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Syntheses and Structures of Three New Copper(II) Coordination Polymers Involving 2,2-(4,6-Dinitro-1,3-phenylenedioxy)diacetic Acid

Dong-Sheng Ma,*[a] Xiu-Mei Zhang,[a] Pei-Jiang Liu,[a] and Shuai Zhang[a]

Keywords: Crystal structure; Coordination complex; Copper; Fluorescence

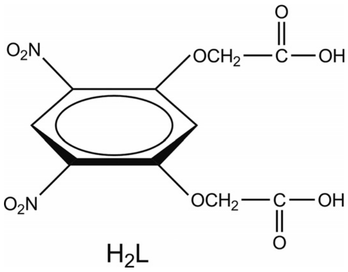
Abstract. Three copper(II) coordination polymers, namely, $\{[CuL(H_2O)_2]\cdot 4H_2O\}_n$(**1**), $[CuL(H_2O)(DMF)]_n$(**2**), and [CuL(2,2′-bipy)(DMSO)]·DMSO (**3**) [H_2L = 2,2′-(4,6-dinitro-1,3-phenylenedioxy)diacetic acid] were synthesized in different solvents (H_2O, DMF, and DMSO). X-ray single crystal diffraction studies show that both complexes **1** and **3** belong to triclinic crystal system and $P\bar{1}$ space group and complex **2** belongs to the monoclinic crystal system and $P2_1/c$ space group. In three complexes, all the central Cu^{II} ions coordinate with the ligand, forming a square pyramidal configuration. Both complexes **1** and **2** show similar 1D chain-like structure and the chains are further connected by hydrogen bonds, forming 3D frameworks. Complex **3** exhibits a 0D structure due to the introduction of the ligand 2,2′-bipy. In addition, the luminescence properties of these complexes were investigated.

1. Introduction

Many functional coordination polymers with carboxylic ligands have been synthesized due to their strong coordination abilities and diverse coordination modes. To date, most of the efforts have been focused on the rigid aromatic carboxylic ligands, which can easily form hydrogen bonds and π–π interactions.[1–4] Among those, studies on coordination polymers with flexible aromatic carboxylic ligands are rare, probably because they have greater deformation ability in coordination process and could adopt diverse configurations according to different coordinating environments, thus increasing the difficulty to predict the structures of coordination polymers. However, these characteristics could make them easily adjust the coordinating orientation to accommodate the coordination environment.[5–8] Therefore, polymers with novel structures and properties could probably be built by adopting flexible aromatic carboxylic ligands as building blocks,[9–12] which may have potentially applications in separation, catalysis, optics, and electrical conductivity, magnetism and bionics etc.[13–16]

Copper chemistry is well-documented through structural and magnetic characterization of different varieties of mono-, di-, and polynuclear complexes. Copper coordination polymers are widely used in many fields such as application in the synthesis of catalysts in heterogeneous and homogeneous reactions, functional materials (super conductive materials, magnetic materials, ceramic materials and electronic materials etc.) and metal enzyme models.[17–23] On the other hand, solvents can also effect the formation of the crystal structure.[24–27] Taking account of the above, our aim was to explore constructing rules and effect of different solvents in the synthesis of copper-containing complexes.

Herein, we report the syntheses, structures, and luminescent properties of three new copper coordination polymers in different solvents (water, DMF, and DMSO) by the reaction of the ligand and copper(II). It is found that three solvents are all coordinated with copper. Complex $\{[CuL(H_2O)_2]\cdot 4H_2O\}_n$ (**1**) achieved from water and complex $[CuL(H_2O)(DMF)]_n$ (**2**) achieved from DMF exhibit the similar 1D infinite chain structures. Complex [CuL(2,2′-bpy)(DMSO)]·DMSO (**3**) achieved from DMSO shows 0D structure due to the presence of 2,2′-bipyridine as a second ligand.



H_2L

2. Experimental Section

2.1. Materials and Measurements

All commercially available chemicals are of reagent grade and were used as received without further purification. Elemental analyses for C, H, and N were carried out with a Vario EL III elemental analyzer. The IR spectra were recorded with a Bruker tensor 27 FT-IR spectrophotometer in the 4000–400 cm^{-1} region by using KBr pellets. The luminescent spectra were taken with a Perkin Elmer Corporation Model Fluorescence Spectrometer LS 55 PL. ^1H NMR spectra was performed with a Bruker AV300 MHz equipment. The melting point was taken on a WRS-2 microscopic meting point meter of Shanghai precision & scientific instrument Co., Ltd.

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* Prof. Dr. D.-S. Ma
E-Mail: rwws8828@sina.com
[a] School of Chemistry and Materials Science
Heilongjiang University
74 XueFu Road, NanGang District
Harbin 150080, P. R. China

2.2. Synthesis of 2,2′-(4,6-Dinitro-1,3-phenylenedioxy)-diacetic Acid (H_2L)

The ligand (H_2L) was synthesized following the references method.[28,29] A mixture of chloroacetic acid (51.60 g, 0.54 mol), sodium hydroxide (36.30 g, 0.90 mol), resorcin (20.00 g, 0.18 mol) was dissolved in distilled water (200 mL) with stirring. The solution was heated to reflux for 6 h, and the pH value was adjusted to about 2.0 by using 25 % hydrochloric acid. After cooling to room temperature, yellow precipitate (10.80 g, 27 %) was obtained. Subsequently, all of the above yellow products were dissolved in concentrated sulfuric acid (100 mL) with stirring, and a mixture of nitric acid (9.45 g, 0.15 mol) and sulfuric acid (20.58 g, 0.21 mol) was dropped into the above solution with keeping the reaction temperature under 0 °C for 1 h. Afterwards, the mixed solution was kept stirring about 5 h at room temperature. The mixture was poured into water (500 mL), the crude product was obtained (37 %). The product was obtained by recrystallization from water. Elemental analysis: $C_{10}H_8N_2O_{10}$: calcd. C 37.99; H 2.55; N 8.86 %; found: C 37.87; H 2.64; N 8.93 %. Melting point: 214.8–215.8 °C. **UV** (solvent: MeOH): 289 nm, [squ] = 2.42×10^3 mol L^{-1} cm^{-1}. **FT-IR** (KBr): $\tilde{\nu}$ = 3558 m, 3468 m, 2927 m, 1772 s, 1741 s, 1614 s, 1596 s, 1520 m, 1426 m, 1244 s, 1220 s, 1085 m, 1064 s, 917 w, 871 w, 834 w, 814 m, 719 m, 662 w cm^{-1}. **^{1}H NMR** ([D_6]DMSO): 5.10 (s, 4 H, CH_2), 7.14 (s, 1 H), 8.66 (s, 1 H), 13.29 (s, 2 H) ppm.

2.3. Synthesis of the Complexes

2.3.1 Synthesis of $\{[CuL(H_2O)_2]\cdot 4H_20\}_n$ (1)

H_2L (0.06 g, 0.20 mmol) and copper nitrate (0.04 g, 0.20 mmol) were dissolved in distilled water (20 mL) with stirring. Afterwards, the pH value was adjusted to about 7 with the aqueous solution of sodium hydroxide (20 %). The mixture was stirred for 2 h and the blue precipitate was filtered off. The filtrate was left at room temperature for several days; dark blue crystals suitable for X-ray diffraction were obtained in 43 % yield. Elemental analysis: $C_{10}H_{18}Cu_1N_2O_{16}$: calcd. C 24.70; H 3.70; N 5.76 %; found: C 24.42; H 3.74; N 5.79 %. **FT-IR** (KBr): $\tilde{\nu}$ = 3435 s, 2071 w, 1519 m, 1446 m, 1426 m, 1405 m, 1361 m, 1197 m, 1082 m, 1047 m, 925 m, 853 m, 834 m, 824 m, 740 m, 713 m, 606 w cm^{-1}.

2.3.2 Synthesis of $[CuL(H_2O)(DMF)]_n$ (2)

The preparation of complex **2** was similar to that of **1** except that the DMF was used instead of water as solvent. Yield 36 %. Elemental analysis: $C_{13}H_{15}Cu_1N_3O_{12}$: calcd. C 33.26; H 3.20; N 8.96 %; found: C 33.00; H 3.22; N 8.64 %. **FT-IR** (KBr): $\tilde{\nu}$ = 3429 s, 2921 w, 2843 w, 1615 s, 1519 m, 1385 m, 1356 m, 1281 m, 1194 w, 1079 w, 1041 w, 915 w, 834 w, 703 w cm^{-1}.

2.3.3 Synthesis of $[CuL(2,2'\text{-bipy})(DMSO)]\cdot DMSO$ (3)

The preparation of complex **3** was similar to that of **1** except that the DMSO was used instead of water as solution, and the 2,2′-bipy was used as the second ligand. Yield 59 %. Elemental analysis: $C_{24}H_{26}Cu_1N_4O_{12}S_2$: calcd. C 41.74, H 3.27; N 9.12 %; found: C 41.59; H 3.15; N 9.46 %. **FT-IR** (KBr): $\tilde{\nu}$ = 3424 m, 1640 s, 1599 s, 1522 m, 1468 w, 1441 w,1402 m, 1357 m, 1271 s, 1198 w, 1102 w, 1078 m, 1032 m, 918 w, 835 m, 790 m, 773 m, 745 w, 732 w, 697 m, 605 w cm^{-1}.

2.4. X-ray Crystallography

Single-crystal X-ray diffraction data for complexes **1**–**3** were collected with a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) at 291 K. Empirical absorption corrections based on equivalent reflections were applied. The structures of complexes **1**–**3** were solved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELXS-97 crystallographic software package.[30,31] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the L and 2,2′-bipy molecules were placed in calculated positions and treated as riding on their parent. The crystal parameters, data collection, and refinement results for **1**–**3** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic

Table 1. Crystallographic data for complexes **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{10}H_{18}CuN_2O_{16}$	$C_{13}H_{15}CuN_3O_{12}$	$C_{24}H_{26}CuN_4O_{12}S_2$
Formula weight	485.81	468.82	690.15
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a /Å	6.9075(14)	6.7169(13)	9.728(4)
b /Å	8.9797(18)	26.680(5)	10.696(5)
c /Å	16.179(3)	10.486(2)	14.163(9)
α /°	84.54(3)	90	94.58(2)
β /°	84.73(3)	106.25(3)	93.25(2)
γ /°	71.43(3)	90	90.009(16)
V /Å^3	945.0(3)	1804.0(6)	1466.6(13)
Z	2	2	2
T /K	291(2)	291(2)	291(2)
d_{calcd} /mg·m^{-3}	1.707	1.726	1.563
μ /mm^{-1}	1.241	1.283	0.955
F(000)	498	956	710
Reflections collected	8773	17554	13899
R_{int}	0.0819	0.0495	0.0267
Goodness-of-fit on F^2	1.062	1.083	1.073
$R_1$$^{a)}$, w$R_2$$^{b)}$ [$I > 2\sigma I$)]	0.0544, 0.1395	0.0420, 0.1082	0.0438, 0.1209
R_1, wR_2 (all data)	0.0764, 0.1712	0.0575, 0.1159	0.0567, 0.1330

a) $R_1 = (\Sigma||F_o|-|F_c|)/\Sigma|F_o|$. b) $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/ \Sigma w (F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths /Å and angles /° of complexes **1**–**3**.

1			
Cu(1)–O(12)	1.931(4)	Cu(1)–O(5)#1	1.947(3)
Cu(1)–O(11)	1.957(3)	Cu(1)–O(1)	2.344(2)
Cu(1)–O(1)#2	1.971(3)		
O(12)–Cu(1)–O(5)#1	89.84(14)	O(12)–Cu(1)–O(1)	92.73(13)
O(12)–Cu(1)–O(11)	176.28(13)	O(12)–Cu(1)–O(1)#2	88.33(13)
O(5)#–Cu(1)–O(1)	101.10(10)	O(5)#1–Cu(1)–O(1)#2	178.10(12)
O(5)#1–Cu(1)–O(11)	90.72(13)	O(11)–Cu(1)–O(1)#2	91.09(12)
O(11)–Cu(1)–O(1)	90.78(11)	O(1)#2–Cu(1)–O(1)	79.47(11)
Symmetry codes: #1 *x*+1, *y*, *z* #2 –*x*+2, –*y*+2, –*z*			
2			
Cu(1)–O(1)	1.922(2)	Cu(1)–O(4)#1	1.959(2)
Cu(1)–O(11)	1.958(3)	Cu(1)–O(12)	1.966(2)
Cu(1)–O(4)#2	2.322(2)		
O(1)–Cu(1)–O(11)	90.84(11)	O(11)–Cu(1)–O(4)#1	88.12(10)
O(1)–Cu(1)–O(4)#1	174.58(9)	O(1)–Cu(1)–O(12)	92.70(10)
O(11)–Cu(1)–O(12)	165.77(10)	O(1)–Cu(1)–O(4)#2	94.45(8)
O(4)#–Cu(1)–O(12)	89.58(9)	O(11)–Cu(1)–O(4)#2	97.88(10)
O(4)#1–Cu(1)–O(4)#2	80.43(8)	O(12)–Cu(1)–O(4)#2	95.58(9)
Symmetry codes: #1 –*x*, –*y*+1, –*z* #2 *x* + 1, *y*, *z*			
3			
Cu(1)–O(1)	1.963(2)	Cu(1)–N(4)	2.006(2)
Cu(1)–O(11)	2.232(2)	Cu(1)–O(5)	1.969(2)
Cu(1)–N(3)	2.010(2)		
O(1)–Cu(1)–O(5)	88.83(9)	O(5)–Cu(1)–N(4)	168.76(9)
N(4)–Cu(1)–N(3)	80.54(10)	O(1)–Cu(1)–N(4)	94.01(9)
O(1)–Cu(1)–N(3)	171.67(9)	O(1)–Cu(1) –O(11)	89.97(9)
O(5)–Cu(1)–N(3)	95.35(9)	N(4)–Cu(1)–O(11)	96.22(10)
O(5)–Cu(1)–O(11)	94.66(9)	N(3)–Cu(1)–O(11)	96.86(10)

Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-734886, CCDC-744660, and CCDC-734887 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

3. Results and Discussion

3.1 Structure Description

Recently, we have reported two types of the crystal structure of H_2L.[28,29] The only difference of the two compounds is the number of the lattice water molecules, which influences the formation of the hydrogen bonding and the stacking fashion of the molecules. From the reported results, one can find that the hydrogen bonds between lattice water molecules and organic components are able to strongly influence the arrangements of the whole molecules. So, what will happen when different solvents were used in the synthesis of coordination complexes? Herein, we used copper as coordination metal and H_2L as ligand to carry out reactions in H_2O, DMF, and DMSO and obtained three different inorganic-organic hybrid complexes.

3.1.1 Crystal Structure of Complex 1

Figure 1 presents a ball-and-stick view of the crystal structure of complex **1**. The asymmetric unit consists of one Cu^{II} cation, one L ligand, two coordinated water molecules, and four lattice water molecules. The central Cu^{II} ion is five-coordinated by three oxygen atoms of three carboxylate groups of three L ligands and two oxygen atoms of two water molecules, resulting in a square pyramid type with $\tau = 0.03$.[32] The basal plane of pyramid is defined by two oxygen atoms (O5, $O1^i$, where i = 2–*x*, 2–*y*, *z*) of two L ligands and two water molecular oxygen atoms (O11, O12), whereas the apical site is occupied by O1 from L ligand, with the Cu1–O1 being almost perpendicular to the least-squares plane. In many cases, the nitro groups of benzene ring do not take part in the coordination with central metal ions, which also exist in these three complexes reported herein.

The molecule can be seen as a dimer of two nearly square-planar monomeric units, which are related to each other by an inversion center located in the middle of the dimer through two bridging oxygen groups, O1 and its symmetry equivalent $O1^i$. The result is a tightly bound pair of CuO5 nuclei, with the distance of copper cations Cu1 and $Cu1^i$ at 3.327(1) Å from each other.

In the crystal structure of complex **1**, two carboxylic groups of L ligand exhibit two kinds of coordination modes, that is, O5 bridges two neighboring Cu^{II} ions into dimer, whereas O1 only coordinates to one Cu^{II} ion. In addition, the two carboxylate groups of L ligand do not locate in a plane with the central benzene ring with the dihedral angles between the carboxylate groups and the benzene ring of 72.56(3)° to 81.52(3)°, which is much larger than those found in free H_2L ligands (nearly 0°).[28,29]

Another structural feature of complex **1** is that it has an infinite chainlike structure along *a* axis, as shown in Figure 1b.

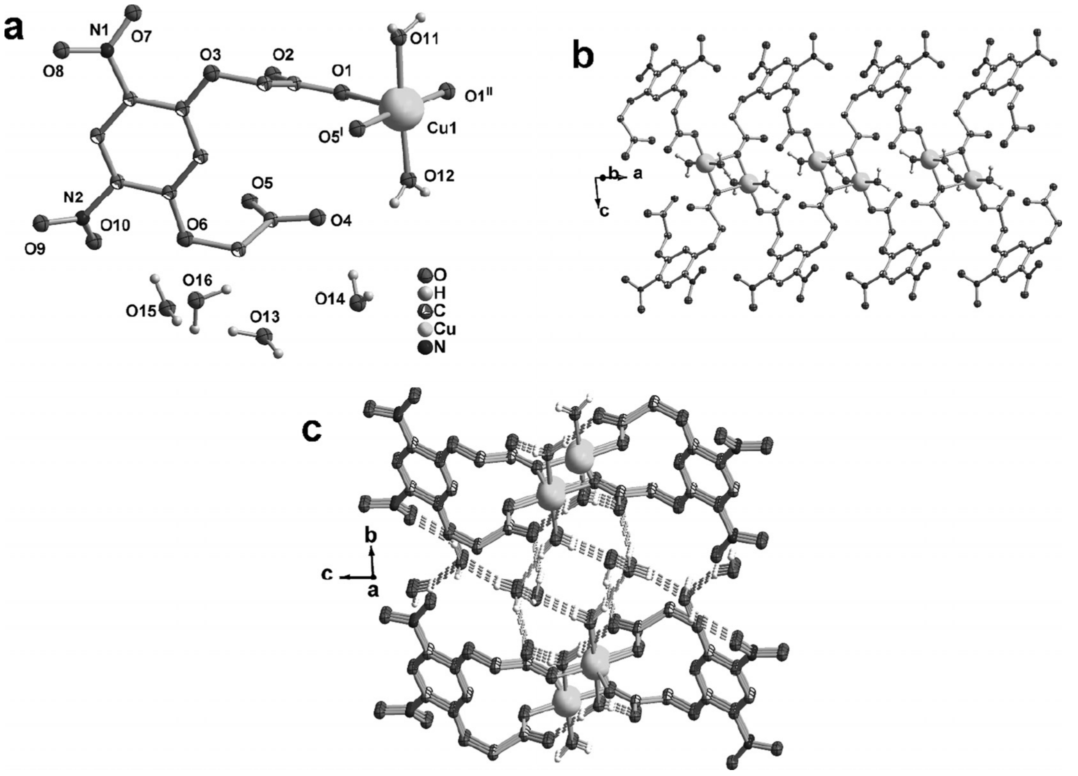

Figure 1. (a) Molecular structure of complex **1**; (b) 1D ladder chain of complex **1**; (c) 2D hydrogen-bonding net of complex **1**. Symmetry codes:I = 1+*x*, *y*, –*z*; II = 2–*x*, 2–*y*, –*z*.

Meanwhile, the interchain weak C–H···O hydrogen bonding C9–H9A···O7^{ii} (where ii = 2–*x*, 3–*y*, –*z*) links the chains to form a 2D structure with (001) plane. In the packing arrangement of complex **1**, the adjacent 2D layers form a 3D framework by O–H···O hydrogen bonding of lattice water molecules (Figure 1c).

3.1.2 Crystal Structure of Complex 2

Single crystal X-ray diffraction analysis indicates that Cu1 in complex **2** is also in a square pyramid coordination environment with $\tau = 0.15$ (Figure 2a), involving three oxygen atoms (O1, O4^{iii}, O4^{iv}, where iii = –*x*, 1–*y*, –*z*; iv = 1+*x*, *y*, *z*) from three different L ligands and two oxygen atoms (O11, O12) from water molecules. The basal of the pyramid is defined by O1, O11, O12, and O4^{iii}, whereas the apical site is occupied by O4^{iv}. The O–Cu–O angles range from 80.43(8)° to 174.59(9)°. It should be noted that no water was added in the synthesis of complex **2**, the coordinated water molecule perhaps comes from the reactants or undried DMF solvent.

As shown in Figure 2b, complex **2** is also a 1D coordination polymer consisting of double metal atoms with the distance of Cu···Cu in dimer of 3.277(1) Å. In complex **2**, all carboxyl groups are completely deprotonated, in agreement with the IR data, in which no absorption peaks around 1731–1651 cm^{-1} for –COOH were observed. Similar with complex **1**, the coordination modes of two carboxylate groups in L ligand are different: one carboxylate group adopts a unidentate coordination mode with one Cu^{II} ion, whereas the other one links two Cu^{II} ions in a bridging fashion. Thus, the copper atoms are infinitely linked by L ligands to generate a one-dimensional chain. The nearest Cu···Cu distance between adjacent chains is 10.486(3) Å. Figure 2c shows the 3D supramolecular framework constructed by hydrogen bonding.

3.1.3 Crystal Structure of Complex 3

Different from complex **1**, complex **3** does not form a 1D coordination chain due to the introduction of 2,2′-bipy. The asymmetric unit of complex **3** consists of one Cu^{II} ion, one 2,2′-bipy ligand, one L ligand, one coordinated DMSO, and one free DMSO molecules. The arrangement around the central metal atom is close to square pyramidal (Figure 3a) with two of the basal positions occupied by the two nitrogen atoms (N3, N4) of 2,2′-bipy ligand and the other ones by two oxygen atoms (O1, O5) of two different carboxylate groups of the same L ligand, whereas the axial position is occupied by the oxygen atom (O11) of the coordinated DMSO molecule ($\tau = 0.05$). The four basal atoms are very nearly coplanar, their maximum deviation from the mean plane not exceeding 0.0350(11) Å. The central copper atom is displaced from this plane by a distance of 2.379(2) Å towards the axial O11 atom. In complexes **1** and **2**, the axial positions of central metal ion's pyramid coordination environment are occupied by the oxygen atoms of L ligands, while it is occupied by DMSO oxygen atom for complex **3**.

The coordination types of L ligand in complex **3** are also different with those in complexes **1** and **2**. In complexes **1**

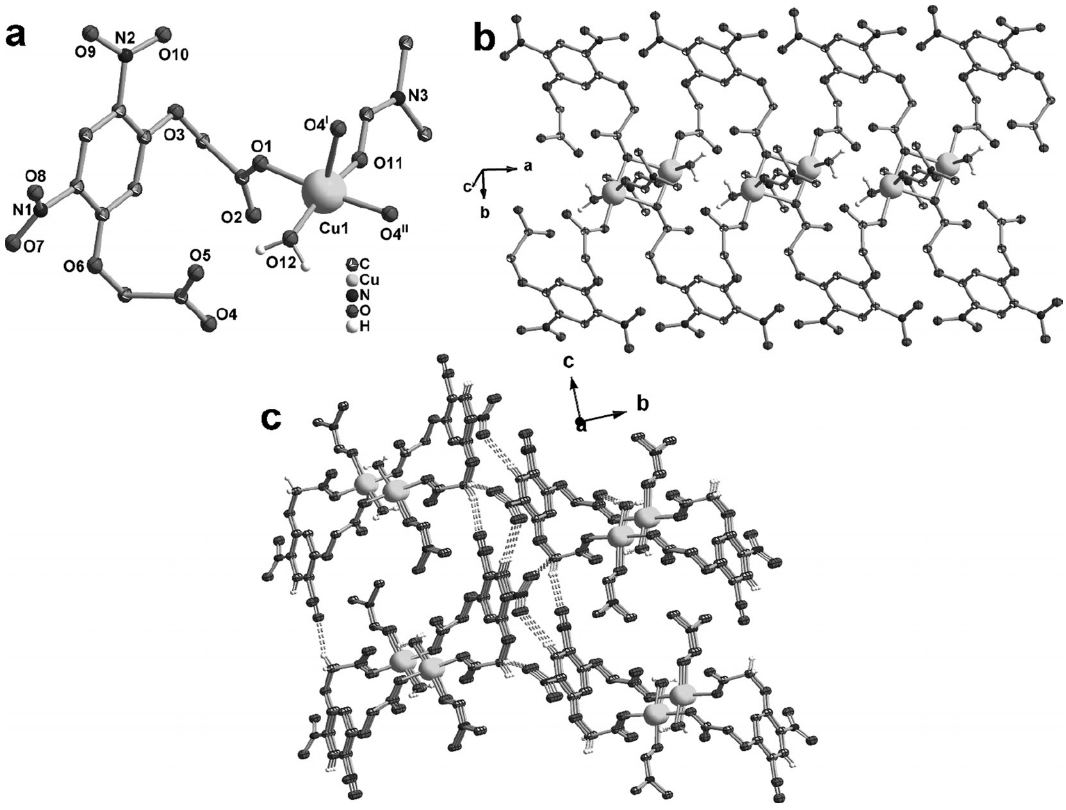

Figure 2. (a) Molecular structure of complex **2**; (b) 1D ladder chain of complex **2**; (c) 3D packing diagram of complex **2**. Symmetry codes: I = –*x*, 1–*y*, –*z*; II = –1–*x*, 1–*y*, –*z*.

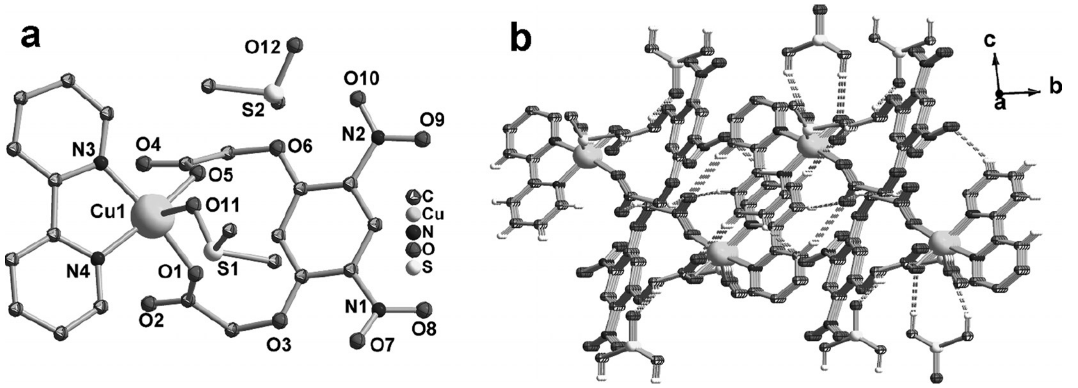

Figure 3. (a) Molecular structure of complex **3**; (b) 3D packing diagram of complex **3**.

and **2**, the two carboxyl groups of L ligand display different coordination modes with copper atoms: one carboxyl group only coordinates to one copper atom with unidentate mode, whereas the other one coordinates to two copper atoms in μ_2-bridging fashion. In complex **3**, the two carboxyl groups of L ligand exhibit the same coordination type and both link with one copper atom in unidentate fashion, which is also responsible for the zero-dimensional crystal structure of complex **3**.

In addition, the crystal structure of complex **3** is stabilized by intra and intermolecular hydrogen bonding (Figure 3b). Firstly, the intermolecular hydrogen bonds C17–H17···O2^{i}, C18–H18···O4^{v} (where v = –*x*, –*y*, –*z*) link the two groups into dimer; secondly, these dimers are further connected by intramolecular hydrogen bonding C9–H9B···O12^{vi} (where vi = –*x*, 1 –*y*, 1 –*z*) and intermolecular hydrogen bonding C24–H24B···O11 into an infinite chain along [100] direction.

In the three complexes reported herein, the solvent molecules (H_2O, DMF, and DMSO) coordinate with the central Cu^{II} ions by oxygen atoms in similar fashion. The coordinated solvent molecules have no influence in the formation of 1D chains in complexes **1** and **2**, whereas they influence the distance of neighboring chains: due to the larger volume of DMF comparing with H_2O, the distance of nearest chains in complex **1** is 8.980(2) Å, which is slightly smaller than that of 10.48 (3) Å in complex **2**. In addition, the coordination of solvent molecules with central metal ions stabilizes the crystal structure, on the other hand, it also prevents the metal ions to coordinate with more L ligands to form a higher dimensional network.

3.2 Luminescent Properties

The emission spectra of complexes **1–3** and H_2L in solid state at room temperature were investigated. As shown in Figure 4, H_2L shows a strong fluorescent emission at 460 nm, which is different with that of the benzene ring (254 nm). The red shift is perhaps caused by the introduction of nitro groups. Complexes **1–3** show similar luminescent spectra with H_2L except for the intensities. The emissions can probably be assigned to the interligand (π–π*) fluorescent emission because similar emission under the same conditions are observed for the free H_2L. It is clear that the coordination bonds significantly influence the luminescence intensities of three complexes. For complexes **1** and **3**, due to the enhanced structural rigidity and reduced fluorescence quenching effect.[33,34] the luminescent intensities are stronger than that of free H_2L. The luminescent intensity of complex **2** is weaker than that of free H_2L perhaps due to the existence of solvent molecule DMF, which destroys the coplanar of the complex.

4. Conclusions

In three common solvents (H_2O, DMF, and DMSO), we synthesized three copper-containing complexes base on the L ligand. In all of the three complexes, solvent molecules coordinate with centered metal atoms through oxygen atoms. For complexes **1** and **2**, due to the existence of nitro groups in L ligands, the large steric hindrances make the copper ions only coordinating with L ligands at one side and form a 1D chain-like structure. In addition, there are abundant hydrogen bonds in the complexes, which link the chains into 3D supramolecular network. For complex **3**, the existence of the second ligand, 2,2′-bipy, occupies the coordination sites of copper atoms and prevents the formation of high dimensional complex. The luminescent curves of complexes **1–3** and H_2L indicate that the good planar can increase the luminescent intensities in coordination complexes.

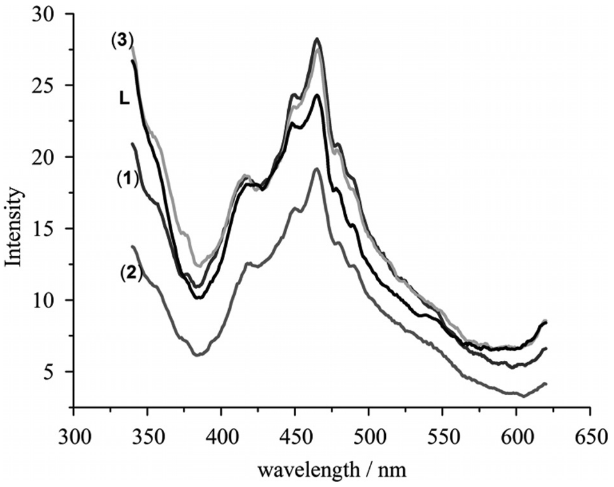

Figure 4. Fluorescent spectra of ligand and complexes **1**–**3**.

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