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A Novel Complex of Copper(II) Derived from Symmetric Five-Dentate Ligand: Synthesis, Crystal Structure, and Characterization[1]

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Abstract—A symmetric five-dentate Schiff-base ligand N,N-bis(pyridine-2-carboxaldehyde)diethylenetriamine (L) was prepared. An unusual copper(II) complex $[CuCl_2(L)] \cdot H_2O$ was obtained, when copper chloride reacted with ligand L. In the course of the coordination reaction, a ring closure reaction happens to ligand L. So, the formation process of the complex can be used for reference to synthesize the ring compound. The complex has been characterized fully by elemental analysis, IR, absorption spectra, emission spectra, and single-crystal X-ray diffraction analysis. Moreover, a reasonable reaction mechanism for forming the complex was presumed. The complex was synthesized by treating an ethanolic solution of the appropriate ligand with an equimolar amount of metallic salt. In the complex, the copper atom is five-coordinated, which can be best described as a distorted square-pyramidal geometry with a N_3Cl_2 donor set, and two parallel one-dimensional chains are formed by packing of the complex.

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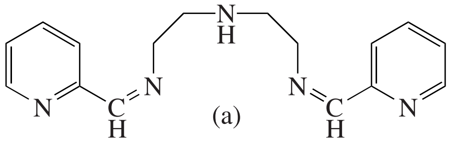
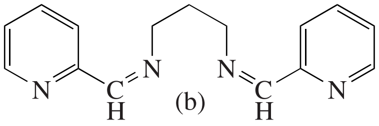
INTRODUCTION

Schiff-base ligands have played an important role in the development of coordination chemistry since the late 19th century. The findings shour that metal complexes of these ligands are ubiquitous. As their facile synthesis, wide application [1], research in this area has been stimulated by amongst other things, biological modeling application, catalysis, design of molecular ferromagnets and materials chemistry [2–6]. To the best of our knowledge, in the past two decades, Schiff-base complexes derived from pyridine-2-carboxaldehyde with diethylenetriamine have been less reported. So, recently we have embarked on the syntheses of a range of ligands that contain N,N-chelating moieties and have chosen pyridine-2-carboxaldehyde as a common starting material. Some representative examples (**a–d**) are shown below:


(a)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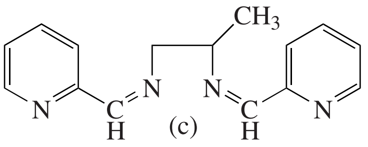
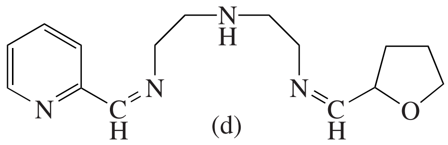

(c)


(d)

The ligand N,N-bis(pyridine-2-carboxaldehyde)diethylenetriamine (**L**) (ligand a), which is used in the present

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study, possesses a remarkable capacity for coordination with transition metals. From a chemical point of view, L is considered to be a good type of chelating ligand with extensive chemical properties. Therefore, this ligand can coordinate to transition metals as a bidentate, tridentate, quadridentate, or pentadentate ligand with consequent variable structural properties.

The metal copper is considered to be an important inorganic element involved in various biological processes. So, a lot of chemical and biological works make great endeavor to study the copper compound. The biologically accessible oxidative/reductive potential made copper complexes to be a class of the most frequently studied metallonucleases. The $[Cu(Phen)_2]^{2+}$ (Phen = 1,10-phenanthroline) compound was the first Cu^{2+} complex displaying high efficiency for the oxidative cleavage of DNA [7, 8]. Copper-ATCUN (amino-terminal Cu(II)-binding) peptide complexes and Cu-PPA (polypyridyl-derived amine) were developed as copper enzyme mimics [9, 10]. These complexes displayed versatile properties due to their different structures and reaction conditions.

In this paper, an unusual copper(II) complex $[CuCl_2(L)] \cdot H_2O$ is reported. The complex was obtained when copper chloride reacted with ligand L. In the course of the coordination reaction, a ring closure reaction happens to the chain Schiff-base ligand L. The spectral properties and the crystal structure of the complex derived from the ligand were described. A reasonable reaction mechanism for forming the complex $[CuCl_2(L)] \cdot H_2O$ was also presumed.

EXPERIMENTAL

Main reagents and apparatus. All reagents and solvents were of analytical or reagent grade, purchased commercially and used without further purification. The C, H, and N analyses were taken with a Perkin Elmer model 2400 elemental analyzer. Crystal structure was obtained on a Bruker Smart–1000CCD diffractometer. IR spectra were recorded on an EQUINOX 55 IR spectrophotometer by using KBr pellets in a range of 4000–400 cm^{-1}. Absorption spectra were recorded on a PE–40P UV spectrometer. Emission spectra were obtained by using an F–4500 fluorescence spectrometer.

Synthesis of Schiff-base ligand (L). When stirring, diethylenetriamine (1.03 g, 10.0 mmol) in ethanol (10 ml) was added to a solution of pyridine–2-carboxaldehyde (2.14 g, 20.0 mmol) in ethanol (10 ml). The resulting mixture turned light yellow immediately and gave out simultaneously a quantity of heat. After stirring at room temperature for 20 min, a little of anhydrous sodium sulfate was added, and the sealed reaction solution was left over night. After filtration, the solvent was all removed by rotary evaporation to obtain a yellow oily liquid. Then, some ether was added to the liquid, and a milky white precipitate appeared. The precipitate was separated from the solution by sucking filtration, and ligand L was obtained when the precipitate dried. The yield was 2.16 g, 76.8%, M.p. 150–151°C.

For $C_{16}H_{19}N_5$			
anal. calcd, %:	C, 68.30;	H, 6.81;	N, 24.89.
Found, %	C, 68.39;	H, 6.44;	N, 24.65.

^{1}H NMR (DMSO, 400 MHz, TMS), δ, ppm: 8.9 (d., 2 H), 8.6 (m., 2 H), 8.0 (t., 2 H), 7.7 (q., 2 H), 7.2 (s., 2 H), 3.3 (q., 4 H), 2.2 (s., 1 H), 1.5 (t., 4 H).

Synthesis of the complex $[CuCl_2(L)] \cdot H_2O$. A mixture of $CuCl_2 \cdot 2H_2O$ (0.171 g, 1.0 mmol) in 3 ml of ethanol and L (0.281 g, 1.0 mmol) in 10 ml ethanol was stirred at room temperature for 2 h. The resulting solution turned black-green and then was filtered. Single crystals suitable for X-ray analysis were grown by direct diffusion of ether into the resulting solution.

For $C_{16}H_{21}Cl_2CuN_5O$			
anal. calcd, %:	C, 44.34;	H, 4.85;	N, 16.17.
Found, %:	C, 44.69;	H, 4.60;	N, 16.55.

Crystal structure determination. The data of complex $[CuCl_2(L)] \cdot H_2O$ were collected on a Bruker Smart–1000CCD diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Intensity measurements were performed using graphite monochromated MoK_α radiation from a sealed tube, and a SMART monocapillary collimator was used for preliminary determination of the cell constants and data collection control. The determination of integral intensities and global cell refinement were performed with the Bruker SAINT software package using a narrow-frame integrative algorithm. The structure was solved by direct methods (SHELXTL-97) and refined by the full-matrix least-squares method on F^2. The final refinement included anisotropic displacement parameters for all atoms and a secondary extinction parameter. In the final difference map, the residuals are 1.455 and –1.140 e Å^{-3}, respectively. The crystallographic data for complex $[CuCl_2(L)] \cdot H_2O$: monoclinic system, space group $P2_1/c$ with cell dimensions a = 14.160(8), b = 17.455(10), c = 7.557(4) Å, β = 95.609(10)°, V = 1858.8(18) Å^3, Z = 4, $F(000)$ = 888, M = 432.81, ρ_c = 1.547 g/cm^3, $\mu(MoK_\alpha)$ = 1.477 mm^{-1}, R_1 = 0.0794, wR_2 = 0.1023. $w = 1/[\sigma^2(F_0^2) + (0.1925P)^2 + 26.7730P]$, $P = (F_0^2 + 2F_0^2)/3$, $(\Delta/\alpha)_{max}$ = 0.079, S = 1.037.

RESULTS AND DISCUSSION

Description of the crystal structure. Selected bond lengths and bond angles of complex $[CuCl_2(L)] \cdot H_2O$ are shown in table. The molecule structure, the cell platform along the y axis and the two-dimensional sand-

Selected bond lengths and bond angles of complex $[CuCl_2(L)] \cdot H_2O$

Bond	*d*, Å	Angle	ω, deg
Cu(1)–N(1)	2.011(14)	N(2)Cu(1)N3	79.2(6)
Cu(1)–N(2)	2.004(13)	N(1)Cu(1)N(2)	81.6(5)
Cu(1)–N(3)	2.048(15)	N(1)Cu(1)N(3)	159.7(6)
Cu(1)–Cl(2)	2.250(5)	N(1)Cu(1)Cl(2)	97.2(4)
Cu(1)–Cl(1)	2.587(5)	N(2)Cu(1)Cl(2)	161.0(4)
N(2)–C(6)	1.48(2)	N(3)Cu(1)Cl(2)	98.6(5)
N(5)–C1(1)	1.42(2)	N(1)Cu(1)Cl(1)	95.5(4)
N(4)–C(6)	1.46(2)	N(2)Cu(1)Cl(1)	95.2(4)
N(2)–C1(1)	1.51(2)	N(3)Cu(1)Cl(1)	93.1(4)
N(2)–C(8)	1.50(2)	Cl(2)Cu(1)Cl(1)	103.8(2)

wich structure of the complex are depicted in Figs. 1–3, respectively.

The molecular structure of $[CuCl_2(L)] \cdot H_2O$ (Fig. 1) shows that in the coordinated unit the copper atom is defined by nitrogen atoms N(1), N(2), and N(3) which come from ligand L and two chlorine atoms. The copper atom is in an N_3Cl_2 environment with ι ($\iota = 0.02$) value for the copper atom about zero as expected for a square pyramidal arrangement [11–13]. The geometry around the copper atom can be best described as a slightly distorted square pyramidal with atoms N(1), N(2), N(3), and Cl(2) making up the undersurface, and atom Cl(1) as the apical point. In the coordinated unit, the dihedral angle of the two pyridine rings is 15.8°, the dihedral angle of the plane determined by N(1), C(5), and C(6) and the plane determined by N(2), C(5), and C(6) is 0.5°. The experimental data indicate that N(1), N(2), C(5), and C(6) are nearly coplanar. The distance of Cl(2) atom to the plane included N(1), N(2), and N(3) is 0.03 Å. The experimental data further indicate that the square pyramide composed of Cu(1) with coordinated atoms is scrambling.

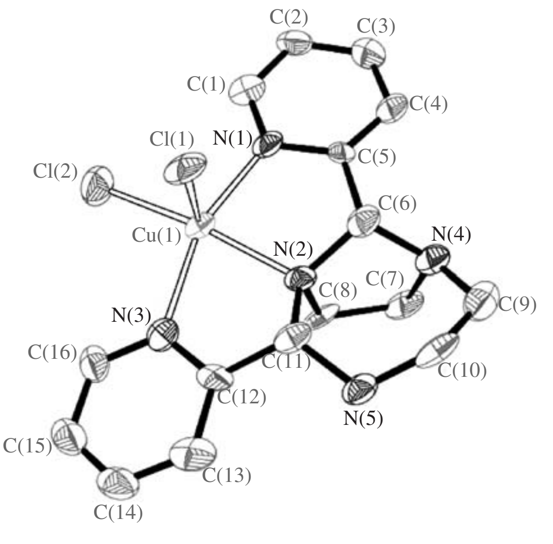


Fig. 1. Crystal structure of complex $[CuCl_2(L)] \cdot H_2O$.

From Figs. 2 and 3, some scientific information can be obtained: (1) two parallel one-dimensional chains are formed by packing of the complex; (2) there is hydrogen bond formed between the H atom, which belongs to the crystal water in the complex, and the coordinate Cl atom. The kind of hydrogen bond is intramolecular; (3) each complex molecule is hanged together by the van der Waals force; (4) Fig. 3 also indicates that the sandwich structure is formed by the compact packing of the complex, and the distance of the nearest metal atoms in the adjacent different layers is 7.557 Å, which shows that very feeble action exists between the metals, and the action can even be ignored.

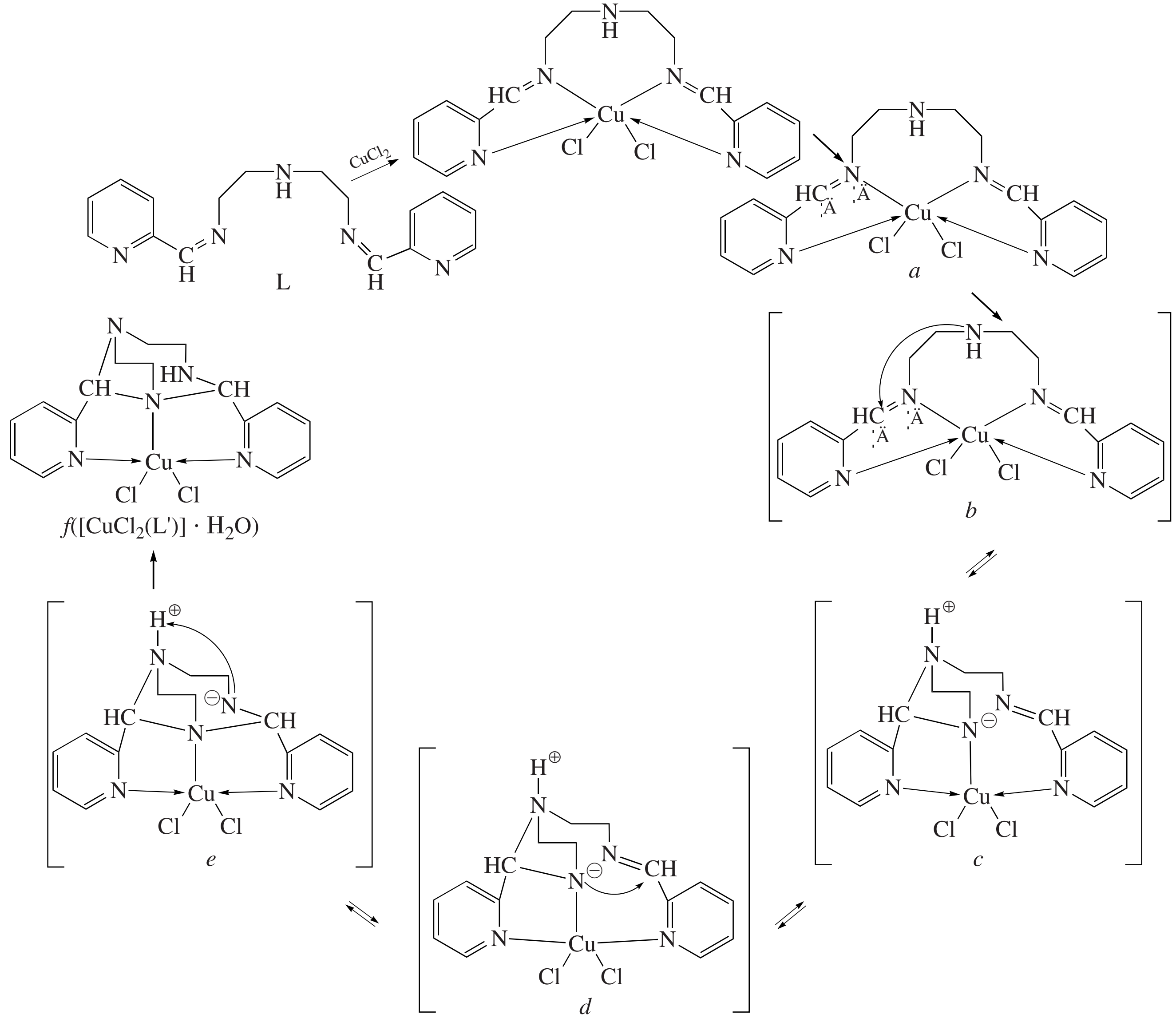
Metal complexes of N-donor ligands are of considerable current interest, because they catalyze many organic transformations [14]. In this work, the complex included N-donor ligands and in the course of forming the complex, a ring closure reaction happens to the line chain Schiff base ligand L (Fig. 1). When L reacts with copper chloride, the two double bonds N(2)–C(6) and N(5)–C1(1) turn into single bonds, and two new single bonds N(4)–C(6) and N(2)–C1(1) are formed. The bond lengths of N(2)–C(6) and N(5)–C1(1) are 1.48(2) and 1.42(2) Å, respectively, which are longer by about 0.200 Å than the typical Schiff-base bond (C = N) length (1.279(5)–1.293(5) Å). The experimental fact proves that a ring closure reaction happens to ligand L. As for the line-chain Schiff-base ligand, the kind of ring closure reaction often occurs [15–17]. So, a significant understanding can be gained from this work, namely, the formation process of the complex $[CuCl_2(L)] \cdot H_2O$ can be used for reference to synthesize a ring compound.

The absorption peaks in IR spectrum of complex $[CuCl_2(L)] \cdot H_2O$ are distributed according to the literature [18, 19]. They are as follows: the absorption peaks of ω(Ar–H) are at 854 and 778 cm^{-1}; the absorption peak of ν(Ar–H) is at 3128 cm^{-1}; the absorption peaks of ν(Ar-ring) are at the range from 1606 to 1356 cm^{-1}; the absorption peak of ν(C–N) is at 1284 cm^{-1}; the absorption peaks of δ(C–H) are at 1152 and 1130 cm^{-1}; the absorption peak of ν(C–H) is at 2920 cm^{-1}; the absorption peak of δ(N–H) is at 1590 cm^{-1}; the absorption peak of ν(N–H) is at 3261 cm^{-1}.

The UV spectra of ligand L and complex $[CuCl_2(L)] \cdot H_2O$ are measured in anhydrous ethanol. Both ligand L and complex $[CuCl_2(L)] \cdot H_2O$ have no transition observed in the visible region. In the UV spectrum of L, there is one peak at 260 nm attributed to the π–π^* transitions of pyridine rings, and in complex $[CuCl_2(L)] \cdot H_2O$ the peak, which belongs to ligand L, is at 257 nm and becomes broader. The peak in complex $[CuCl_2(L)] \cdot H_2O$ is slightly blue-shifted as a result of the incorporation of the metal ion with ligand L.

The emission spectra of L and complex $[CuCl_2(L)] \cdot H_2O$ are shown in Fig. 4. The measurements are all in anhydrous ethanol. There are two fluorescence peaks in the ligand L emission spectra located in 327 and 403 nm, which are owing to the $n \longrightarrow \pi^*$ and $\pi \longrightarrow \pi^*$ transitions of the ligand, respectively. The fluorescence peak of complex $[CuCl_2(L)] \cdot H_2O$ is at 405 nm, which is in agreement with the λ_{max} of ligand L. So, the fluorescence peak of complex $[CuCl_2(L)] \cdot H_2O$ should be owing to the $\pi \longrightarrow \pi^*$ transition of the ligand. The emission spectra of L and complex $[CuCl_2(L)] \cdot H_2O$ are directly associated with the conjugated system of the ligand. Generally, the molar absorption coefficient of $\pi \longrightarrow \pi^*$ transition is greater, and the fluorescence of this type compounds is accordingly strong. In complex $[CuCl_2(L)] \cdot H_2O$, the formation of the coordination bonds and the introduction of the counterion anions affect the conjugation of the ligand decreased, which results in no $n \longrightarrow \pi^*$ transition in the complex. In fact, the molar absorption coefficient of $n \longrightarrow \pi^*$ transition is essentially small.

The crystal structure $[CuCl_2(L)] \cdot H_2O$ indicates that when ligand L coordinates with Cu(II), a ring closure reaction happens to it. The formation mechanism of complex $[CuCl_2(L)] \cdot H_2O$ which we proposed, is shown below:



First, when $CuCl_2$ reacts with L, the coordinate bonds are formed between the nitrogen atoms coming from ligand L and the metal atom. The coordinate bonds result in the electron cloud density of the atoms

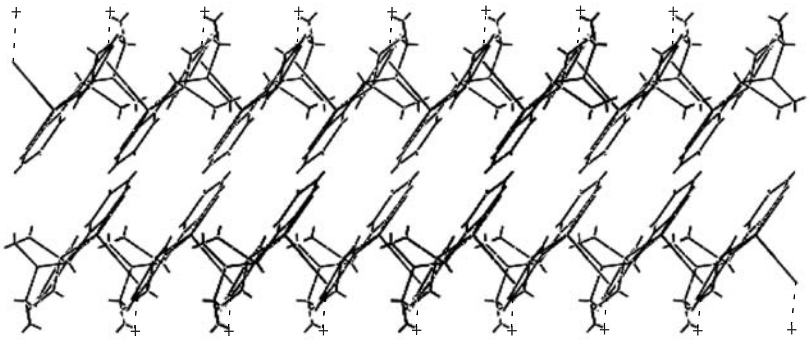


Fig. 2. Cell platform along the *y* axis of complex $[CuCl_2(L)] \cdot H_2O$.

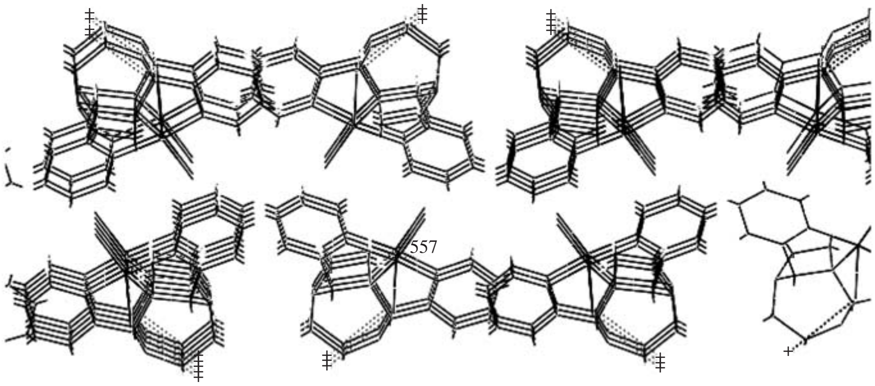


Fig. 3. Two-dimensional sandwich structure of complex $[CuCl_2(L)] \cdot H_2O$.

in ligand L to change and distribute newly, concretely, in the C=N bonds in which the nitrogen atom takes part in coordination, the nitrogen atom has a partial negative charge, and the carbon atom has a partial positive charge (structure *a*). Second, the middle nitrogen atom of ligand L attacks the carbon atom with a partial posi-

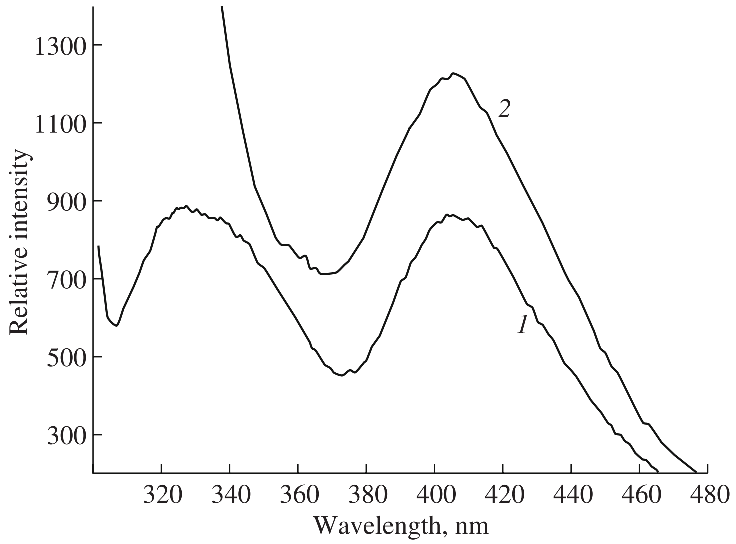


Fig. 4. Emission spectra of (*1*) L and complex (*2*) $[CuCl_2(L)] \cdot H_2O$.

tive charge (structure *b*), and the result is that two new C–N bonds are formed and the old C=N bond is broken simultaneously. A new nitrogen negative ion and a new hydrogen positive ion are formed (structure *c*). Third, the new nitrogen negative ion attacks the carbon atom, which belongs to an other old C=N bond in ligand L (structure *d*). Two new C–N bonds are formed, and the double bond C=N is broken also at the same time. The negative charge in the attacking nitrogen atom transfers to the nitrogen atom of the old Schiff-base bond (structure *e*). Finally, a new N–H bond is formed between the nitrogen negative ion and the hydrogen positive ion, and the old N–H is broken. Thus the complex $[CuCl_2(L)] \cdot H_2O$ is formed (structures *e* and *f*).

Thus, in a search for new metal complexes with interesting features, we have synthesized and structurally characterized the novel copper(II) complex with symmetrical Schiff-base five-dentate ligand L. In the course of forming the complex, a ring closure reaction happens to the line-chain Schiff-base ligand L. The reaction mechanism for forming complex $[CuCl_2(L)] \cdot H_2O$ was proposed. The experimental results can be used for reference to synthesize a ring compound. Moreover, further studies on other derivatives (e.g., complex of Co(II) and Ni(II) with L) are underway in our laboratory.

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