

Three new 2-D metal-organic frameworks containing 1-D metal chains bridged by *N*-benzesulfonyl-glutamic acid: Syntheses, crystal structures and properties

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Abstract

To explore the possibility of obtaining the metal-organic frameworks (MOFs) bearing the *bsglu*H₂ ligand, two new Cd(II) and one Cu(II) coordination polymers, [Cd(*bsglu*)(*bipy*)_{*n*}] (1), [Cd(*bsglu*)·(H₂O)]_{*n*} (2) and {[Cu₂(*bsglu*)₂(*bipy*)₂]·4H₂O}_{*n*} (3) (*bsglu* = *N*-benzesulfonyl-glutamic acid bianion, *bipy* = 2,2'-bipyridine) were synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis. Compounds 1 and 3 exhibit one-dimensional coordination chains, which are further connected to form two-dimensional supramolecular networks through π - π aromatic stacking interactions in a novel zipper-like way. Compound 2 presents a two-dimensional layer structure. To the best of our knowledge, 2 is the first two-dimensional complex formed from transition metal and *bsglu*H₂ ligand. Interestingly, the *bsglu* anion exhibits remarkable versatile coordination modes in these complexes. Fluorescent analyses show that 1 exhibits photoluminescence in the solid state. Magnetic measurements for 3 revealed that the Cu(II) chain exhibit a weak antiferromagnetic behavior with a *J* value of -0.606 cm^{-1} .

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Keywords: *N*-benzesulfonyl-glutamic acid; Crystal structures; Luminescence; Magnetic properties

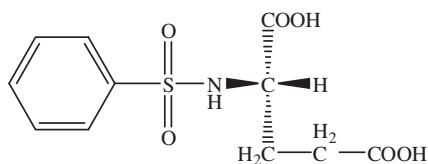
1. Introduction

Recently in material science and chemical research, much attention has been paid to the rational design and syntheses of metal-organic frameworks (MOFs) not only for their intrinsic aesthetic appeal, but also for the fact that they may provide a new strategy for achieving solid functional materials with the potential applications in magnetism, ion exchange, catalysis, photoluminescence, gas storage and electric conductivity [1–10]. Although many efforts have been devoted to the preparation of specific frameworks including one-, two- and three-dimensional structures [11–15], the preparation of the MOFs under rational control is still of great challenge. The formation of MOFs is greatly influenced by the organic ligands, the nature of the metal ions, the counterions and

sometimes the ratio of the metal ions to ligands [15–20]. Presently, a rational synthetic strategy widely used in this area is linking metal ions with polydentate ligands that function as connectors. Recently, the remarkable multi-dentate ligand *N*-benzesulfonyl-glutamic acid (Scheme 1) seized our attention for the following reasons: (i) the substitution of an Ar–SO₂-group on amine increases the number of coordination donors in the substituted amine, which may result in different coordination modes [21–24]; (ii) *bsglu*H₂ ligand has two carboxyl functions, which can lead to various coordination modes and provide abundant structure motifs; (iii) it can act not only as the hydrogen bond donors but also as acceptors, which make it a wonderful candidate for the construction of supramolecular structures. Thus, it is of great interest to study the coordination chemistry of *N*-benzesulfonyl-glutamic acid. To our knowledge, two-dimensional coordination polymers containing *N*-sulfonyl-glutamic acid have not been reported. In this work, we present two new Cd(II) and one

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Scheme 1.

Cu(II) bsglu complexes, $[\text{Cd}(\text{bsglu})(\text{bipy})]_n$ (**1**), $[\text{Cd}(\text{bsglu}) \cdot (\text{H}_2\text{O})]_n$ (**2**) and $\{[\text{Cu}_2(\text{bsglu})_2(\text{bipy})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**3**), alongside with their photoluminescence or magnetic properties.

2. Experimental

2.1. General

All reagents used in the syntheses were of analytical grade. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN Elemental analyzer. The IR spectra were in the range of $4000\text{--}400\text{ cm}^{-1}$ on a Shimadzu IR-408 IR spectrophotometer using KBr pellets. The crystal data collection were performed on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Fluorescence experiments used a HITACHI F-4500 Fluorescence Spectrophotometer at room temperature. Variable-temperature magnetic susceptibilities were measured using a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.2. Preparation of complexes 1–3

2.2.1. Preparation of 1

A mixture of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.5 mmol, 0.133 g) and bsgluH_2 (1.0 mmol, 0.275 g) was added in 10 mL of water with stirring and the resulting mixture was stirred at room temperature for 20 min giving a clear solution. Subsequently, the pH value of the reaction mixture was carefully adjusted to 5 using 0.1 M NaOH solution. After 3 h of stirring at $65\text{ }^\circ\text{C}$, an ethanol solution (5 mL) of 2,2'-bipyridine (0.5 mmol, 0.078 g) was added and the solution was heated at $65\text{ }^\circ\text{C}$ for 7 h with stirring, and then filtered. The slow evaporation of the filtrate at room temperature gave colorless prisms after 30 days. Anal. Calcd. for $\text{C}_{21}\text{H}_{19}\text{CdN}_3\text{O}_6\text{S}$: C, 45.54; H, 3.60; N, 7.59; Found: C, 45.63; H, 3.55; N, 7.67%.

2.2.2. Preparation of 2

The mixture of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.5 mmol, 0.133 g) and bsgluH_2 (2.0 mmol, 0.550 g) was added into 10 mL of water with stirring at room temperature, giving a clear solution after 20 min. Then the pH value of the reaction mixture was adjusted to 4 by careful addition of 0.1 M NaOH solution. The mixture solution was heated at $65\text{ }^\circ\text{C}$ for 7 h,

and then filtered. The colorless prisms were separated from the filtrate after 25 days by slow evaporation at room temperature. Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{CdNO}_7\text{S}$: C, 31.78; H, 3.15; N, 3.37; Found: C, 31.69; H, 3.23; N, 3.31%.

2.2.3. Preparation of 3

Compound **3** was prepared using a similar method to that for **1** by using $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.5 mmol, 0.100 g) instead of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$. Light blue crystal was obtained after 3 weeks. Anal. Calcd. for $\text{C}_{42}\text{H}_{46}\text{Cu}_2\text{N}_6\text{O}_{16}\text{S}_2$: C, 46.62; H, 4.26; N, 7.77; Found: C, 46.71; H, 4.18; N, 7.70%.

2.3. Crystal structure determination

The structures were solved by direct methods with SHELXS-97. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [25,26]. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by the use of geometrical restraints. Further details of X-ray structure analyses are given in Table 1, and selected bond distances and angles for **1**, **2** and **3** are listed in Table 2.

3. Results and discussion

3.1. Infrared spectra

In comparison of the infrared spectra of the free ligand to those of its complexes, we can get some information about the coordination nature of the ligand. Based on some general references and previous studies on bsgluH_2 complexes [22,27–29], a tentative assignment of most important bands is achieved and the bands are listed in Table 3. Complexes **1–3** show very similar infrared bands in the range of $400\text{--}4000\text{ cm}^{-1}$, which are different from the free ligand. The $\nu(\text{NH})$ of the ligand and its complexes suffer only minor changes in excellent agreement with the fact that this group is not coordinated. Bands assigned to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, which are observed for the free ligand at 1707 and 1452 cm^{-1} , respectively, shift to $1566\text{--}1593\text{ cm}^{-1}$ and $1398\text{--}1408\text{ cm}^{-1}$ in **1–3**, which indicates that the carboxylate groups was deprotonated upon coordination. The $\nu_{\text{as}}(-\text{SO}_2-)$ and $\nu_{\text{s}}(-\text{SO}_2-)$ exhibit almost the same feature as in the ligand, suggesting that this group keeps free of coordination. All these spectroscopic features of **1–3** were further confirmed by the corresponding crystal structure determinations.

3.2. Structural analyses of 1–3

The asymmetric unit of **1** comprises one Cd^{2+} cation, one bsglu bianion and one 2,2'-bipyridine molecule. As shown in Fig. 1, the Cd atoms are six coordinated by two N atoms from a chelating 2,2'-bipyridine ligand and four oxygen atoms from three different bsglu bianion motifs to form an octahedral geometry. The Cd–O bond distances

Table 1
Crystallographic data for 1–3

	1	2	3
Empirical formula	C ₂₁ H ₁₉ CdN ₃ O ₆ S	C ₁₁ H ₁₃ CdNO ₇ S	C ₄₂ H ₄₆ Cu ₂ N ₆ O ₁₆ S ₂
Formula weight	553.85	415.68	1082.07
Temperature (K)	291(2)	291(2)	291(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁
Unit cell dimensions			
<i>a</i> (Å)	8.4947(6)	8.022(3)	13.5122(9)
<i>b</i> (Å)	10.4886(8)	5.1670(2)	14.0553(9)
<i>c</i> (Å)	12.9341(1)	17.229(6)	25.2257(2)
α (deg)	78.8110(1)	90	90
β (deg)	72.7770(1)	96.806(5)	90
γ (deg)	81.0530(1)	90	90
<i>V</i> (Å ³)	1073.87(14)	709.1(5)	4790.8(5)
<i>Z</i>	2	2	4
<i>D</i> _{calc} (mg m ⁻³)	1.713	1.947	1.486
<i>F</i> (000)	556	412	2192
Goodness-of-fit on <i>F</i> ²	1.100	1.099	1.043
Crystal size (mm ³)	0.42 × 0.30 × 0.23	0.30 × 0.19 × 0.12	0.25 × 0.17 × 0.12
θ range for data collection (deg)	2.39–27.50	2.69–25.49	2.64–27.50
Reflection collected	6469	5914	42533
Independent	4736	2425	11009
Reflections	<i>R</i> (int) = 0.0074	<i>R</i> (int) = 0.0403	<i>R</i> (int) = 0.0389
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0191, <i>wR</i> ₂ = 0.0504	<i>R</i> ₁ = 0.0516, <i>wR</i> ₂ = 0.1290	<i>R</i> ₁ = 0.0470, <i>wR</i> ₂ = 0.1182

fall in the range of 2.326(1)–2.380(1) Å, and the Cd–N bond distances are 2.324(2) and 2.355(2) Å, respectively, which are in agreement with previous data of carboxylate- and bipy-containing Cd(II) complexes. In **1**, each bsglu ligand adopts a μ_3 -bridging mode to connect three cadmium atoms and the carboxylate groups adopt monodentate or bidentate chelating coordination modes (Scheme 2a). Thus, each bsglu ligand links three cadmium atoms and each cadmium center interacts with three bsglu ligands. One pair of the nearest Cd atoms are connected by double oxygen atoms from two carboxyl groups of two different bsglu ligands with the distance of 3.663 Å, while another pair of Cd atoms are bridged by two carboxyl groups of bsglu ligand with the separation of 8.023 Å (Fig. 2a). The two types of Cd pairs are extended into a ladder chain running along the *a* axis. These chains are decorated with 2,2'-bipyridine ligands alternating at the two sides and the pyridine rings of 2,2'-bipyridine at each side of the ladder chain are arranged in a nearly parallel fashion with an inter-ring distance of 8.495 Å (Fig. 2b).

These adjacent chains stack along the *b*-axis by π – π stacking interactions through the intercalation of the lateral pyridine rings in a zipper-like way into a two-dimensional layer nearly parallel to the *ab* plane. Their interfacial (inter-pyridine-plane) distance of 3.841 Å indicates relatively weak π – π aromatic stacking interactions which plays an important role in molecular aggregation [30–33]. Similar zipper-like intercalations have been reported previously in some two-dimensional coordination architectures [34]. However, up to now, the molecular ladders owning different inner lungs and lateral arms are seldom reported [35,36].

Usually the multicarboxyl MOFs show 2-D or 3-D structures. The formation of one-dimensional chain of **1** may be mainly due to the 2,2'-bipyridine ligand which is usually used to reduce the available binding sites of the metal ions to interdict polymer growth in other directions [37–39]. Without these terminal ligands, a single-crystal X-ray analysis reveals that **2** shows a 2-D polymeric coordination layer structure.

In the unit of **2**, there is one cadmium atom, one coordination water molecule and one bsglu ligand (Fig. 3). The Cd(II) center is six coordinated in an octahedron by one oxygen atom from water molecule and five oxygen atoms from four bsglu ligands. The equatorial positions are occupied by one water oxygen atom O15, two γ -carboxyl oxygen atoms (O4A, O3A) of bsglu ligand and one oxygen atom O2B from α -carboxyl group of another bsglu ligand. Another two oxygen atoms (O1C, O4) from two other bsglu ligands are located at the axial positions. The Cd–O bond lengths are in the range of 2.297(4) and 2.454(4) Å (Table 2), which are comparable to those reported for the Cd(II) complexes with amino acids [40–43].

In **2**, each bsglu ligand adopts a μ_4 -bridging mode to connect four cadmium atoms (Scheme 2b). Each pair of the nearest Cd atoms is connected by two oxygen atoms from γ -carboxyl group of two bsglu ligands with a distance of 4.304 Å. Each bsglu molecule unit links two cadmium–cadmium pairs, and adjacent cadmium–cadmium pairs are linked by four bsglu with a separation of 9.542 Å. This connection motif was then propagated to result in a one-dimensional coordination polymeric structure (Fig. 4a). One remarkable feature of **2** is that the two neighboring chains are connected into a two-dimensional layer structure

Table 2
Selected bond lengths (Å) and angles (deg) of **1–3**

Compound 1			
Cd(1)–N(3)	2.3243(2)	Cd(1)–N(2)	2.3552(2)
Cd(1)–O(2) ^a	2.3262(1)	Cd(1)–O(3) ^b	2.3559(1)
Cd(1)–O(2)	2.3449(1)	Cd(1)–O(4) ^b	2.3801(1)
N(3)–Cd(1)–O(2) ^a	88.41(5)	O(2)–Cd(1)–O(3) ^b	86.25(5)
N(3)–Cd(1)–O(2)	116.22(5)	N(2)–Cd(1)–O(3) ^b	91.55(5)
O(2) ^a –Cd(1)–O(2)	76.73(5)	N(3)–Cd(1)–O(4) ^b	157.58(5)
N(3)–Cd(1)–N(2)	70.17(5)	O(2) ^a –Cd(1)–O(4) ^b	83.29(5)
O(2) ^a –Cd(1)–N(2)	100.36(5)	O(2)–Cd(1)–O(4) ^b	82.11(5)
O(2)–Cd(1)–N(2)	172.61(5)	N(2)–Cd(1)–O(4) ^b	90.83(5)
N(3)–Cd(1)–O(3) ^b	133.92(5)	O(3) ^b –Cd(1)–O(4) ^b	55.46(5)
O(2) ^a –Cd(1)–O(3) ^b	137.30(5)	N(3)–Cd(1)–C(5) ^b	158.11(5)
Compound 2			
Cd(1)–O(4) ^c	2.259(4)	Cd(1)–O(15)	2.306(5)
Cd(1)–O(2) ^d	2.278(5)	Cd(1)–O(3) ^e	2.318(4)
Cd(1)–O(1)	2.301(5)	Cd(1)–O(4) ^e	2.450(5)
O(4) ^c –Cd(1)–O(2) ^d	86.74(2)	O(2) ^d –Cd(1)–O(3) ^e	94.23(2)
O(4) ^c –Cd(1)–O(1)	174.96(2)	O(1)–Cd(1)–O(3) ^e	86.3(2)
O(2) ^d –Cd(1)–O(1)	97.23(2)	O(15)–Cd(1)–O(3) ^e	162.2(2)
O(4) ^c –Cd(1)–O(15)	100.30(2)	O(4) ^e –Cd(1)–O(4) ^e	85.54(9)
O(2) ^d –Cd(1)–O(15)	100.6(2)	O(1)–Cd(1)–O(4) ^e	89.45(2)
O(1)–Cd(1)–O(15)	82.08(2)	O(15)–Cd(1)–O(4) ^e	111.8(2)
O(4) ^c –Cd(1)–O(3) ^e	90.28(2)	O(3) ^e –Cd(1)–O(4) ^e	54.34(2)
Compound 3			
Cu(1)–O(10) ^f	1.936(3)	Cu(2)–O(8)	1.925(4)
Cu(1)–O(1)	1.947(3)	Cu(2)–O(4) ^g	1.951(4)
Cu(1)–N(6)	2.007(4)	Cu(2)–N(3)	1.993(4)
Cu(1)–N(5)	2.019(3)	Cu(2)–N(4)	1.997(4)
Cu(1)–O(7)	2.322(3)	S(1)–O(6)	1.413(7)
O(10) ^f –Cu(1)–N(6)	170.80(2)	N(5)–Cu(1)–O(7)	93.18(1)
O(1)–Cu(1)–N(6)	94.69(2)	O(8)–Cu(2)–O(4) ^g	90.05(2)
O(10) ^f –Cu(1)–N(5)	94.57(2)	O(8)–Cu(2)–N(3)	174.54(2)
O(1)–Cu(1)–N(5)	174.93(2)	O(4) ^g –Cu(2)–N(3)	94.05(2)
N(6)–Cu(1)–N(5)	80.24(1)	O(8)–Cu(2)–N(4)	95.11(2)
O(10) ^f –Cu(1)–O(7)	90.50(1)	O(4) ^g –Cu(2)–N(4)	172.63(2)
O(1)–Cu(1)–O(7)	87.16(1)	N(3)–Cu(2)–N(4)	81.15(2)

Symmetry codes for **1–3**: a = $-x+2, -y, -z+1$; b = $-x+3, -y, -z+1$; c = $x+1, y-1, z$; d = $x, y-1, z$; e = $-x+1, y-1/2, -z+1$; f = $x-1/2, -y+3/2, -z$; g = $x+1/2, -y+3/2, -z$.

Table 3
Characteristic IR bands (cm⁻¹) of the spectra of the ligand and its complexes **1–3**

bsglu	1	2	3	Assignment
3246m	3230m	3234m	3221m	ν (NH)
1707s	1580s	1566s	1593s	$\nu_{\text{as}}(\text{COO}^-)$
1452s	1408s	1398s	1405s	$\nu_{\text{s}}(\text{COO}^-)$
1341m	1361m	1352m	1321m	$\nu_{\text{as}}(-\text{SO}_2^-)$
1172s	1160s	1152s	1156s	$\nu_{\text{s}}(-\text{SO}_2^-)$

by alternating γ -carboxyl group and α -carboxyl group of bsglu ligands (as shown in Fig. 4b) with alternating large open rectangular and rhombus-shaped channels (Fig. 4c). As far as we know, **2** is the first two-dimensional coordination polymer constructed from metal ions and bsglu ligand.

To explore the influence of metal ions on the formation of MOFs bearing the bsgluH₂ ligand, we synthesized **3** by

utilizing Cu salt instead of Cd salt. As illustrated in Fig. 5, two crystallographically independent Cu(II) atoms exhibit two different coordination geometries in **3**. Cu(1) adopts a distorted square-pyramid geometry by the coordination of three oxygen atoms from three bsglu ligands [Cu1–O10 = 1.936(3) Å, Cu1–O1 = 1.947(3) Å and Cu1–O7 = 2.322(3) Å] and two nitrogen atoms [Cu1–N6 = 2.007(4) Å; Cu1–N5 = 2.019(3) Å] from a bipy molecule. Cu2A is four-coordinated with two oxygen atoms [Cu2A–O8A = 1.925(4) Å, Cu2A–O4 = 1.951(4) Å] from two bsglu ligands and two nitrogen atoms [Cu2A–N3A = 1.993(4) Å, Cu2A–N4A = 1.997(4) Å] from a bipy molecule to furnish a rectangle geometry.

In **3**, the carboxylate groups of the bsglu ligand adopts two types of coordinated modes: monodentate–monodentate and bidentate–monodentate, which differ from those in **1** and **2**, as schematically shown in Scheme 2c and d, respectively. The adjacent Cu atoms in the asymmetric unit are connected by two bsglu ligands with a separation of

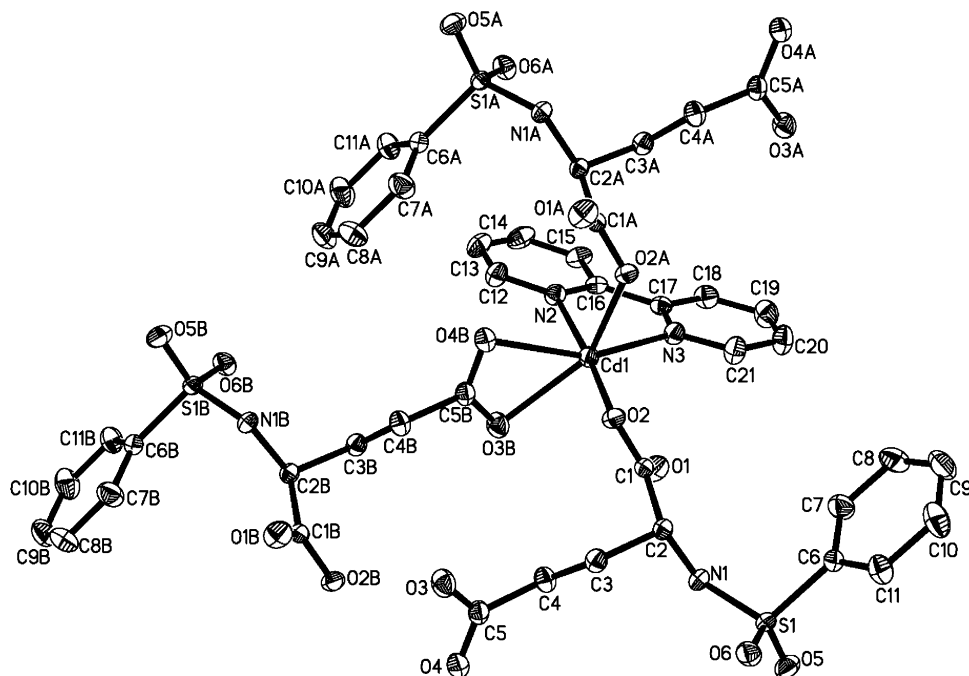
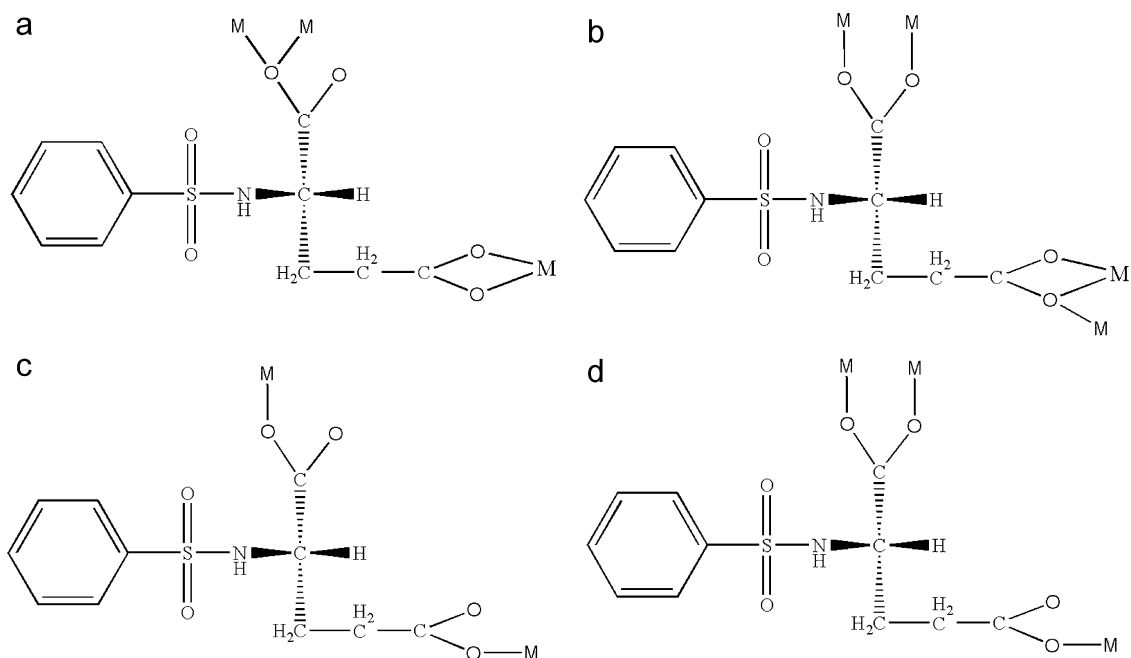


Fig. 1. Coordination environment around Cd atom with the thermal ellipsoids at 30% probability level.



Scheme 2. Coordination modes of bsglu ligand in 1–3.

8.267 Å, and the neighboring copper–copper pairs are linked into a square-wave alternating chain motif by one carboxyl oxygen atom of the bsglu with the separation 4.389 Å (Fig. 6a).

In the structure of **3**, relatively strong π – π aromatic stacking interactions can be found. The chains are decorated with 2,2′-bipyridine at two sides and the pyridine rings at each side of the square-wave chains are arranged in a nearly parallel fashion with an inter-ring-plane distance

of 3.709 and 3.797 Å, and the plane–plane distances of neighboring pyridine rings from adjacent chains are 3.573 and 3.641 Å, respectively. This indicates that there exist two types of π – π aromatic stacking interactions in **3**: intra- and inter-chain π – π aromatic stacking interactions. The two kinds of π – π aromatic stacking interactions are in a novel stacking fashion which consolidate the stacked arrangement leading to a two-dimensional supramolecular architecture (Fig. 6b).

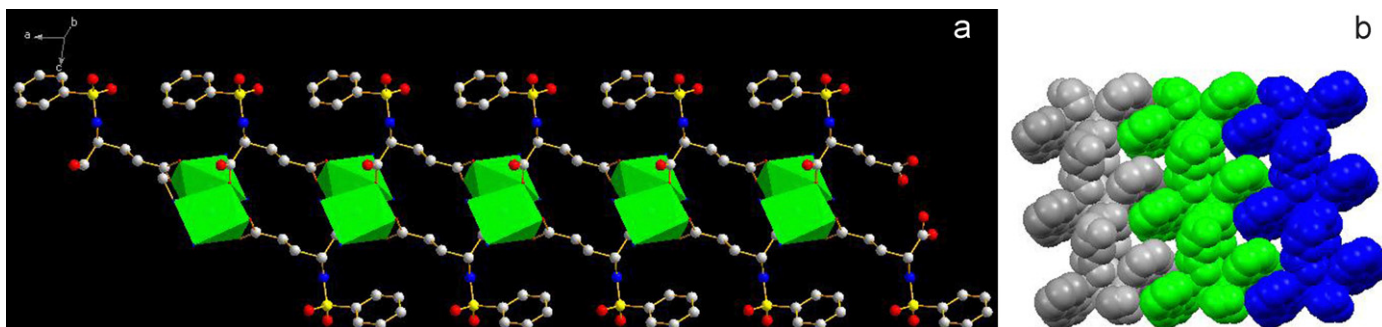


Fig. 2. (a) A view of the 1-D ladder framework of **1** (bipy ligands are omitted for clarity); (b) a space-filling mode of the 2-D layer supramolecular coordination polymer constructed by the intermolecular π - π aromatic stacking interactions.

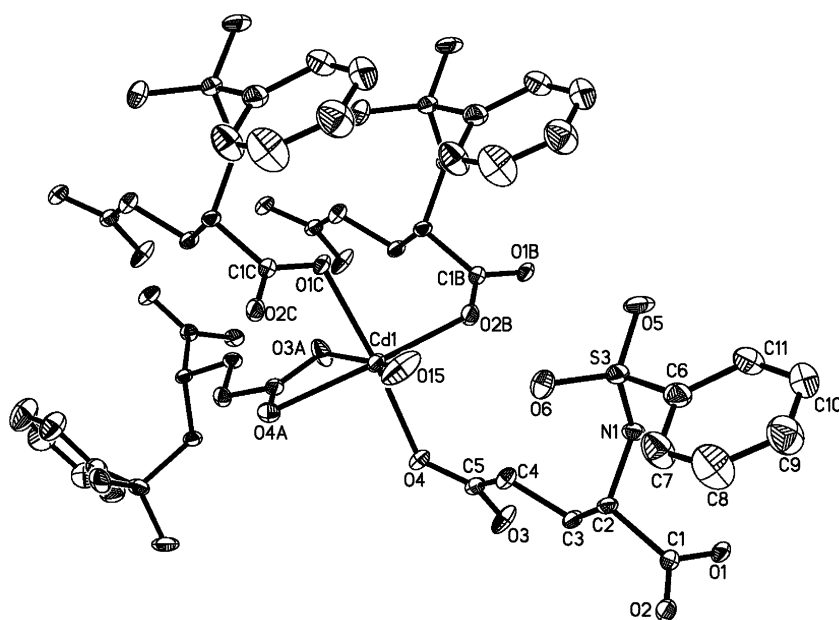


Fig. 3. ORTEP drawing of **2** with the atom numbering scheme showing the local geometry of the metal center and ligand.

In the three complexes, the bsgluH_2 ligand behaves as just simple carboxylate group coordinated to the metal ions with the sulfonamide nitrogen free. This is consistent with the reported cases where *N*-benzenesulfonyl-amino acids behave as the simple carboxylate ligands under low pH value. While with the pH value increasing, it switches to dianionic *N,O*-bidentate chelating ligands due to the environment of the deprotonated amide nitrogen as an additional donating site [21,44–48]. It seems that bsglu ligand should perform different coordinating behavior in the reaction with transitional metal ions at higher pH value which is to be confirmed in the future.

3.3. Fluorescent properties of **1**

Coordination frameworks are fascinating luminescent materials owing to their higher thermal stability than the free organic ligand and the ability to tune the emission wavelength of the organic material upon coordination [49,50]. The luminescent properties of **1** were investigated

in the solid state at room temperature, as shown in Fig. 7. Compound **1** gave an emission band in the range of 530–560 nm with a maximum at 539 nm upon excitation at 337 nm. In comparison to the emission at 287 nm for the free bsgluH_2 ligand [27] and at 530 nm for free 2,2'-bipyridine in the solid state at room temperature [51], the fluorescence may be assigned to the intraligand emission from the 2,2'-bipyridine ligand. The luminescent properties of **2** were also investigated in the solid state at room temperature. It displays no luminescence as expected. This might be caused by the coordination of water molecules instead of bipy ligands to Cd(II) ion and water molecules possessing high-energy OH-vibrations ($\nu = 3700 \text{ cm}^{-1}$) are the most efficient quencher [52].

3.4. Magnetic properties of **3**

The magnetic susceptibilities, χ_M , of **3** were measured in the 2–300 K temperature range at 10,000 G, and the plots of $\chi_M T$ and χ_M versus T are shown in Fig. 8. The $\chi_M T$

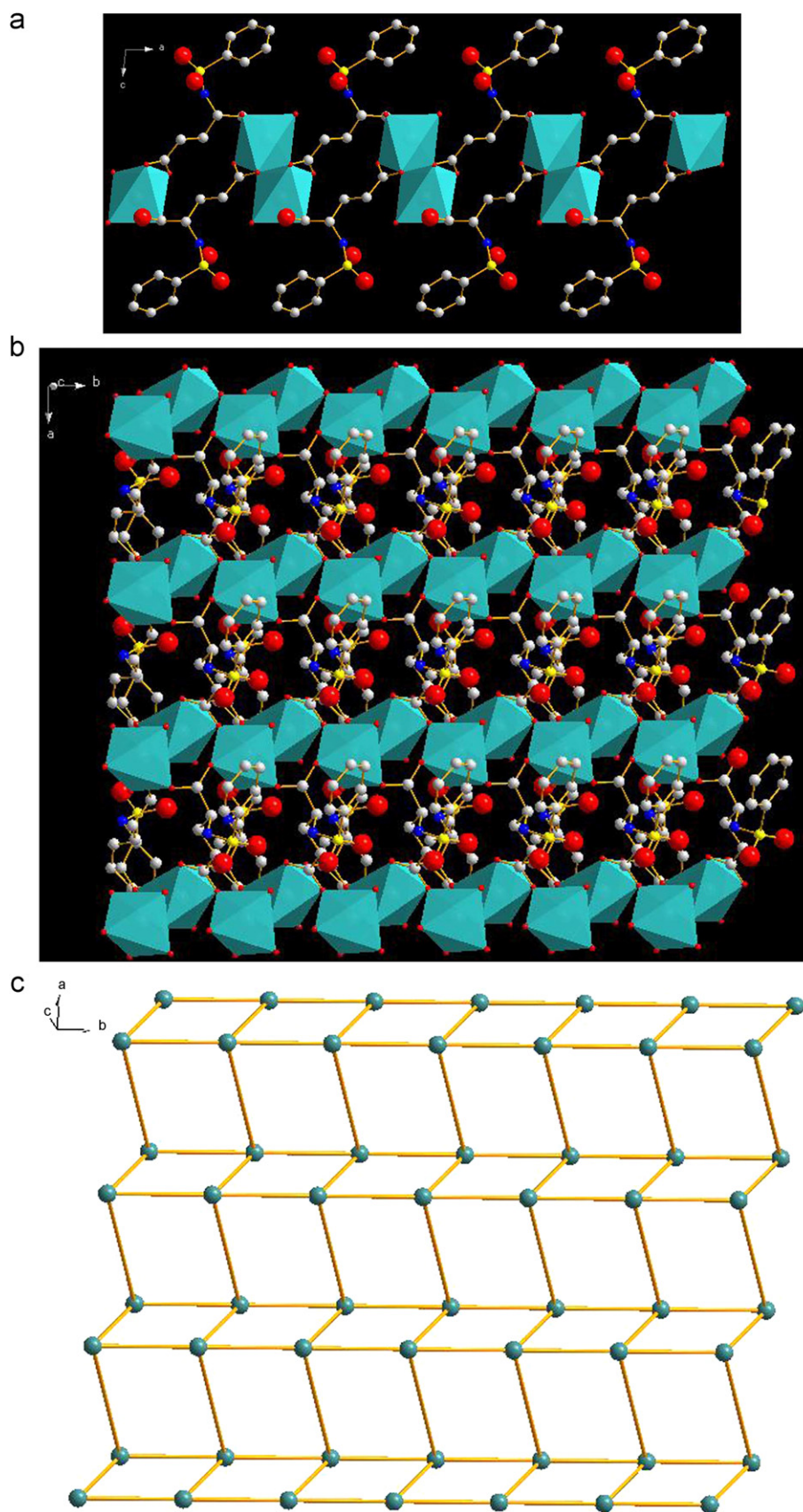


Fig. 4. (a) A view of the double chain framework of **2**; (b) 2-D layer structure of **2** constructed from the 1-D chain through alternating γ - and α -carboxyl group; (c) schematic representation of 2-D layer structure.

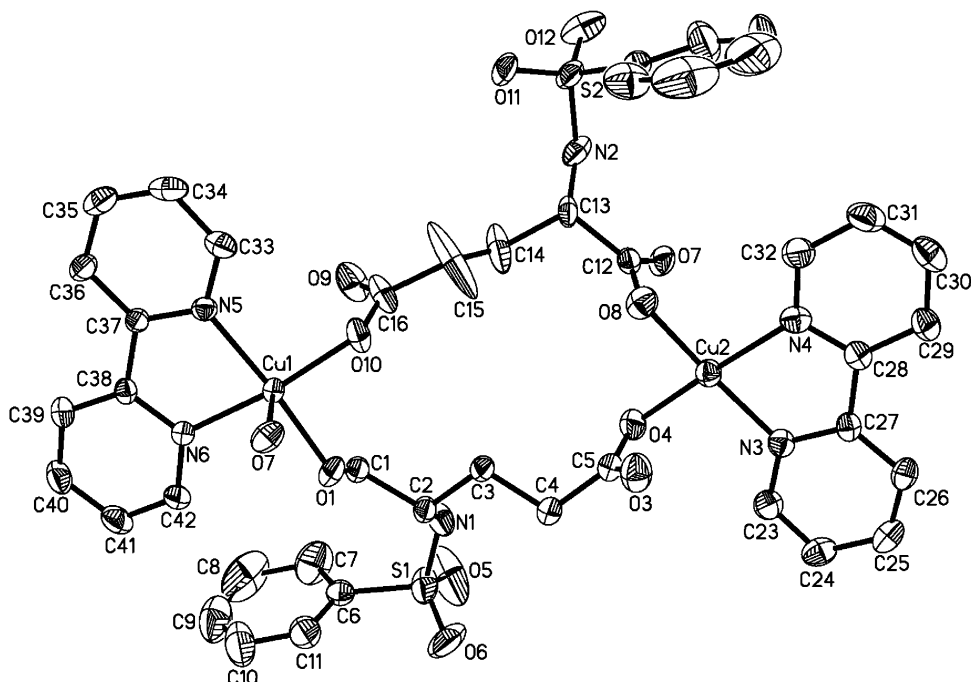


Fig. 5. Molecular structure of **3**, showing two different coordination geometries of Cu centers.

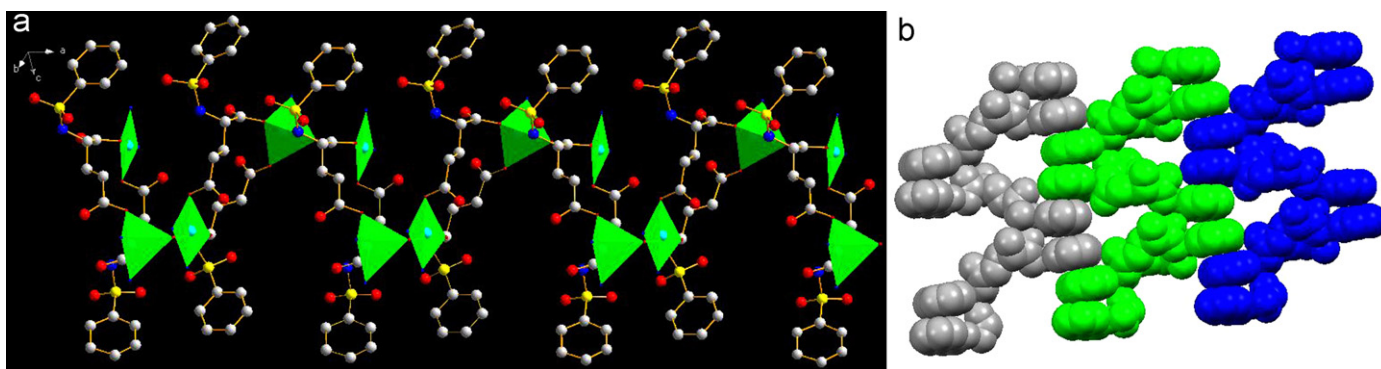


Fig. 6. (a) The square-wave-like 1-D chain polymer motif of **3**; (b) a space-filling mode of 2-D layer supramolecular coordination polymer constructed by the inter- and intra-molecular π - π aromatic stacking interactions.

value at room temperature is $0.381 \text{ cm}^3 \text{ K mol}^{-1}$, which is close to that expected for uncoupled one independent spin ($0.375 \text{ cm}^3 \text{ K mol}^{-1}$, $S = 1/2$) of the Cu(II) ion. As the temperature is lowered, the $\chi_M T$ value decreases gradually, which indicates the presence of antiferromagnetic interactions between the two Cu(II) ions through the bridging carboxylate. There are two pathways of magnetic interaction in the present system, namely: (i) the adjacent Cu(II) ions bridged by the α -carboxyl O atoms and (ii) neighboring Cu(II) ions bridged by the α -carboxyl and γ -carboxyl O atoms of extended bsglu. In order to quantitatively understand the magnitude of the spin-exchange interaction, for similar 1-D alternating Cu(II) complexes, the following Eq. (1) is induced from the Hamiltonian for a chain behavior in the Heisenberg model which is good fit

for antiferromagnetic exchange ($J < 0$) and for $0 \leq \alpha \leq 1$ (α is the alternation parameter) [53]. At the extremes, when $\alpha = 0$, the model reduces to the dimer model with pairwise interactions and when $\alpha = 1$, the model reduces to the regular linear-chain model:

$$\hat{H} = -2J \sum_{i=1}^{n/2} [\hat{S}_{2i} \hat{S}_{2i-1} + \alpha \hat{S}_{2i} \hat{S}_{2i+1}],$$

where J is the parameter of exchange integral between a spin and its right neighbor and αJ is the exchange integral between a spin and its left neighbor:

$$\chi_M = \frac{Ng^2 \mu_B^2}{KT} \frac{A + Bx + Cx^2}{1 + Dx + Ex^2 + Fx^3}, \quad (1)$$

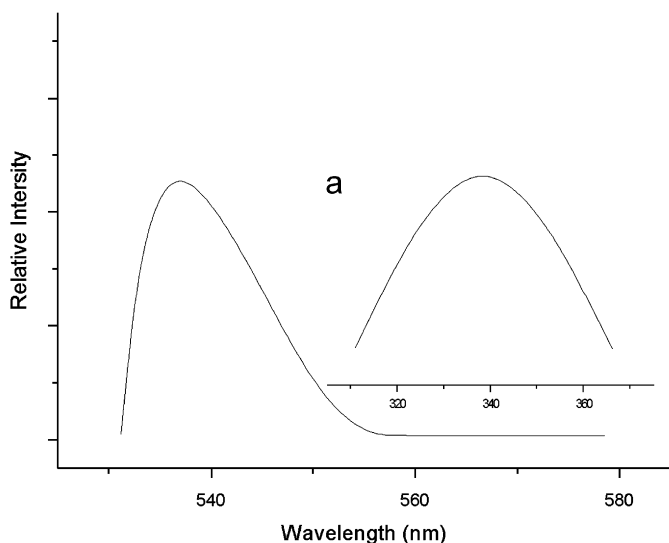


Fig. 7. The emission spectra of **1** in the solid state at room temperature; (a) the excitation spectra of the **1** in the solid state at room temperature.

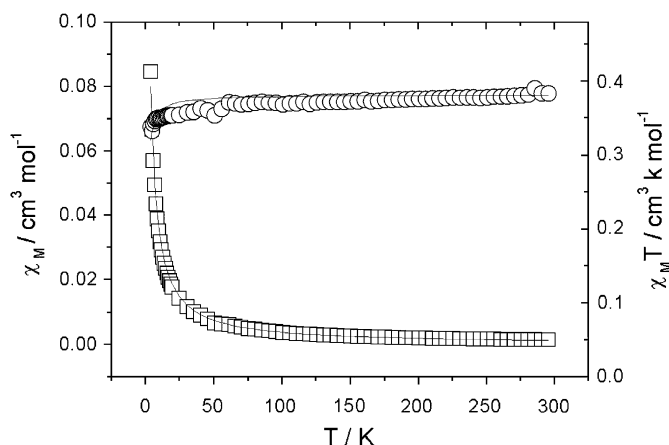


Fig. 8. Temperature dependence of $\chi_M T$ and χ_M for **3**. The solid line represents the theoretical values based on Eq. (1) described in the text.

where $x = |J|/KT$ and the values for the parameters A – F for $0 \leq \alpha \leq 0.4$ are

$$A = 0.25,$$

$$B = -0.12587 + 0.22752\alpha,$$

$$C = 0.019111 - 0.13307\alpha + 0.50967\alpha^2 - 1.3167\alpha^3 + 1.0081\alpha^4,$$

$$D = 0.10772 + 1.4192\alpha,$$

$$E = -0.0028521 - 0.42346\alpha + 2.1953\alpha^2 - 0.8241\alpha^3,$$

$$F = 0.7754 - 0.067022\alpha + 6.9805\alpha^2 - 21.678\alpha^3 + 15.838\alpha^4$$

and the values for the parameters A – F for $0.4 < \alpha \leq 1$ are

$$A = 0.25,$$

$$B = -0.13695 + 0.26387\alpha,$$

$$C = 0.017025 - 0.12668\alpha + 0.49113\alpha^2 - 1.1977\alpha^3 + 0.87257\alpha^4,$$

$$D = 0.070509 + 1.3042\alpha,$$

$$E = -0.0035767 - 0.40837\alpha + 3.4862\alpha^2 - 0.73888\alpha^3,$$

$$F = 0.36184 - 0.065528\alpha + 6.65875\alpha^2 - 20.945\alpha^3 + 15.452\alpha^4,$$

$$\alpha = 0.5.$$

In order to quantitatively evaluate magnetic interaction on the system, all of our attempts to reproduce the susceptibility data through this isotropic Heisenberg form of interaction were not successful when $\alpha = 0, 0.1, 0.2, 0.4, 0.6, 0.7, 0.9, 1.0$ except for $\alpha = 0.5$. When $\alpha = 0.5$, the results of solid line were in excellent agreement with the experimental data.

The least-squares analysis of magnetic susceptibilities data led to $J = -0.606 \text{ cm}^{-1}$, $g = 1.99$, $zJ' = -0.024 \text{ cm}^{-1}$ and $R = 7.35 \times 10^{-4}$ (the agreement factor defined as $R = \sum[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calc}}]^2 / \sum[(\chi_M)_{\text{obs}}]^2$). The J value indicates a weak antiferromagnetic between the two Cu(II) ions bridged by the α -carboxyl O atoms. The more weak antiferromagnetic coupling zJ' accounts for the interaction through the extended bs glu bridge. Its low magnitude can be associated with the excessive span (8.267 Å) of the bs glu bridge.

In the literature, the successful examples of quantitative calculation for the magnetic interaction on the 1-D alternating chain copper polymeric complexes were seldom reported. The metal ions in the reported cases were usually connected by simple inorganic ions such as chlorine and bromine atoms [53–55]. The 1-D alternating copper chain polymers constructed from organic molecules are still scarcely explored and we believe that this study will provide new information on the magnetic properties of them.

4. Conclusion

In summary, three coordination polymers with different structure motifs have been synthesized and characterized. Interestingly, the bs $gluH_2$ ligand exhibits versatile coordination modes in these complexes. It is not yet fully understood what is the major factor affecting the coordination modes in the given complexes, some conclusions can still be made: (i) the ancillary ligand has important effects on the formation of the complexes and physical properties because of its rigidity and steric hindrance; (ii) each transition metal ion has its own specific preference and different geometries derived from different ion radii and d electron numbers, which can affect the interaction with the carboxyl groups; (iii) the experimental conditions, such as pH value and temperature, also play important roles in the formation of the complexes. The luminescent properties of **1** indicate that the coordination of metal ion can affect the emission intensity of the organic material. The magnetic susceptibility measurement of **3** reveals that antiferromagnetic coupling among the copper ions has been transferred through the bs glu ligand. On the basis of this work and our previous work, further syntheses, structural diffraction studies and physical

characterization of other transition metals and rare-earth metals as well as their heterometal centers with the bsgluH_2 ligand are also underway in our lab. We anticipate that this ligand will result in a variety of coordination polymers or supramolecules with unique topologies and fascinating properties.

5. Supplementary data

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 615477 for **1**, 615478 for **2** and 615479 for **3**. 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; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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