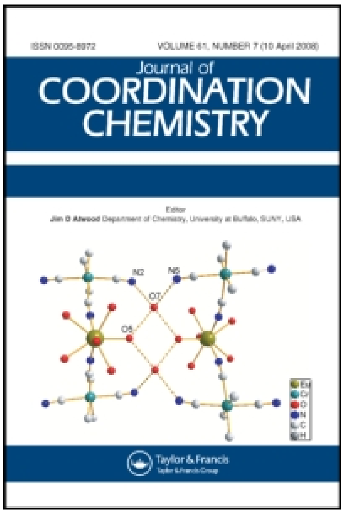

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structures and characterization of two Cu(II) complexes with asymmetric sulfonamide Schiff-base ligands

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To cite this Article Li, Shu-Ni , Zhai, Quan-Guo , Hu, Man-Cheng and Jiang, Yu-Cheng(2009) 'Synthesis, crystal structures and characterization of two Cu(II) complexes with asymmetric sulfonamide Schiff-base ligands', Journal of Coordination Chemistry, 62: 16, 2709 — 2718, First published on: 24 May 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970902912373

URL: http://dx.doi.org/10.1080/00958970902912373

Journal of Coordination Chemistry
Vol. 62, No. 16, 20 August 2009, 2709–2718

Synthesis, crystal structures and characterization of two Cu(II) complexes with asymmetric sulfonamide Schiff-base ligands

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(*Received 3 November 2008; in final form 30 December 2008*)

Reaction of the *N*-tosyl-1,2-diaminopropane or *N*-tosyl-1,2-diaminobenzene with salicylaldehyde forms two new asymmetric sulfonamide Schiff bases, *N*-[2-(2-hydroxybenzylideneamino)propyl]-4-methylbenzenesulfonamide (**H_2L^1**) and *N*-[2-(2-hydroxybenzylideneamino) phenyl]-4-methylbenzenesulfonamide (**H_2L^2**). Two new complexes [Cu$L^x(H_2O)$] ($x=1$ for **1**, $x=2$ for **2**) constructed from **H_2L^x** have been prepared and characterized *via* X-ray single-crystal diffraction, elemental analysis, FT-IR, UV-Vis, TGA, quantum chemical calculations, and photoluminescence measurements. Weak C–H $\cdots\pi$, hydrogen bonds, π–π, and Cu$\cdots$O weak interactions lead to 3-D supramolecular architecture, **1**, and 1-D double chain, **2**.

Keywords: *N*-tosyl-1,2-propanediamine; *N*-tosyl-o-phenyldiamine; Sulfonamide Schiff base; Quantum chemical calculation; Fluorescence

1. Introduction

Metal complexes with Schiff bases played an important role in the development of coordination chemistry [1–9] and a number of reviews [3, 7, 10–12] have been reported on salen like Schiff-base complexes. The salen and sulfonamide Schiff-base ligands are electronically very different. There have been many reports on transition metal complexes with sulfonamide Schiff bases [13, 14], mainly focused on two types of sulfonamide Schiff base, one derived from condensation of 2-tosylaminobenzaldehyde and diamines [15–19] and the other from condensation of *N*-tosyl-diamine and aldehydes [20–22].

As part of our study on the coordination chemistry of Schiff bases, we recently turned our attention to asymmetric sulfonamide Schiff bases in contrast to salen. There have been few reports on asymmetric Schiff bases derived from 1,2-diaminopropane or *o*-phenyldiamine [23–26]. In this work, two new asymmetric sulfonamide Schiff bases *N*-[2-(2-hydroxybenzylideneamino)propyl]-4-methylbenzenesulfonamide (**H_2L^1**) and *N*-[2-(2-hydroxybenzylideneamino)phenyl]-4-methylbenzenesulfonamide (**H_2L^2**) (scheme 1) were obtained, and two complexes [Cu$L^x(H_2O)$] ($x=1$ for **1**, $x=2$ for **2**) have been prepared and characterized. Weak C–H $\cdots\pi$, hydrogen bonds, π–π, and

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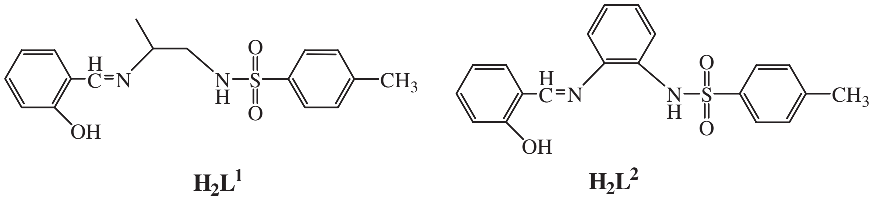
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970902912373



Scheme 1. $\mathbf{H_2L^1}$ and $\mathbf{H_2L^2}$.

Cu···O weak interactions lead to 3-D supramolecular architecture, **1**, and 1-D double chain, **2**, respectively.

2. Experimental

2.1. *Materials*

All solvents and 1,2-propanediamine, *o*-phenyldiamine, tosyl chloride, $Cu(NO_3)_2 \cdot 3H_2O$ were commercial products and used without purification. $Cu(ClO_4)_2 \cdot 6H_2O$ was prepared by reaction of $Cu_2(OH)_2CO_3$ and dilute $HClO_4$.

2.2. *Analyses and physical measurements*

C, H, and N elemental analyses were performed on a Vario EL-III analyzer. Infrared spectra were recorded as KBr pellets on a Nicolet Avatar 360 spectrophotometer in the range 4000–400 cm^{-1}. UV-Vis absorptions were recorded on a SHIMADZU UV-1700 spectrophotometer. Luminescence emission and excitation spectra were recorded with a Perkin-Elmer LS55 luminescence spectrometer at room temperature. Thermogravimetric analysis was performed on a Q1000 DSC with a heating rate of 10°C min^{-1} under N_2.

2.3. *Synthesis*

2.3.1. *N*-[2-(2-hydroxybenzylideneamino)propyl]-4-methylbenzenesulfonamide ($\mathbf{H_2L^1}$). *N*-tosyl-1,2-diaminopropane was prepared similar to the synthesis of *N*-tosyl-ethylenediamine [27]. The slimy crude product was recrystallized twice from ethanol–water (V/V = 1 : 1) and white precipitate collected by filtration. $\mathbf{H_2L^1}$ was obtained by refluxing an ethanol solution (30 mL) of *N*-tosyl-propyldiamine (0.228 g, 1 mmol) and salicylaldehyde (0.122 g, 1 mmol) for 1 h. The resulting yellow solution containing the product was concentrated with a rotary evaporator and used without purification.

2.3.2. *N*-[2-(2-hydroxybenzylideneamino)phenyl]-4-methylbenzenesulfonamide ($\mathbf{H_2L^2}$). *N*-tosyl-1,2-diaminobenzene was prepared according to the literature method [28]. $\mathbf{H_2L^2}$ was obtained by refluxing an ethanol solution (60 mL) of *N*-tosyl-propyldiamine (1.31 g, 5 mmol) and salicylaldehyde (0.61 g, 5 mmol) for 2 h; yellow precipitation formed after cooling the solution. It was collected and dried in air, m.p. 139.3–140.1°C. Anal. Calcd for $C_{16}H_{18}N_2O_3S$ (%): C, 60.38; H, 5.660; N, 8.805. Found: C, 60.52; H, 5.487; N, 8.595.

2.3.3. [$CuL^1(H_2O)$] (1). To a methanol solution (3 mL) of salicylaldehyde (0.122 g, 1 mmol), an aqueous solution (3 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1 mmol) was added slowly. The solution turned from light yellow to bright green. The mixture was stirred at 60°C for 30 min and then 0.15 mL pyridine was added. After 20 min, a methanol solution (10 mL) of *N*-tosyl-1,2-diaminopropane (0.228 g, 1 mmol) was added and solution was stirred for an additional time of 3 h. Dark green crystals were collected from the filtrate 2 days later. Block-shaped crystals suitable for X-ray diffraction were obtained after 3 days by standing the filtrate in a vacuum flask in a 70°C water bath, collected, and air dried. Anal. Calcd for $C_{17}H_{20}N_2O_4SCu$ (%): C, 49.81; H, 4.396; N, 6.838. Found: C, 49.75; H, 4.099; N, 6.606.

2.3.4. [$CuL^2(H_2O)$] (2). To an ethanol solution (20 mL) of $\mathbf{H_2L^2}$ (0.318 g, 1 mmol), an ethanol solution (10 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1 mmol) was added slowly. The mixture was refluxed under continuous stirring for 3 h with change from yellow to brown-green. Needle-shaped crystals suitable for X-ray diffraction were obtained after 2 days, collected by filtration and air dried. Anal. Calcd for $C_{20}H_{18}N_2O_4SCu$ (%): C, 53.99; H, 4.040; N, 6.285. Found: C, 53.98; H, 3.969; N, 5.983.

2.4. *Single-crystal X-ray diffraction studies*

The crystal determination was performed at room temperature on a Bruker Smart APEX CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were made using SADABS [29] and structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using SHELX-97 [30]. All non-hydrogen atoms were anisotropically refined; hydrogens were included at geometrically calculated positions and refined using a riding model except those of water. The crystal data, experimental details, refinement results, and details of structure determinations are shown in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Quantum chemical calculations of* N*-tosyl-1,2-diaminopropane*

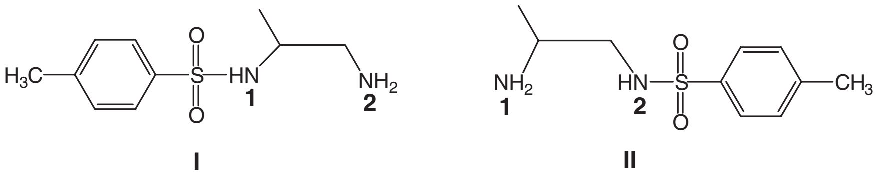
1,2-diaminopropane is an asymmetrical diamine, when reacted with tosyl chloride, isomers possessing configuration I and II (scheme 2) may be produced. Possible configurations were studied using B3LYP [31] of density functional theory (DFT) with the 6-31G basis set [32]. The calculations were done using Gaussian 03 [33]. The frequency analysis was performed on the optimized structures and there is no imaginary frequency for each structure. The theoretical calculation shows that the total energies are −2752674.11 and −2752690.64 kJ mol^{-1}, and the dipole moments are

Table 1. Crystal data and structure refinements for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{17}H_{20}CuN_2O_4S$	$C_{20}H_{18}CuN_2O_4S$
Formula weight	411.95	445.96
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2(1)/c$
Unit cell dimensions (Å, °)		
a	18.460(18)	6.1402(9)
b	12.647(13)	16.870(3)
c	15.94(2)	17.822(3)
β	95.614(17)	94.349(3)
V (Å^3)	3704(7)	1840.8(5)
Z	8	4
D_{Calcd}(Mg m^{-3})	1.478	1.609
Absorption coefficient (mm^{-1})	1.315	1.330
F(000)	1704	916
Crystal size (mm^3)	$0.36 \times 0.30 \times 0.18$	$0.23 \times 0.12 \times 0.06$
Limiting indices	$-21 \le h \le 21$; $-6 \le k \le 15$; $-17 \le l \le 19$	$-7 \le h \le 4$; $-18 \le k \le 20$; $-21 \le l \le 20$
Reflections collected	8330	9213
Independent reflections	3272 [$R_{(\text{int})} = 0.1570$]	3281 [$R_{(\text{int})} = 0.0576$]
Completeness to $\theta = 25.09$	99.1%	99.9%
Data/restraints/parameters	3272/3/205	3281/2/226
Goodness-of-fit on F^2	1.003	1.000
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0951$, $wR_2 = 0.2334$	$R_1 = 0.0441$, $wR_2 = 0.0768$
R indices (all data)	$R_1 = 0.1534$, $wR_2 = 0.2740$	$R_1 = 0.0985$, $wR_2 = 0.0847$
Largest difference peak and hole (e Å^{-3})	1.072 and −1.173	0.328 and −0.401

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

	1	**2**
Cu(1)–O(1)	1.922(5)	1.910(3)
Cu(1)–O(4)	1.971(6)	1.950(3)
Cu(1)–N(1)	1.937(6)	1.921(3)
Cu(1)–N(2)	1.984(6)	1.999(3)
O(1)–Cu(1)–N(1)	94.6(2)	93.84(13)
O(1)–Cu(1)–O(4)	89.9(2)	84.89(13)
N(1)–Cu(1)–N(2)	84.3(3)	83.34(14)
O(4)–Cu(1)–N(2)	95.6(2)	98.18(14)
N(1)–Cu(1)–O(4)	158.9(3)	177.24(16)
O(1)–Cu(1)–N(2)	167.4(2)	173.15(13)



Scheme 2. The possible structure of *N*-tosyl-1,2-diaminopropane.

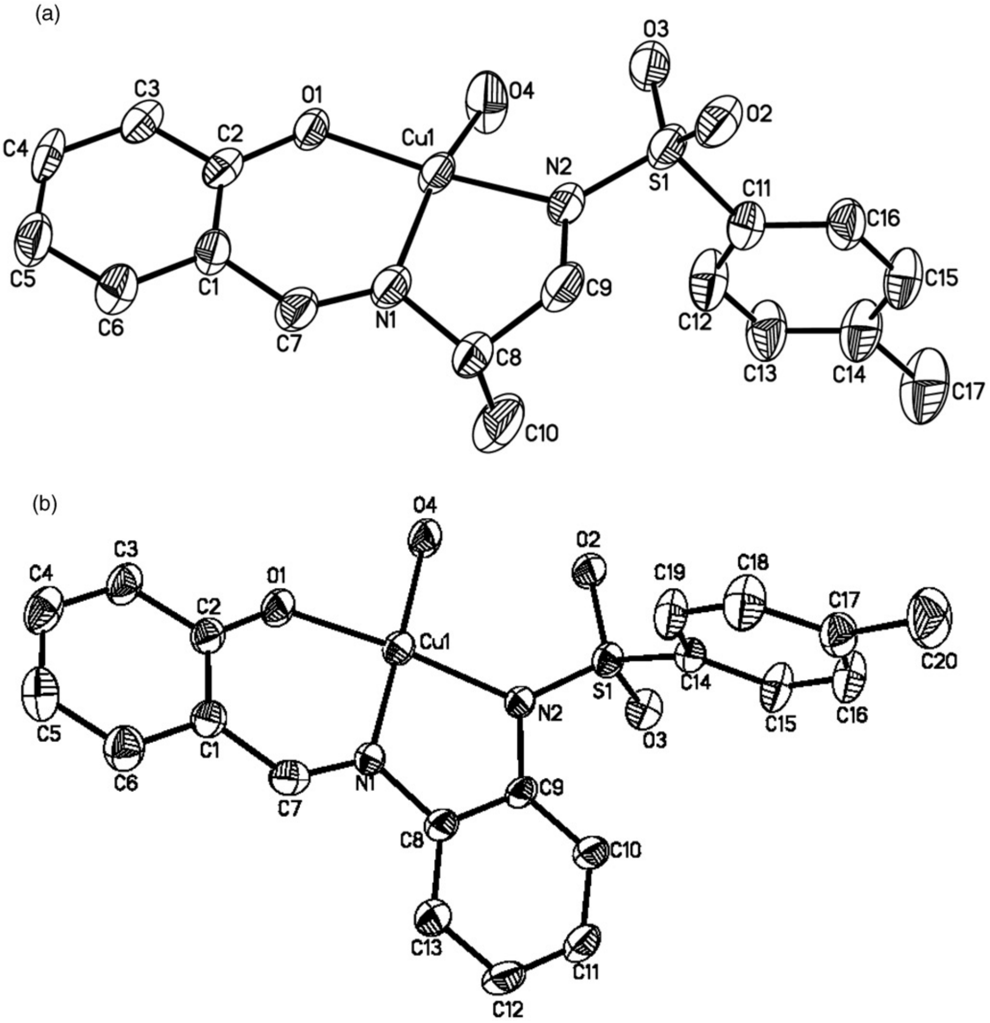


Figure 1. Molecular structure of **1** (a) and **2** (b) (H atoms omitted for clarity).

9.2695 and 6.4314 Debye, respectively, indicating that **I** is less stable than **II**, which can be further proved by the larger separation between the tosyl group and methyl group in configuration **II** (Supplementary material).

3.2. *Crystal structures of [CuL^1(H$_2$O)] (1) and [CuL^2(H$_2$O)] (2)*

The molecular structures of **1** and **2** are shown in figure 1. In both complexes, the copper(II) is coordinated to one dianionic tridentate Schiff base and one water molecule. The Schiff base coordinates through the imine and sulfonamide nitrogens and phenol oxygen. The coordination geometry around Cu(II) is a slightly distorted square plane with N_2O_2 in a *cis* arrangement. The *cis* angles are from 84.3(3) to 95.6(2)° for **1** and 83.38(12) to 98.06(12)° for **2**. The *trans* angles are 158.8(3) and 167.5(2)° for **1** and

177.33(14) and 173.21(11)° for **2**. In both complexes, the bond lengths increase as Cu–$O_{phenolate}$ < Cu–N_{imine} < Cu–O_{water} < Cu–N_{amide}. The longer Cu–N_{amide} distances than Cu-N_{imine} indicate stronger coordination of imine because the electron withdrawing of the tosyl group decreases the electron density of the amide nitrogen. The Cu–N_{amide}, Cu–N_{imine}, and Cu–$O_{phenolate}$ bond lengths (table 2) in **2** are all shorter than in five-coordinate [CuL^2phen] [34] possessing the same ligand. Coordination mode of the ligand in **1** and **2** is much different than in $[M^{II}(HL')_2]$ (M = Cu, Ni, Zn; H_2L' = *N*-[2-(2-hydroxybenzylideneamino)ethyl]-4-methylbenzenesulfonamide) [35], indicating that deprotonation of amide NH depends on the metal center, the reaction medium, and the replacing group on the ligand.

The molecular structures of **1** and **2** differ in the propyl and phenyl in the ligand and the different packing of the two complexes is driven by the conformational freedom of tosyl, which assumes a different orientation in the two complexes.

For **1**, two molecules are linked as a centrosymmetric head-to-tail subunit by weak $\pi \cdots \pi$ interactions (center-to-center distance of about 3.6 Å) [36–38]. Then, four weak C17–H17B $\cdots \pi$ interactions (C $\cdots$ centroid 3.9 Å) link the units into a 2-D layered structure in the *ab* plane (figure 2a). Coordinated waters contributed to formation of the 3-D supramolecular structure through O4–H4A $\cdots$ O$1_{phenolate}$ intermolecular hydrogen bonds (O4 $\cdots$ O1, 2.697(9) Å) from different layers (figure 2b).

For **2**, molecules are linked into a chain structure through weak $\pi \cdots \pi$ interactions (center-to-center distance of 3.5 Å). The Cu $\cdots$ O_{tosyl} distance of 2.9 Å is too long to be considered as a true coordinate bond, but can be described as a secondary intermolecular interaction, linking molecules into a single chain structure. The single chain is further connected to a double chain by the O4–H4A $\cdots$ O$1_{phenolate}$ intermolecular hydrogen bonds (O4 $\cdots$ O1, 2.69 Å) (figure 2c).

3.3. *FT-IR spectra*

In IR spectra of free ligands, ν(N–H) at 3260 and 3273 cm^{-1} (figure S1) disappear in **1** and **2** indicating deprotonation of amide N–H. A broad band from 3260 to 3444 cm^{-1} attributed to O–H vibration reveals the presence of phenol in the ligands and water in the two complexes. Bands at 1650 and 1615 cm^{-1} for $\mathbf{H_2L^1}$ and $\mathbf{H_2L^2}$, 1635 and 1604 cm^{-1} for **1** and **2** are attributed to ν(C=N). $\mathbf{H_2L^2}$ and **2** show a lower frequency of 30 cm^{-1} compared with $\mathbf{H_2L^1}$ and **1**, caused by the conjugated system of C=N and phenyl of *o*-phenyldiamine in $\mathbf{H_2L^2}$ and **2**, reducing the electron density of C=N. Compounds **1** and **2** show a red-shift of 10 cm^{-1} compared with the free ligands, suggesting coordination through the imine nitrogen. Two bands at 1158 and 1330 cm^{-1} are attributed to asymmetric and symmetric vibrations of SO_2 [39].

3.4. *UV-Vis absorption and fluorescence studies*

The UV-Vis absorption spectra of the ligands and complexes in ethanol are given in "Supplementary material". Absorptions at 320 and 411 nm for $\mathbf{H_2L^1}$ and $\mathbf{H_2L^2}$ shift to 368 and 420 nm in **1** and **2**, respectively, indicating coordination of C=N to the metal. $\mathbf{H_2L^2}$ and **2** show a red shift of about 90 and 50 nm compared to $\mathbf{H_2L^1}$ and complex **1** because of the conjugated system in $\mathbf{H_2L^2}$. These bands can be assigned to intraligand

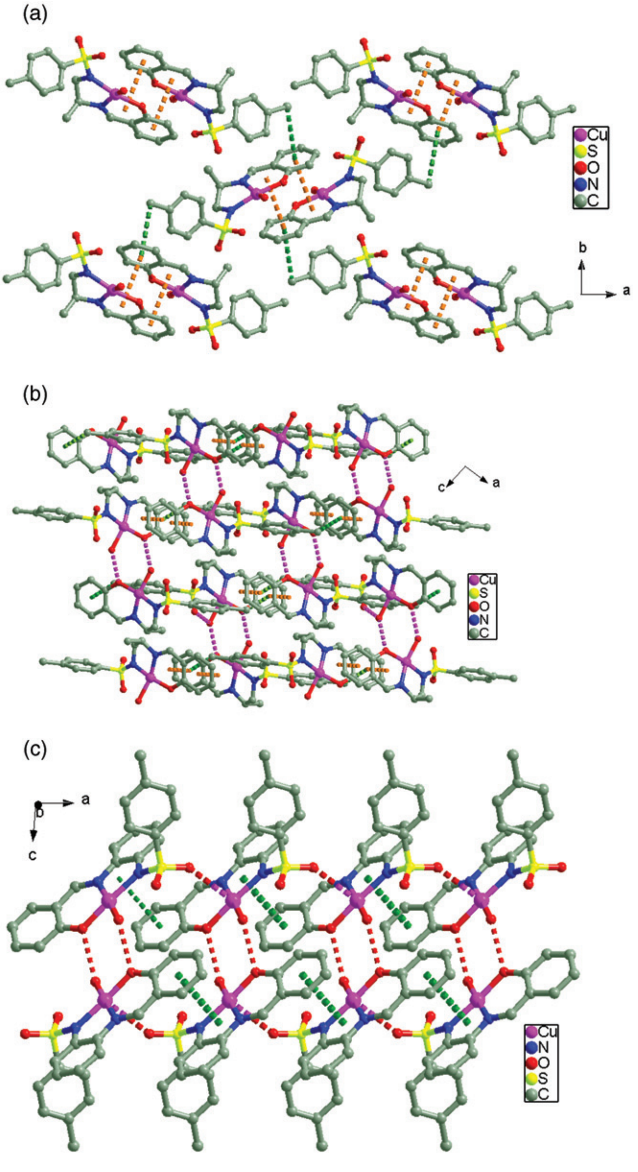


Figure 2. (a) 2-D structure of **1**; (b) 3-D supramolecular structure of **1** from *b*-axis; (c) 1-D double chain structure of **2**.

$\pi \rightarrow \pi^*$ transition of C=N group. There exist a weak d–d transition at about 596 and 643 nm for **1** and **2**.

Solid state fluorescence spectra shows that $\mathbf{H_2L^2}$, **1**, and **2** have similar excitation at 210 nm and emission at 367 nm at room temperature (figure S2). The solution fluorescence properties were studied at room temperature in ethanol (figure 3). The emission spectra of $\mathbf{H_2L^1}$ and $\mathbf{H_2L^2}$ are similar ($\lambda = 450$ nm), but the excitation of $\mathbf{H_2L^1}$ ($\lambda = 375$ nm) is strongly red-shifted compared to $\mathbf{H_2L^2}$ ($\lambda = 320$ nm), in agreement with the UV absorptions. For **1** and **2**, the large red shift of the excitation and emission

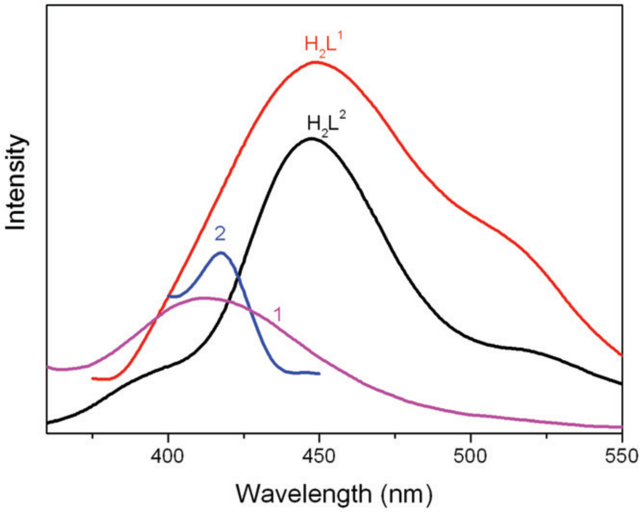


Figure 3. Solution fluorescence spectra of the ligands and complexes.

from 418 and 477 nm for **2** to 310 and 412 nm for **1** may also be caused by conjugation. No emission can be assigned to MLCT or LMCT transitions. Thus, the emission of the complexes and the ligand can be assigned to intraligand $\pi \rightarrow \pi^*$ fluorescence [40, 41].

3.5. *Thermogravimetric analysis*

The complexes were investigated by thermal analysis in nitrogen from 30 to 1000°C. The TG/DSC curves are provided in figure S3. The first weight loss observed from 30–150°C was due to the loss of coordinated water. Then the compounds were stable to 260 and 200°C for **1** and **2**, respectively. Ligand decomposition takes place at 350°C and the TG curves show rapid weight loss. The residue may be CuO for **1** (Exptl. 21.52%, Calcd 19.32%), but for **2** the observed residue content is only 6.50%, which is much less than 14.25% corresponding to the residue of Cu.

Supplementary material

CCDC 707716 and 707715 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif

Acknowledgment

We thank the National Natural Science Foundation of China (Nos. 20801033 and 20871079).

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