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Self Assembly of Three New Copper Coordination Polymers Based on N-[(3-Pyridine)-Sulfonyl]aspartate: Synthesis and Structure[1]

B. L. Liao[a, b], **S. X. Li**[a, b], **J. J. Guo**[b], **J. J. Jia**[b], **and Y. M. Jiang**[b, *]
[a] *College of Chemistry and Biological Engineering, Hechi University, Yizhou, 546300 P.R. China*
[b] *College of Chemistry and Pharmacy, Guangxi Normal University, Guilin, 541004 P.R. CHINA*
**e-mail: lsx1324@163.com*

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Abstract—Three new copper coordination polymers $[Cu(L) \cdot 6H_2O]_n$ (**I**), $[Cu_2(L)_2]_n$ (**II**), and $[Cu(HL)_2]_n$ (**III**), where H_2L is N-[(3-pyridine)-sulfonyl]aspartate, have been synthesized and characterized by single-crystal X-ray diffraction (CIF files CCDC nos. 1435871 (**I**), 1435872 (**II**), 1435873 **III**), elemental analysis and IR spectra. Moreover, the variable-temperature magnetic susceptibility had been studied for complex **I**. A structural comparison of these polymers suggests that different reaction temperatures play important role in the construction of resulting architectures for **I**–**III**.

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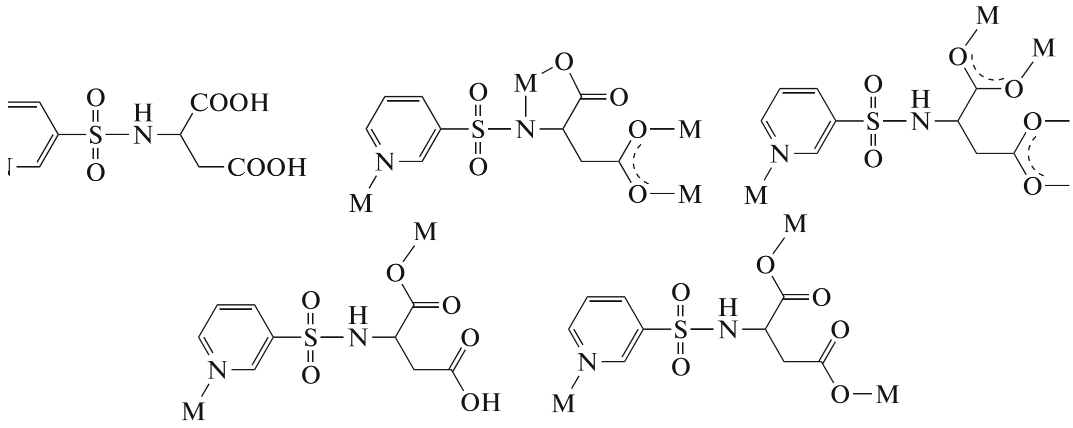
INTRODUCTION

In the past few decades, the design and synthesis of the novel coordination polymers has attracted great attention owing to their fascinating structures and functional application, such as magnetic, electronic, optical, catalytic materials and fluorescent materials [1–6]. In general, the structural motifs of these compounds are closely related to the geometries of metal centers and the numbers of coordination sites provided by multidentate ligands. Reasonable selection of a suitable organic ligand with certain features, such as versatile bonding modes and the ability to undergo supramolecular interactions, is helpful for constructing metal-organic architectures with desirable properties [7–11].

Recently, multidentate ligand, N-[(3-pyridine)-sulfonyl]aspartate (H_2L) based on 3-(chlorosulfonyl)pyridine and aspartic acid, seized our attention for the following reasons: (i) Aspartic acid is a basic building unit inproteins for study in medical applications. Recent work has shown that aspartic acid is capable of binding to metals via two carboxylate groups and the single amino functional group to form extended open frameworks [12], which can be porous and displays enantioselective sorption [13]. (ii) It holds multipotential groups, i.e., the nitrogen atom and four oxygen atoms of the aspartatic group, one nitrogen atoms of the pyridine and two oxygen atoms of sulfonate group which can afford interesting structures with tunable dimensionality and our group also has interest in heterocyclic sulfonate-coordinated transition-metal complexes [14–20].

In this article we report three copper coordination polymers $[Cu(L) \cdot 6H_2O]_n$ (**I**), $[Cu_2(L)_2]_n$ (**II**), and $[Cu(HL)_2]_n$ (**III**) (H_2L = N-[(3-pyridine)-sulfonyl]aspartate). H_2L and its coordination modes, observed in **I**–**III**, are below:



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EXPERIMENTAL

Physical measurements. All solvents, chemicals were commercial reagents and used without further purification. Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Perkin-Elmer 240 elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet 5DX FT-IR spectrometer. The emission spectra were recorded on Time-resolved fluorescence spectrometer FL3-TCSPC. The crystal structure was determined by a Bruker APEX-II CCD diffractometer.

Synthesis of H_2L. To a solution of aspartate (6.66 g, 0.05 mol) in 4 M NaOH (10 mL), 3-(chlorosulfonyl) pyridine (8.88 g, 0.05 mol) was added. The mixture was stirred at room temperature for 3 h, and then the aqueous solution is acidified to pH 3 with 6 M hydrochloric acid; white solid derivative begins to crystallize at once. The crystals were collected on a filter and recrystallized from hot water, the yield was ~73% (based on aspartate).

For $C_9H_{10}N_2O_6S$

anal. calcd., %:	C, 39.32;	H, 3.62;	N, 10.29.
Found, %:	C, 39.42;	H, 3.68;	N, 10.22.

Synthesis of I. A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.048 g, 0.2 mmol), H_2L (0.0548 g, 0.02 mmol) and NaOH (0.008 g, 0.2 mmol) in 10 mL distilled H_2O was sealed in a 25 mL Teflon-linged stainless steel container and heated at 160°C for 3 days. The mixture cooled to room temperture at a rate of 10°C/h, thin blue block crystals of **I** were obtained, the yield was 46% (based on Cu).

For $C_9H_{12}CuN_2O_8S$

anal. calcd., %:	C, 24.38;	H, 2.76;	N, 6.28;	S, 7.33.
Found, %:	C, 24.33;	H, 2.70;	N, 6.30;	S, 7.20.

Synthesis of II. The procedures were similar to the synthesis of **I** except that the reaction temperature was 120°C. Green block crystals of **II** were obtained with a yield of 23% (based on Cu).

For $C_9H_8N_2O_6SCu_2$

anal. calcd., %:	C, 27.12;	H, 2.05;	N, 7.13;	S, 8.06.
Found, %:	C, 27.04;	H, 2.00;	N, 7.01;	S, 8.01.

Synthesis of III. The procedures were similar to the synthesis of **I** except that the reaction temperature was 90°C. The yield was 55% (based on Cu).

For $C_{18}H_{18}N_4O_{12}S_2Cu$

anal. calcd., %:	C, 35.47;	H, 2.87;	N, 9.20;	S, 10.45.
Found, %:	C, 35.41;	H, 2.95;	N, 9.18;	S, 10.49.

X-ray crystallography. Diffraction intensities were collected on a Bruker Apex CCD area-detector diffractometer (MoK_α, $\lambda = 0.71073$ Å). The structure was solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package [21]. 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 **I–III** are summarized in Table 1. Selected bond lengths and bond angles for complexe **I–III** are listed in Table 2. Hydrogen bonds for complexes **I–III** are listed in Table 3.

Supplementary material for **I–III** has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1435871 (**I**), 1435872 (**II**), 1435873 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

A single-crystal X-ray diffraction study reveals that **I** adopt a 3D coordination polymer. The asymmetric unit contains one Cu^{2+} cation, one ligand and six water molecules.

As illustrated in Fig. 1a, the Cu(II) center adopts a distorted tetragonal pyramid coordination environment, which is completed by two nitrogen atoms from pyridine (N(1*A*)) and sulfamine (N(2)) of two ligands as well as two oxygen atoms (O(1), O(4*B*)) from two carboxylates located at the equatorial plane, and one oxygen (O(3)) from carboxylate at the axial positions. Carboxylic acid of the ligands both coordinated with *cis-trans*-bridged bidentate and monodentate. Because of Jahn–Teller effect the bonds, so the Cu–O(1) and Cu–O(4) bonds are much shorter than Cu-$O(3)_{ax}$ bonds (Cu–O(1) 2.013(13), Cu–O(4) 1.906(11), Cu–O(3) 2.422(11) Å). Bonds Cu(1)–N(2) 1.964(13), Cu(1)–N(1) 2.055 Å are similar to the reported bond length [22–24].

Three Cu^{2+} cations are bridged by one ligand to construct 2D sheet (Fig. 1b). Each three of Cu^{2+} cations are bridged by two carboxylate groups from two L^{2-} anions in *cis-trans*-bridged bidentate mode. The further link by ligand bridging the Cu_3 unit with 2_1 helicity along the *z* axis direction, in which the helical pitch of 9.834 Å is equal to the length of the *z* axis (Fig. 1c). As shown in Fig. 1d, the extension of the structure into a 3D framework is accomplished by one ligand bearing two Cu from the different 2D layers along *z* axis.

The asymmetric unit of crystal **II** contains two crystallographically independent Cu^{2+} cations and one ligand. As illustrated in Fig. 2a, Cu(1) cations adopts a distorted tetrahedral coordination environment, which is completed by Cu(2) cations and two bridging carboxylate oxygen atoms (O(2), O(3*A*)) from two different ligands as well as one nitrogen atom

Table 1. Crystallographic data and structure refinement for complexes **I–III**

Parameter	Value		
	I	**II**	**III**
Fw	443.89	399.34	610.05
T	296(2)	298(2)	293(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a, Å	9.572(10)	8.6642(8)	10.156(5)
b, Å	18.029(17)	15.0934(12)	7.282(3)
c, Å	9.834(10)	10.0909(9)	15.954(7)
β, deg	90	112.8860(10)	100.554(6)
V, Å^3	1697(3)	1215.73(18)	1160.1(9)
Z	13	2	15
ρ_{calcd}, g/cm^3	1.674	2.154	1.741
F(000)	865	783	619
θ Range, deg	2.3–25.6	2.–28.5	3.0–25.2
Collected reflections	1741	2143	2145
Independent reflectios	1674	1439	1914
R_{int}	0.1362	0.0643	0.0276
GOOF	1.024	1.061	1.103
Refinement parameter	228	180	171
R_1, wR_2 ($I > 2\sigma(I)$)	0.084, 0.249	0.0546, 0.1137	0.0360, 0.0947
R_1, wR_2 (all data)	0.1441, 0.3314	0.0902, 0.1259	0.0402, 0.0968
Large diff. peak and hole, e Å^{-3}	0.96 and –1.23	2.31 and –2.23	0.53 and –0.35

Table 2. Selected bond lengths (Å) and bond angles (deg) for **I–III***

Bond	d, Å	Bond	d, Å	Bond	d, Å
		I			
Cu(1)–O(4*B*) Cu(1)–O(1)	1.906(11) 2.013(13)	Cu(1)–N(2) Cu(1)–N(1*A*)	1.964(13) 2.055(14)	Cu(1)–O(3)	2.422(11)
		II			
Cu(1)–O(2) Cu(1)–N(2)	1.948(5) 2.102(6)	Cu(1)–O(3) Cu(1)–Cu(2)	2.015(4) 2.619(13)	Cu(2)–O(4) Cu(2)–O(1)	1.876(5) 1.883(5)
		III			
Cu(1)–O(2*B*)	1.9435(19)	Cu(1)–N(1)	2.014(2)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
		I			
O(4*B*)Cu(1)N(2)	167.9(5)	O(4*B*)Cu(1)O(1)	93.7(5)	N(2)Cu(1)N(1*A*)	97.6(5)
N(2)Cu(1)O(1)	82.9(5)	O(4*B*)Cu(1)N(1*A*)	86.7(5)	O(4*B*)Cu(1)O(3)	85.9(4)
O(1)Cu(1)N(1*A*)	175.6(5)	O(1)Cu(1)O(3)	87.9(6)	N(1*A*)Cu(1)O(3)	96.5(6)
N(2)Cu(1)O(3)	82.4(4)				
		II			
O(2)Cu(1)O(3)	150.8(2)	O(2)Cu(1)N(2)	112.2(2)	O(1)Cu(2)Cu(1)	86.52(16)
O(3)Cu(1)N(2)	96.8(2)	O(2)Cu(1)Cu(2)	81.14(16)	C(5)N(2)Cu(1)	118.7(5)
O(3)Cu(1)Cu(2)	76.94(13)	N(2)Cu(1)Cu(2)	143.43(17)	C(1)O(2)Cu(1)	124.1(5)
O(4)Cu(2)O(1)	174.1(2)	O(4)Cu(2)Cu(1)	89.78(15)	C(4)O(4)Cu(2)	119.4(4)
C(9)N(2)Cu(1)	120.4(5)	C(1)O(1)Cu(2)	121(4)	C(4)O(3)Cu(1)	127.4(4)
		III			
O(2)C–Cu(1)–O(2*B*)	180(8)	O(2)C–Cu(1)–N(1*A*)	90.97(9)	O(2*B*)–Cu(1)–N(1)	90.97(9)
O(2)B–Cu(1)–N(1*A*)	89.03(9)	O(2)C–Cu(1)–N(1)	89.03(9)	N(1*A*)–Cu(1)–N(1)	180(8)

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

Table 3. Geometric parameters of hydrogen bonds for complexes **I–III***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
I				
O(7)–H(7*A*)···O(4)	0.85	1.92	2.769(18)	179
O(7)–H(7*B*)···O(9)	0.85	1.98	2.83(18)	179
O(2)–H(8*C*)···O(8)	1.26	0.86	2.12(17)	175
O(8)–H(8*D*)···O(3)	0.86	2.37	2.99(9)	128
O(8)–H(8*D*)···O(4)	0.86	2.35	3.21(8)	174
O(9)–H(9*A*)···O(2*D*)	0.87	2.29	3.15(18)	179
O(9)–H(9*B*)···O(6*C*)	0.84	2.13	2.97(18)	179
O(12)–H(12*A*)···O(1)	0.82	2.21	2.965(14)	153
C(1)–H(1*A*)···O(8*E*)	0.93	1.57	2.48(10)	165
II				
N(1)–H(1)···O(5*C*)	0.9	2.36	3.18(8)	151
III				
N(2)–H(2*A*)···O(6*D*)	0.9	2.16	2.852(3)	133
C(5)–H(1)···O(5*E*)	0.93	2.34	3.12(3)	141
O(5)–H(5)···O(3*F*)	0.93	2.33	3.023(3)	131

* Symmetry codes: (*A*) $-x + 1/2, -y, z + 1/2$; (*B*) $x - 1/2, -y + 1/2, -z + 2$; (*C*) $x + 1/2, -y + 1/2, -z + 1$; (*D*) $-x + 1/2, -y, z - 1/2$; (*E*) $-x + 1, y - 1/2, -z + 3/2$.

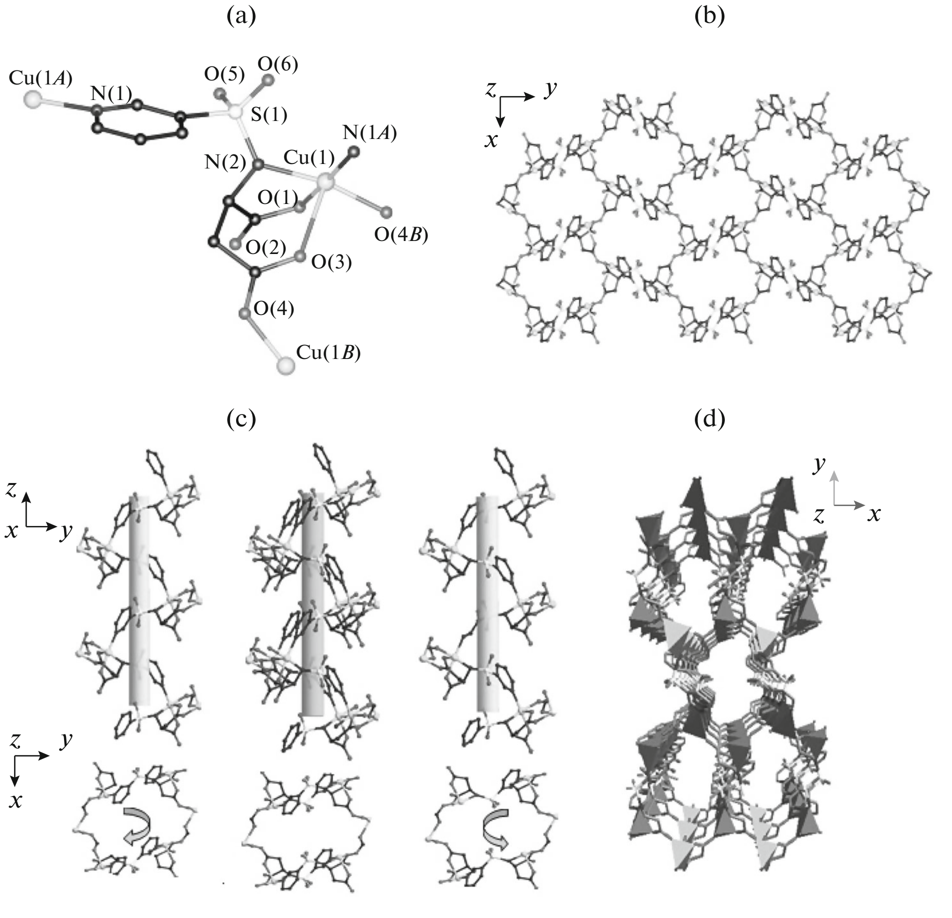

Fig. 1. Coordination environment of Cu^{2+} ions in **I** with hydrogen atoms omitted for clarity with thermal ellipsoids at 50% level (a); 2D sheet along the *z* axis of ploymer **I** (b); the left- and right-handed helical chains along *z* axis (c); extended 3D network viewed along the *z* axis (d).

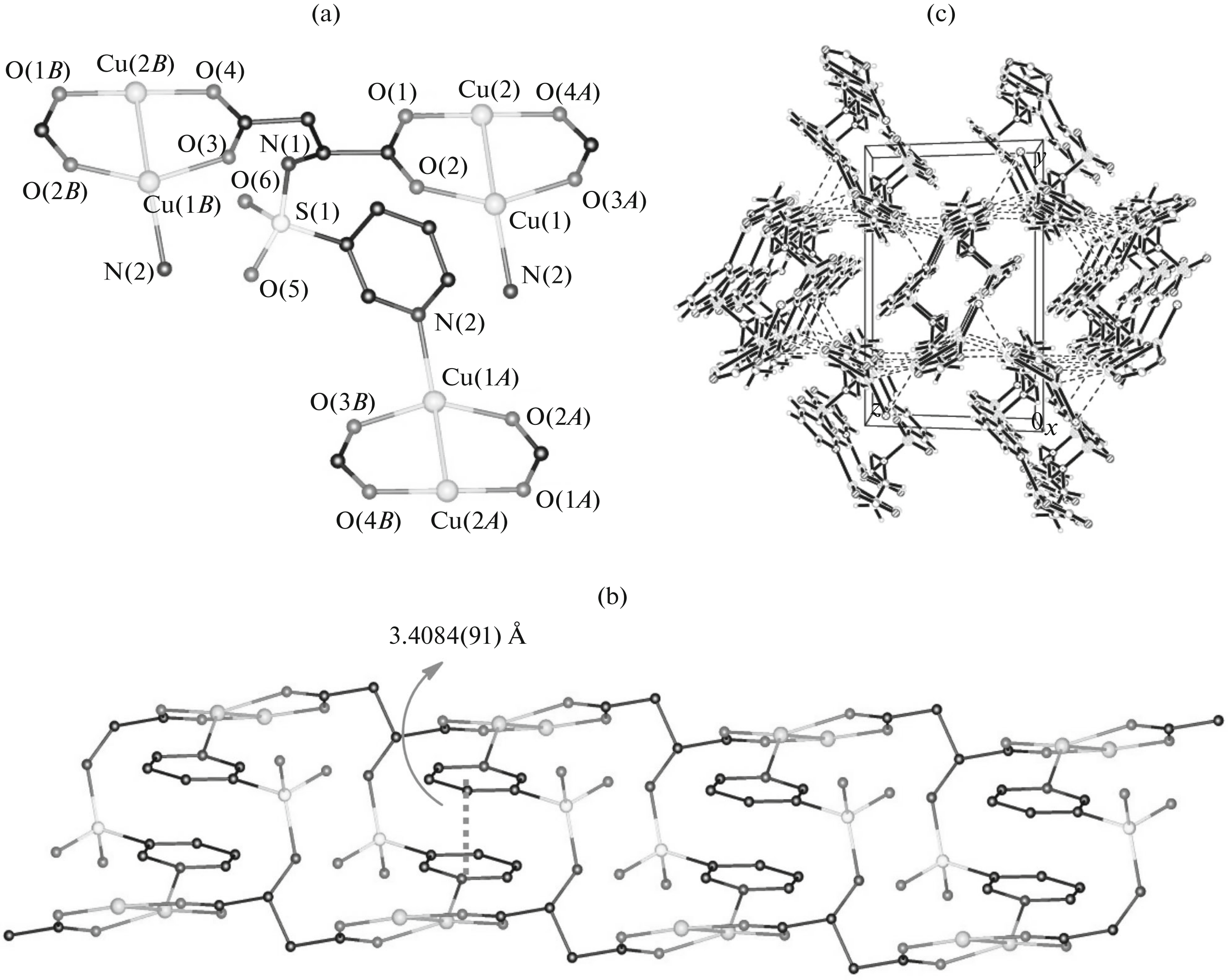

Fig. 2. Coordination environment of Cu^{2+} ions in **II** with hydrogen atoms omitted for clarity with thermal ellipsoids at 60% level (a); 1D ladder of ploymer **II** and distance of centroid-to-centroid of pyrazine rings (b); hydrogen bonds that make up a 3D network polymer (c).

(N(2)) from sulfamine at the axial position. Cu(2) cations is completed by Cu(1) cations and bridging carboxylate oxygen atoms (O(1), O(4)) from two different ligands. The Cu(1) cations is four-coordinated, Cu(2) cations is three-coordinated. Both carboxylate groups of the ligand adopt *cis*-*cis*-bridged bidentate mode coordinating with two Cu(1) cations and two Cu(2) cations. The Cu-Cu bond length is 2.619 Å, which is in the normal range [22–24].

Three Cu(1)–Cu(2) units are bridged by one ligand to contruct an 1D ladder coordination polymer in which Cu–Cu unit take as handraill and pyridine is foodboard in the equatorial direction. From the crystal packing of the coordination polymer, the pyridine are parallel to each other with a centroid-to-centroid distance of 3.4084 Å, which supports the presence of π-π stacking interactions (Fig. 2b). The non-coordinated sulfamine and sulfonic acid groups participate in N–H···O hydrogen bonds, which defind 3D hydrogen-bonded network and support the supramolecular architecture (Fig. 2c).

A single-crystal X-ray diffraction study reveals that **III** adopts a 1D coordination polymer. The asymmetric unit contains one Cu^{2+} cation and two ligands. As illustrated in Fig. 3a, the Cu(II) cation is four-coordinated by two nitrogen atoms from pyridine of two ligands (Cu(1)–N(1) 2.014) and two carboxylate oxygen atoms of two ligands (Cu(1)–O(2*B*) 1.9435). Four coordination sites of Cu(II) are coplanar in a perfectly symmetric and form an approximate spuare that Cu^{2+} cation is located in the center and coordinated atoms are occupied four vertex position of the spuare. The bond lengths and bond angles are in the normal range [22–24].

Two Cu^{2+} cations are bridged by one ligand to contruct an 1D coordination polymer in the equatorial direction (Fig. 3b). Notably, the presence of sulfonic

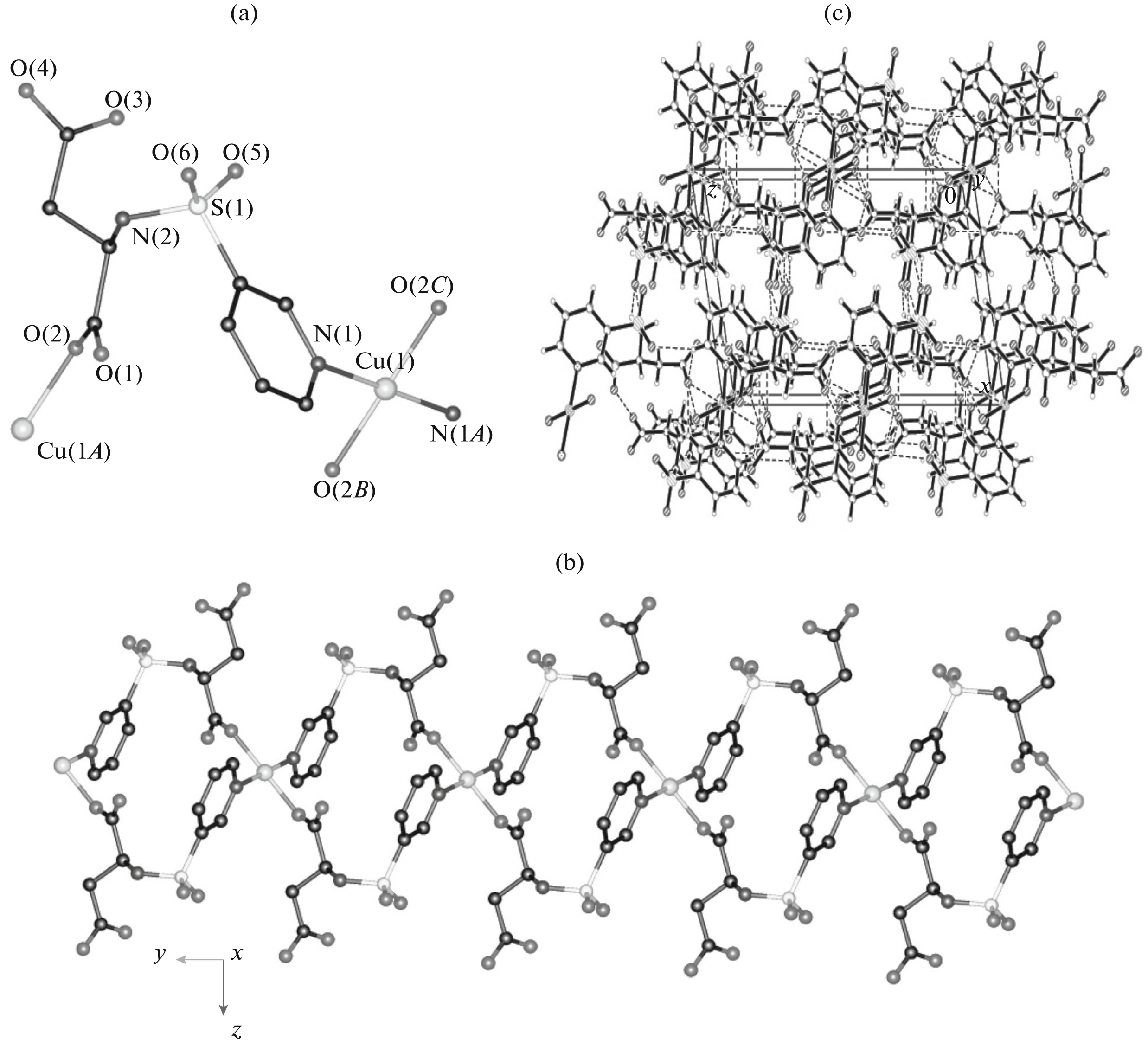

Fig. 3. Coordination environment of Cu^{2+} ions in **III** with hydrogen atoms omitted for clarity with thermal ellipsoids at 50% level (a); 1D chain of ploymer **III** (b); hydrogen bonds that make up a 3D network polymer (c).

acid groups and sulfamine leads to the formation of N–H···O and C–H···O hydrogen bonds interactions, which defines a 3D hydrogen-bonded network and, thus, supports the supramolecular architecture (Fig. 3c).

In order to check the purity of complex **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 complex.

The magnetic property of the complex **I** was investigated over the temperature range 2.0–300.0 K, and the resulting data is shown in Fig. 4. For **I**, the $\chi_M T$ value at 300 K is 0.51 $cm^3 mol^{-1}$ K, which is much higher than the expected value (0.16 $cm^3 mol^{-1}$ K) of two isolated spin-only Cu^{2+} ions ($S = 1/2, g = 2.0$). As T is lowered, $\chi_M T$ decreases continuously to a value of 3.22 $cm^3 mol^{-1}$ K at 2 K. This behavior in dicatesa dominant antiferromagnetic interaction between the Cu(II) is in correspondence with the Curie–Weiss law in the range of 45–300 K with $C = 0.53$ $cm^3 mol^{-1}$ K and $\theta = -17.43$ K.

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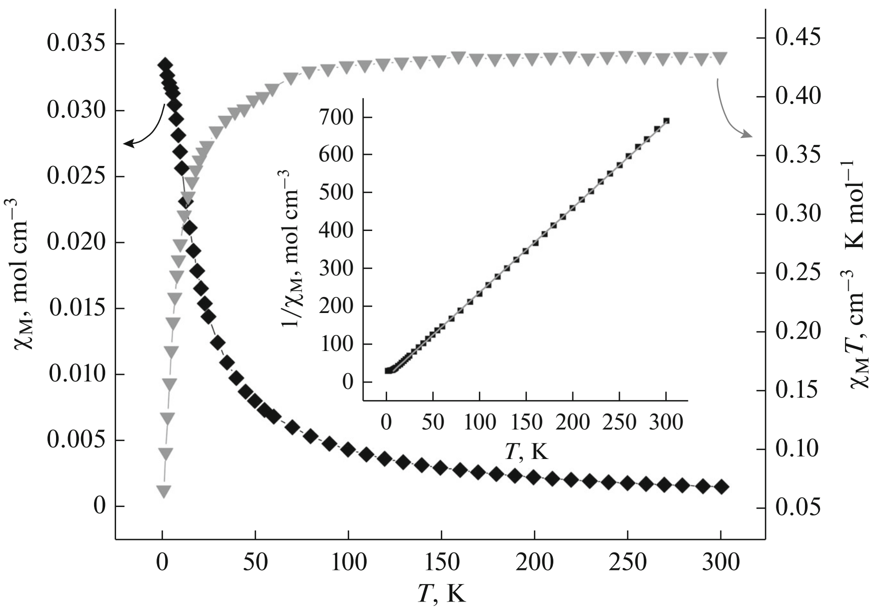

Fig. 4. Temperature dependence of χ_M, $\chi_M T$ vs. T and χ_M^{-1} vs. T (inset) for **I**.

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