N(1)–C(2)	120.62(15)
N(3)–N(4)–Ag(1)	127.48(12)		
Complex 2			
Cu(1)–O(1)♯5	1.9293(13)	N(4)–N(3)	1.363(2)
Cu(1)–N(4)	1.9991(16)	N(3)–N(2)	1.283(2)
C(1)–N(1)	1.323(2)	N(2)–N(1)	1.355(2)
C(1)–N(4)	1.313(2)		
O(1)♯5–Cu(1)–N(4)	87.78(6)	N(4)–C(1)–N(1)	108.18(16)
O(1)♯6–Cu(1)–N(4)	92.22(6)	C(1)–N(4)–N(3)	106.77(15)
C(1)–N(4)–Cu(1)	126.09(13)	N(2)–N(3)–N(4)	109.68(15)
C(3)–O(1)–Cu(1)♯7	115.03(11)	N(3)–N(2)–N(1)	106.88(15)
N(3)–N(4)–Cu(1)	127.06(12)	C(1)–N(1)–N(2)	108.51(14)

Symmetry transformations used to generate equivalent atoms:♯1: $-x+1/2$, $y-1/2$, $-z+1/2$; ♯2: $-x+1$, $-y$, $-z+1$; ♯3: $-x$, $-y$, $-z+1$; ♯4: $-x+1/2$, $y+1/2$, $-z+1/2$; ♯5: $x-1$, $-y+1/2$, $z-1/2$; ♯6: $-x+1$, $y+1/2$, $-z+3/2$; ♯7: $-x+1$, $y-1/2$, $-z+3/2$.

3. Results and discussions

3.1. Synthesis

Compounds 1 and 2 were obtained as pure crystalline precipitates from reaction solutions at room temperature. The reactions of AgNO$_3$ (or CuCl$_2$ · 2H$_2$O) with Htza in the varied molar ratio of 1:1, 1:2 or 2:1 (1:3) afford the charge-balanced products [Ag(tza)]$_\infty$ (1) or [Cu(tza)$_2$]$_\infty$ (2) only. The reactions of Htza with different silver salts such as AgNO$_3$ or CH$_3$COOAg have also been found to produce the single silver complex [Ag(tza)]$_\infty$ (1).

3.2. Structural description of [Ag(tza)]$_\infty$ (1)

Compound 1 crystallizes in monoclinic space group $P2_1/n$ and the asymmetric unit consists of one crystallographically independent tza and silver ion as shown in Fig. 1. Ag(I) center is almost linearly coordinated to N4 and O1 atoms (N(4)–Ag(1)–O(1), 163.44°), resulting in alternatively arranged R- and L-handed 1-D helical chains (Fig. 2a). The bond lengths of Ag(1)–N(4) and Ag(1)–O(1) are 2.1842(16) and 2.1896(15) Å (Table 2), respectively, which are the typical values for Ag(I)–N$_{tetrazol}$ and Ag(I)–O$_{carboxyl}$ coordination distances [6,30]. Interestingly, the adjacent chains are linked together through strong Ag•••Ag interactions (Ag•••⊀•Ag, 2.9996(8) Å) to form 2-D extended double-stranded helical chains running along a crystallographic 2$_1$ axis with a pitch of 13.717 Å (Fig. 2b). The 2-D undulated layers are further linked together through inter-lamellar Ag•••Ag interactions (Ag•••Ag, 3.3595(8) Å) between the adjacent layers resulting in a 3-D structure (Fig. 3).

3.3. Structural description of [Cu(tza)$_2$]$_\infty$ (2)

As shown in Fig. 4a, Cu(II) ion is coordinated to two carboxylate oxygen atoms and two tetrazole nitrogen atoms from four different tza ligands to exhibit a square planar coordination geometry, with the Cu–O and Cu–N bond lengths of 1.929 (1) Å
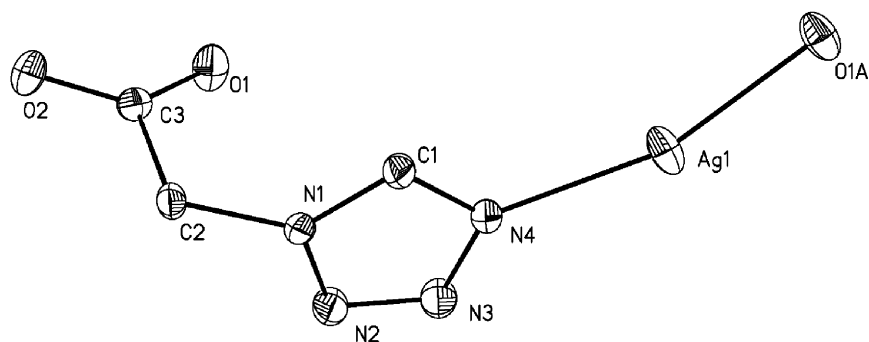
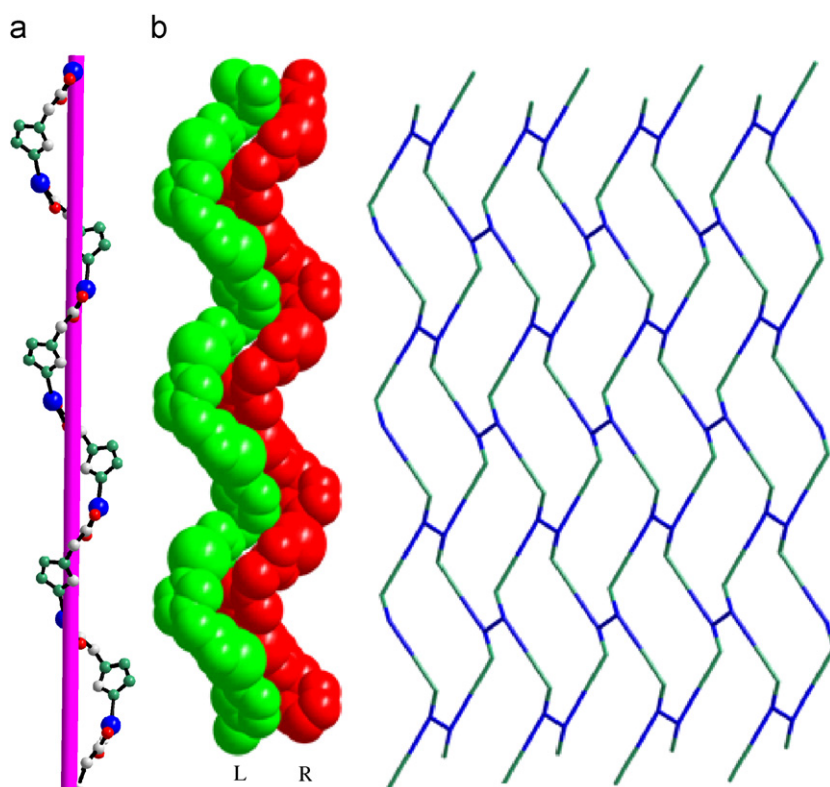**Fig. 1.** ORTEP drawing of **1** with 30% probability thermal ellipsoids.

Fig. 2. (a) View of a single helical chain. (b) Left: space-filling diagram of one parallel double-stranded helical chain. Right: a 2-D helical layer consists of parallel double-stranded helical chains through Ag•••Ag interactions.

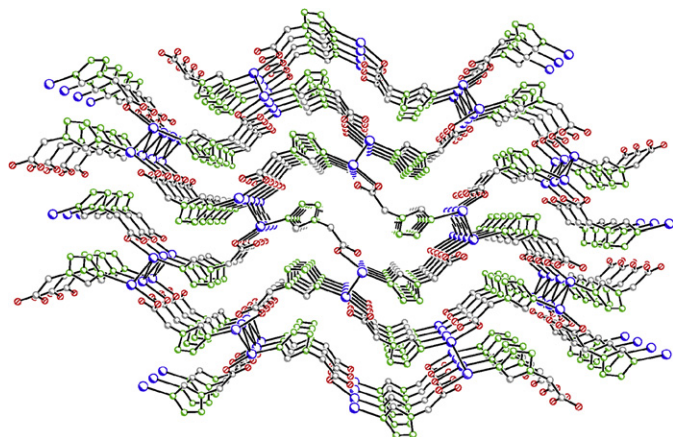**Fig. 3.** Packing diagram of the 3-D framework formed mainly by the Ag•••Ag interactions.

and 1.999 (2) Å, respectively. As in the case of **1**, the tza ligand in **2** adopts two-coordinated μ-tza-N_4, O_1 bridging mode. However, the square planar coordination geometry of the Cu atoms are linked by the linear tza ligands into a layered structure (Fig. 4b). The inter-lamellar Cu•••Cu distance of 4.806 Å is much longer than the sum of the vander Waals radii (3.56 Å), indicating no Cu•••Cu interactions. Unlike the case of **1**, the two tetrazole rings coordinated to Cu(II) ion are coplanar that leads to a undulated layer (Fig. 5a). As shown in Fig. 5b, the layered structure are further stabilized by the C–H•••O hydrogen bonds between uncoordinated carboxylate oxygen atoms and carbon atoms of the tetrazole rings [C(1)•••O(2), 3.025 Å, $\angle$ C(1)–H•••O(2), 157°], leading to a 3-D supramolecular frameworks.

3.4. Luminescent properties of 1

Ag(I) coordination complexes usually exhibit weak photoluminescence at low temperatures. Those exhibiting luminescent

a

b

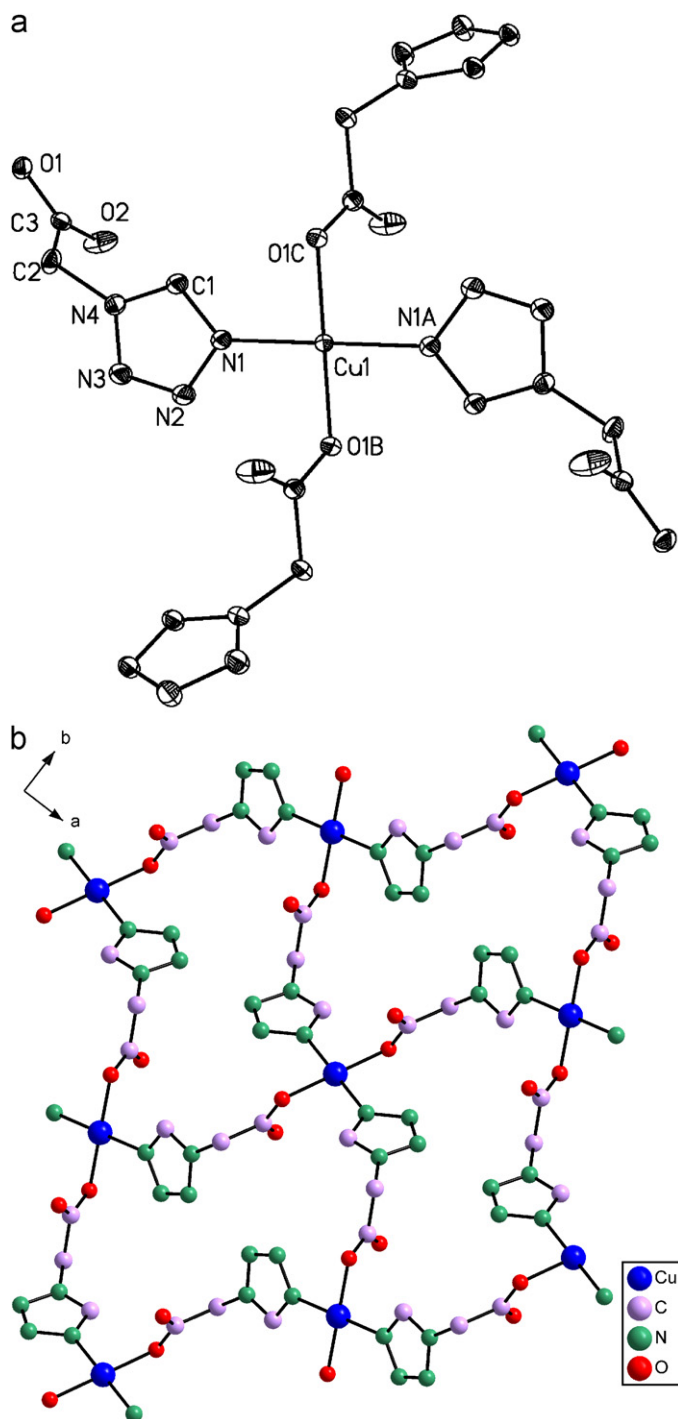**Fig. 4.** (a) ORTEP drawing of **2** with 30% probability thermal ellipsoids and (b) the 2-D [Cu$_4$(tza)$_4$] layer (view along the **c**-axis).
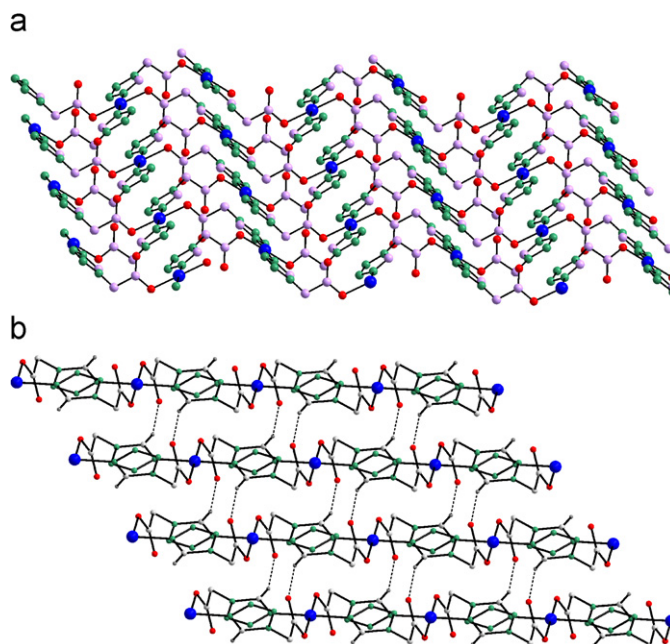
a

b

Fig. 5. (a) Undulated layered structure and (b) the 2-D packing of the layers through hydrogen bonds viewed along the *b*-axis.

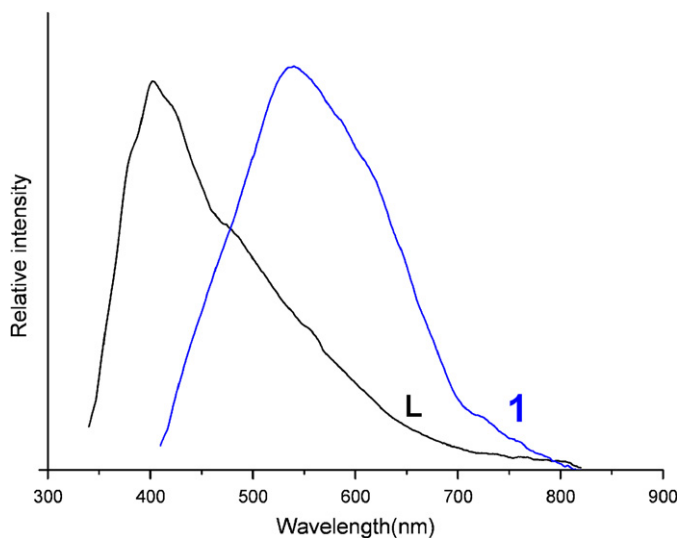**Fig. 6.** The solid-state luminescence spectra for the free ligand (*L*) and compound **1**.

properties at room temperature are very limited [31–34]. Interestingly, compound **1** exhibits the green photoluminescence at room temperature with the emission maximum at 540 nm (excited at 372 nm), which means a red shift of ca. 140 nm relative to that of the free Htza ligand (excited at 286 nm and emitted at 403 nm) as shown in Fig. 6. We tentatively believe that is closely related to the extended Ag•••Ag interactions (Ag•••Ag, 2.9996(8) and 3.3595(8) Å). The reported compound [Ag$_2$(pidc)(H$_2$O)] (H$_3$podc = 3,5-pyrazoledicarboylic acid) [35] with short Ag•••Ag interactions (Ag•••Ag, 3.158(1) Å), which exhibits close emission maximum at 518 nm upon excitation at 325 nm while

the free ligand displays very weak luminescence, thus the presence of metal–metal interactions has been recognized as one of the important factors contributing to the photoluminescent properties of coinage d^{10} metal coordination compounds. The solid UV–vis spectra of the Ag(I) complex shows a peak at 210 nm from the ligand and a shoulder peak at 260 nm due to the Ag–Ag interaction similar to those in [Ag$_2$(μ-dcpm)$_2$]X_2 (266 nm) (dcpm = bis(dicyclohexylphosphino)methane, X = CF$_3$SO$_3^-$ and PF$_6^-$) and [Ag$_3$(dpmp)$_2$(CH$_3$CN)$_2$(ClO$_4$)$_2$]ClO$_4$·(Et$_2$O)$_2$ (288 nm) (dpmp = bis(diphenylphosphinomethyl)phenylphosphine) [36]. And also we studied the solid UV–vis of the copper (II) compound **2**, which shows the maximum absorptions at 210 nm from the ligand, 300 and 600 nm from copper (II) ions. However, the copper (II) compound **2** has been found to be florescence-silent, indicating that the luminescence of the ligand has been quenched
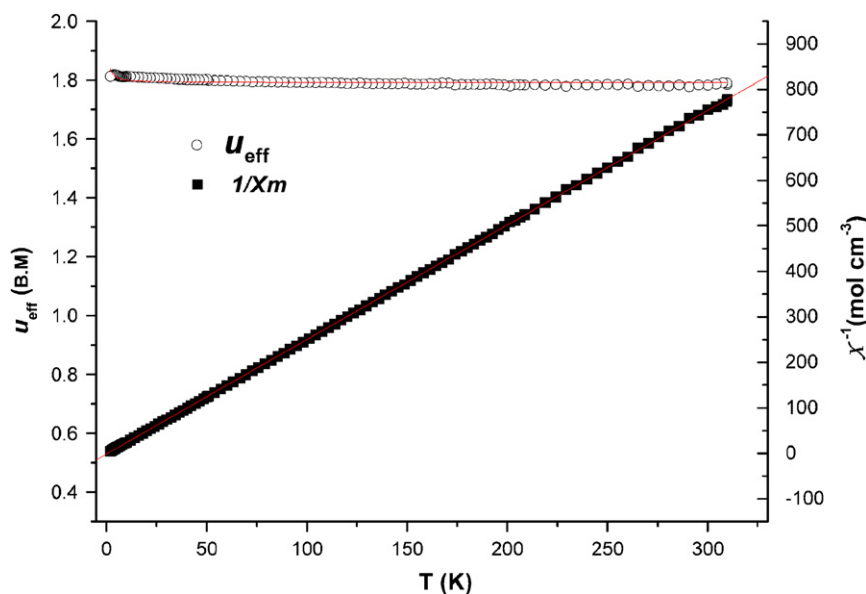
Fig. 7. Plots of μ_{eff} ($\bigcirc$) and χ^{-1} ($\blacksquare$) vs. temperature for **2**; the solid lines represent the best fit.

by the coordination the copper (II) ions. Similar case has also been observed from the zinc and cadmium complexes of tza [37]. This is in consistent with the fact that only single fluorescent emission due to the Ag•••Ag interactions in the silver (I) compound **1**.

3.5. Magnetic properties of **2**

Temperature-dependent magnetic susceptibilities of **2** over the temperature range 2–300 K have been measured to investigate the magnetic interactions between the copper (II) ions. The plots of the magnetic moment and χ_m^{-1} versus temperature are depicted in Fig. 7. The magnetic moment of the copper (II) compound **2** at 300 K is 1.78 μ_B close to the magnetically isolated spin only value of 1.73 μ_B. This value keeps almost unchanged from 300 to 2 K (1.81 μ_B), indicating that there is no significant interaction between the copper (II) ions [38] because of the long metal–metal separations and poor communication ability of the –CH_2– spacer.

4. Conclusions

The present study demonstrates that the carboxylate arm and the *trans*-nitrogen atom are able to interconnect the two-coordinated silver (I) ions into double-stranded helical chains, which are further linked together by Ag•••Ag interactions into 3-D framework structures. The planar square-coordinated metal ions can be interconnected by tza in the same coordinating mode into 2-D modulate structure. The fluorescent emission of the ligand has been found to be quenched by the coordination to the metal ions and new fluorescent emission caused by Ag•••Ag interactions has been found in the silver (I) complex **1**. The magnetic interactions between the metal ions interconnected by tza via the present coordinating mode have been found not to be significant.

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 663453 and 663454 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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