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# Unprecedented Dinuclear Cu<sup>II</sup> N,O-Donor Complex: Synthesis, Structural Characterization, Fluorescence Property, and Hirshfeld Analysis

# Yin-Xia Sun \*, Ying-Qi Pan, Xin Xu and Yang Zhang

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, Gansu, China; Panyq0329@163.com (Y.-Q.P.); xxchemistry@163.com (X.X.); zhangyang@mail.lzjtu.cn (Y.Z.) \* Correspondence: sunyinxia@mail.lzjtu.cn; Tel.: +86-931-4938-755

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**Abstract:** An unprecedented dinuclear Cu<sup>II</sup> complex, [Cu<sub>2</sub>(L<sup>2</sup>)<sub>2</sub>], derived from a salamo-like chelating ligand H<sub>2</sub>L<sup>2</sup>, was produced by the cleavage of a newly synthesized, half-salamo-like ligand HL<sup>1</sup> (2-[*O*-(1-ethyloxyamide)]oxime-3,5-dichloro-phenol). This was synthesized and characterized by elemental analyses, IR, UV–Vis and fluorescent spectra, single crystal X-ray diffraction analysis, and Hirshfeld surface analysis. X-ray crystallographic analysis indicated that the two Cu<sup>II</sup> (Cu1 and Cu2) ions bore different (N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>2</sub>) coordination environments, the penta-coordinated Cu1 ion possessed a slightly twisted tetragonal pyramid geometry with the  $\tau$  value  $\tau = 0.004$ , and the tetra-coordinated Cu2 ion showed a slightly twisted square planar geometry. Interestingly, one oxime oxygen atom participated in the coordination reported previously. Moreover, an infinite two-dimensional layered supramolecular network was formed. Compared with HL<sup>1</sup>, the Cu<sup>II</sup> complex possessed the characteristic of fluorescence quenching.

Keywords: half-salamo-like ligand; Cu<sup>II</sup> complex; synthesis; crystal structure; fluorescent property

# 1. Introduction

Salen-like ligand and its derivatives  $(R-CH=N-(CH_2)_n-N=CH-R)$  have received extensive attention in the field of coordination chemistry in the past decades. This is due to their use as essential Schiff bases. They can coordinate with alkaline earth, rare earth, and d-block transition metal ions to form stable mononuclear or multinuclear metal coordination compounds [1-5]. It has been found that these salen-like complexes have various special structures and interesting properties [6–8]. In recent years, based on the research of salen and its derivatives, a new salamo-like ligand and its derivatives  $(R-CH=N-O-(CH_2)_n-O-N=CH-R)$  have been developed, as the cavity formed by  $N_2O_2$  is easier to bind with metal ions [9–13]. When different metal ions are added, mononuclear and multinuclear metal complexes with different structures are expected, which show superior stability and flexibility compared with salen-like compounds [14–17]. The salamo-like ligands and their metal complexes have special properties and potential applications. For example, they are widely used in the fields of magnetic materials [18–21], electrochemistry [22–25], catalysis [26–30], luminescence [31–36], ion recognition [37-40], biological antibacterial [41-43], and supramolecular architecture [44-49]. In addition, the potential applications of polynuclear metal N<sub>2</sub>O<sub>2</sub>-donor complexes in photoelectric, magnetic, and porous materials are interesting [50,51]. In the salamo-like metal complexes mentioned above, the metal ions always coordinate with the N<sub>2</sub>O<sub>2</sub>-donor cavities of salamo-like ligands, and at the same time, the metal ions can also coordinate with the three-position hydroxyl and alkoxy oxygen atoms from salicylaldehydes of salamo-like ligands, without the oxime oxygen atoms participating in the coordination reported previously. With the development of salamo-like metal

complexes, the participation of oxime oxygen atoms of salamo-like ligands in coordination should be constantly emerging.

In order to study the structures and properties of metal salamo-like complexes, we have designed and synthesized a new half-salamo-like ligand,  $HL^1$ , and a  $Cu^{II}$  complex  $[Cu_2(L^2)_2]$ . The  $Cu^{II}$  complex  $[Cu_2(L^2)_2]$  was obtained by the reaction of the ligand  $HL^1$  with  $Cu(OAc)_2 \cdot H_2O$  and contained no acetate ion. This contrasts with the salamo-like complexes previously reported [52,53], in which an acetate ion often accompanied and coordinated with metal ions. The fluorescence property and Hirshfeld surface analysis of the  $Cu^{II}$  complex were studied [54].

#### 2. Experimental

#### 2.1. Materials and Instrumentation

2-Hydroxy-3,5-dichlorobenzaldehyde of 99% purity was obtained from the Alfa Aesar. The other reagents and solvents used in the experiment were purchased from the Tianjin Chemical Reagent Factory at the analytical reagent level and used without further purification [55]. Elemental analyses of metal element (Cu) and non-metallic elements (C, H, and N) were measured by an atomic emission spectrometer (IRIS ER/S·WP-1 ICP) and automatic elemental detection analyzer (GmbH VariuoEL V3.00) from Berlin, Germany, respectively, melting points were measured by the use of a microscopic melting point apparatus made by the Beijing Taike Instrument Limited Company (Beijing, China) and was uncorrected, 1H NMR (nuclear magnetic resonance) spectra were measured by German Bruker AVANCE DRX-400/600 spectroscopy (Bruker AVANCE, Billerica, MA, USA), single crystal X-ray structure data was collected by a CCD surface detecting diffractometer (Bruker, Germany), and Mo-K $\alpha$  ( $\lambda$  = 0.71073 Å) ray radiation was monochromated with graphite, IR spectra were recorded on a VERTEX 70 spectrophotometer with samples prepared as KBr (500–4000 cm<sup>-1</sup>) from Bruker, Germany, UV-Vis spectra were measured on a UV-3900 spectrophotometer from Hitachi, Tokyo, Japan, fluorescence spectra were recorded on a F-7000 FL 220-240V spectrophotometer from Hitachi, Tokyo, Japan, and Hirshfeld surface analysis of the Cu<sup>II</sup> complex was performed using the Crystal Explorer program were all made according to similar methods previously reported [56].

#### 2.2. Preparation of the Ligand $HL^1$

The preparation of 1,2-bis(aminooxy)ethane has been reported in previous studies [57,58]. 2-Hydroxy-3,5-dichlorobenzaldehyde (382.02 mg, 2.0 mmol) in chloroform solution (30 mL) was slowly added to 1,2-bis(aminooxy)ethane (368.4 mg, 4.0 mmol) in chloroform solution (30 mL) for ~4–5 h. The mixture was heated and stirred at ~ 40–45 °C for 5 h. Finally, the mixed solution was concentrated under reduced pressure. The ligand HL<sup>1</sup> (2-[*O*-(1-ethyloxyamide)]oxime-3,5-dichloro-phenol) was purified and obtained by column chromatography (v/v, chloroform/ethyl acetate = 20:1) (Scheme 1). Yield: 58.5%. m.p.: 58–60 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  10.47 (s, 1H), 8.14 (s, 1H), 7.37 (s, 1H), 7.17 (s, 1H), 4.47 (d, *J* = 8.5 Hz, 2H), 3.98 (d, *J* = 5.0 Hz, 2H). IR (KBr, cm<sup>-1</sup>): 3438 (m), 2966 (m), 2953 (m), 2897 (m), 1737 (m), 1615 (s), 1470 (s), 1449 (m), 1385 (s), 1380 (s), 1347 (s), 1271 (s), 1214 (m), 1181 (s), 1067 (w), 978 (w), 940 (s), 850 (s), 742 (m), 662 (s), 601 (s), 532 (s). UV–Vis (CH<sub>3</sub>CH<sub>2</sub>OH),  $\lambda_{max}$ : 266 and 324 nm. Anal. Calc. for C<sub>9</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>3</sub> (%): C, 40.78; H, 3.80; N, 10.57. Found: C, 40.86; H, 3.96; N, 10.43.



Scheme 1. Synthetic route to the half-salamo-like ligand HL<sup>1</sup>.

## 2.3. Preparation of the Cu<sup>II</sup> Complex

The synthetic route to the Cu<sup>II</sup> complex is depicted in Scheme 2. An acetone solution (3 mL) of HL<sup>1</sup> (10.60 mg, 0.04 mmol) was added to a methanol solution (3 mL) of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (7.96 mg, 0.04 mmol). The mixed solution was stirred for 15 min and then filtered into a vial, which was sealed with aluminum foil. About two weeks later, some bright brown block-like crystals suitable for X-ray diffraction were gained and collected carefully. Yield: 54.5%. IR (KBr, cm<sup>-1</sup>): 3423 (m), 2992 (m), 2945 (m), 2926 (m), 1609 (s), 1507 (s), 1443 (m), 1396 (s), 1358 (m), 1320 (s), 1263 (s), 1205 (s), 1169 (w), 1073 (s), 973 (w), 949 (s), 864 (m), 759 (s), 693 (s), 626 (s), 559 (w), 531 (w). UV–Vis (CH<sub>3</sub>CH<sub>2</sub>OH),  $\lambda_{max}$  (nm): 271 and 382 nm. Anal. Calc. for C<sub>32</sub>H<sub>20</sub>Cl<sub>8</sub>Cu<sub>2</sub>N<sub>4</sub>O<sub>8</sub> (%): C, 38.46; H, 2.02; N, 5.61; Cu, 12.72. Found: C, 38.61; H, 1.86; N, 5.48; Cu, 12.65.



Scheme 2. Synthetic route to the Cu<sup>II</sup> complex.

## 2.4. Crystal Structure Determination of the Cu<sup>II</sup> Complex

The crystal structure determination of the Cu<sup>II</sup> complex is given in the Supplementary Materials. The key crystal data and structural parameters of the Cu<sup>II</sup> complex are summarized in Table 1. CCDC: 1959387.

Compound	The Cu <sup>II</sup> Complex		
Empirical formula	C <sub>32</sub> H <sub>20</sub> Cl <sub>8</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>8</sub>		
Molecular weight, $g \cdot mol^{-1}$	999.22		
Temperature (K)	273 K		
Wavelength (Å)	0.71073		
Color	Brown		
Crystal size, mm <sup>3</sup>	$0.25 \times 0.18 \times 0.13$		
Crystal shape	Parallelepiped		
Crystal system	Triclinic		
Space group	<i>P</i> -1		
Unit cell dimension			
a (Å)	10.7507(5)		
b (Å)	13.5169(6)		
<i>c</i> (Å)	14.3611(6)		
α (°)	86.689(2)		
β (°)	68.572(2)		
γ (°)	67.681(2)		
V (Å <sup>3</sup> )	1789.15(14)		
Z	2		
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.855		
$\mu (mm^{-1})$	1.845		
F(000)	996		
$\theta$ Range (°)	3.024–27.186		
Index ranges	$-13 \le h \le 13, -17 \le k \le 16, -18 \le l \le 17$		
Reflections collected	17905		
Completeness (%)	97.0		
Data/restraints/parameters	7728/0/487		
Final $R_1/wR_2$ [ $I > 2\sigma(I)$ ]	$R_1 = 0.0349, wR_2 = 0.0919$		
Final $R_1/wR_2$ (all data)	$R_1 = 0.0459, wR_2 = 0.0969$		
$\Delta \rho_{\text{max/min}}$ (e·Å <sup>-3</sup> )	0.381 and -0.337		

**Table 1.** Crystal data and structure parameters for the Cu<sup>II</sup> complex.

 $R_1 = \overline{\Sigma ||F_o|} - |F_c|| \Sigma |F_o|; \quad wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}, \quad w = 1/[s^2 (F_o^2) + (0.0330P)^2 + 1.9700P],$ where  $P = (F_o^2 + 2F_c^2)/3;$  GOF  $= [\Sigma w (F_o^2 - F_c^2)^2 / n_{obs} - n_{param})]^{1/2}.$ 

#### 3. Results and Discussion

#### 3.1. Infrared Spectra

The infrared spectra of HL<sup>1</sup> and the Cu<sup>II</sup> complex exhibited various bands in the 500–4000 cm<sup>-1</sup> range. As shown in Table 2 and Figure S1, the infrared spectrum of the ligand HL<sup>1</sup> exhibited a broad characteristic band at ca. 3438 cm<sup>-1</sup> and can be attributed to the characteristic band of the  $v_{OH}$  group. This band is weakened in the IR spectrum of the Cu<sup>II</sup> complex, which is indicative of the fact that the phenolic OH groups of the ligand H<sub>2</sub>L<sup>2</sup> have been deprotonated and coordinated to the Cu<sup>II</sup> ions [59,60]. The ligand HL<sup>1</sup> showed a characteristic C=N stretching band at ca. 1615 cm<sup>-1</sup>, while the C=N stretching band of the Cu<sup>II</sup> complex appeared at ca. 1609 cm<sup>-1</sup> [61]. In addition, the ligand HL<sup>1</sup> exhibited typical aromatic C=C skeleton vibration bands at ca. 1449 and 1470 cm<sup>-1</sup> and appeared at ca. 1443 and 1507 cm<sup>-1</sup> for the Cu<sup>II</sup> complex [62]. Meanwhile, the free ligand HL<sup>1</sup> exhibited an Ar–O stretching band at ca. 1214 cm<sup>-1</sup> and that of the Cu<sup>II</sup> complex appeared at ca. 1205 cm<sup>-1</sup>, meaning the Ar–O stretching vibration frequency had shifted to a lower frequency. It is indicated that the Cu–O bonds are formed between the Cu<sup>II</sup> ions and the phenoxy atoms of the free ligand H<sub>2</sub>L<sup>2</sup> [63].

**Table 2.** Main infrared data (cm<sup>-1</sup>) for the ligand HL<sup>1</sup> and the Cu<sup>II</sup> complex.

Compound	$\nu_{(O-H)}$	ν <sub>(C=N)</sub>	$\nu_{(Ar-O)}$	$\nu_{(C=C)}$
HL <sup>1</sup>	3438	1615	1214	1470, 1449
The Cu <sup>II</sup> complex	-	1609	1205	1507, 1443

#### 3.2. UV-Vis Spectra

The UV–Vis absorption and titration spectra of HL<sup>1</sup> and the Cu<sup>II</sup> complex at room temperature are depicted in Figure 1. In the UV–Vis titration experiment (micro drop), an ethanol solution of the ligand HL<sup>1</sup> was prepared at a concentration of  $5.0 \times 10^{-5}$  M, and an aqueous solution of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O was prepared with distilled water at a concentration of  $1.0 \times 10^{-3}$  M.



**Figure 1.** (a) The UV–Vis spectra of HL<sup>1</sup> (c =  $5.0 \times 10^{-5}$  M) and the Cu<sup>II</sup> complex (c =  $5.0 \times 10^{-5}$  M). (b) UV–Vis spectral changes of HL<sup>1</sup> upon addition of the Cu<sup>II</sup> ion (CH<sub>3</sub>CH<sub>2</sub>OH, HL<sup>1</sup> =  $5.0 \times 10^{-5}$  M,  $0 \le [Cu^{2+}]/[HL^1] \le 1.2$ ). The inset shows the plot of absorbance at 382 nm against the molar ratio of  $[Cu^{2+}]/[HL^1]$ .

Two typical absorption peaks of HL<sup>1</sup> at ca. 266 and 324 nm were clearly observed. The two peaks can be attributed respectively to the  $\pi$ - $\pi$ \* transitions of the benzene ring and the oxime group [64,65]. When the concentration of the Cu<sup>II</sup> ion increased gradually, the absorption peaks had evidently changed to 271 nm. Compared with the peak (266 nm) of the free ligand HL<sup>1</sup>, this absorption peak was

red-shifted, and another absorption peak at 324 nm disappeared in the UV–Vis absorption spectrum of the Cu<sup>II</sup> complex, which indicated that the oxime nitrogen atoms of the ligand  $H_2L^2$  have coordinated to the Cu<sup>II</sup> ions [14,16].

Meanwhile, a new absorption peak appeared at ca. 382 nm, which was attributed to the characteristic LMCT of salamo-like transition metal complexes [66,67]. When the amount of  $Cu^{2+}$  droplets was added to 1.0 equivalent, the absorption peak at 382 nm reached the maximum value and did not change. The titration spectral data indicated that the ratio of displacement reaction was 1:1 ([ $Cu^{2+}$ ]/[ $HL^1$ ]).

#### 3.3. Crystal Structure Description

The crystal structure of the Cu<sup>II</sup> complex and the coordination polyhedra of the Cu<sup>II</sup> ions are depicted in Figure 2. Significant bond lengths and angles are summarized in Table 3.



Figure 2. (a) Crystal structure of the Cu<sup>II</sup> complex. (b) Coordination polyhedra for the Cu<sup>II</sup> ions.

The Cu<sup>II</sup> complex crystallized in the triclinic system, space group *P*-1, which clearly indicated that the structure of the resulting complex was an unexpected dinuclear Cu<sup>II</sup> complex of salamo-like ligand  $H_2L^2$ , not an expected Cu<sup>II</sup> complex of half-salamo-like ligand HL<sup>1</sup>. Here, the half-salamo-like ligand HL<sup>1</sup> was converted to a salamo-like ligand  $H_2L^2$ . This phenomenon of oxime oxygen atom participating in coordination has not been previously reported in the literature [6,9,11–13] and may be due to the catalysis of the Cu<sup>II</sup> ion upon coordination [16]. Compared with the previously reported M/L as 1:2 [68], 3:2 [69], and 2:2 [70] complexes, it consisted of two Cu<sup>II</sup> ions and two wholly deprotonated ( $L^2$ )<sup>2–</sup> units. The two Cu<sup>II</sup> ions (Cu1 and Cu2) have different (N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>2</sub>) coordination environments. The Cu<sup>II</sup> ion (Cu1) is penta-coordinated with the donor N<sub>2</sub>O<sub>2</sub> atoms (N1, N2, O1, and O4) of the ( $L^2$ )<sup>2–</sup> unit and one oxime oxygen atom (O6) from another deprotonated ( $L^2$ )<sup>2–</sup> unit. The four donor atoms (N1, N2, O1, and O4) formed a base plane, and the dihedral angle of the N1–Cu1–O1 and O4–Cu1–N2 planes was at 2.09(3)°. The axial position was occupied by the oxime oxygen atom (O6); thus, the Cu1 ion possessed a slightly twisted square pyramidal geometry with the  $\tau$  value  $\tau = 0.004$  ( $\tau < 0.5$ ) [15,61].

The distance of Cu1–O6 (2.508(2)) was considerably longer than the Cu–O and Cu–N bonds (Cu1–O1, 1.914(2); Cu1–O4, 1.921(2); Cu1–N1, 2.014(3) and Cu1–N2, 1.964(3)) in  $[Cu_2(L^2)_2]$ , indicating a weaker interaction. The lengthening of Cu1-O6 should be assigned to the involvement of O6 in a dimer bridge formation; similar elongation of the M–O bond has also been found in the dimer of  $[Cu_2(L^2)_2]$  [71]. The Cu<sup>II</sup> ion labelled as Cu2 shows a twisted square planar coordination sphere, being the donor atoms N3, N4, O5, and O8 provided by the deprotonated  $(L^2)^{2-}$  unit, and the dihedral angle of the N3–Cu2–O5 and O8–Cu2–N4 planes was about 10.29(3)°.

Bond	Bond Lengths Bond		Lengths
Cu101	1.914(2)	Cu2-O5	1.923(2)
Cu1–O4	1.921(2)	Cu2-08	1.897(2)
Cu1-O6	2.508(2)	Cu2–N3	1.958(3)
Cu1–N1	2.014(3)	Cu2–N4	2.007(3)
Cu1–N2	1.964(3)		
Bond	Angles	Bond	Angles
O1-Cu1-O4	84.20(10)	O6Cu1N2	86.93(9)
O1-Cu1-O6	92.95(9)	N1-Cu1-N2	98.06(12)
O1-Cu1-N1	88.86(11)	O5-Cu2-O8	84.87(10)
O1-Cu1-N2	173.03(11)	O5-Cu2-N3	88.47(10)
O4-Cu1-O6	97.49(9)	O5-Cu2-N4	168.37(10)
O4-Cu1-N1	172.79(11)	O8-Cu2-N3	172.25(10)
O4-Cu1-N2	88.91(10)	O8-Cu2-N3	88.93(10)
O6-Cu1-N1	84.76(9)	N3-Cu2-N4	98.30(11)

**Table 3.** Significant bond lengths (Å) and angles (°) for the Cu<sup>II</sup> complex.

# 3.4. Supramolecular Interactions and Hirshfeld Surface Analysis

In the crystal structure of the Cu<sup>II</sup> complex, there were three intermolecular (C8–H8A···O1, C24–H24A···Cl5, and C25–H25A···O8) and one intramolecular (C24–H24A···O3) hydrogen bondings (see Table 4), which played a role in stabilizing the crystal structure of the Cu<sup>II</sup> complex [72,73]. As a result, the Cu<sup>II</sup> complex formed a self-assembled infinite two-dimensional supramolecular structure via intermolecular hydrogen bondings, as shown in Figure 3. In particular the chlorine atom (Cl5) of the ligand formed intermolecular hydrogen bondings, which gave rise to a supramolecular structure that differs from most of the salamo-like metal complexes previously reported. In fact, the latter always assembled supramolecular structures through the formation of intermolecular hydrogen bondings involving solvent molecules [22,30,35–37].

D-H…A	d(H…A)	d(D…A)	∠DHA	Symmetry Code
C24–H24A…O3	2.51	3.234(5)	131	
C8-H8A…O1	2.52	3.488(5)	173	– x, 1 – y, 2 – z
C24-H24A…Cl5	2.71	3.427(4)	132	-1 + x, y, z
C25-H25A…O8	2.46	3.394(6)	163	1 – x, 1 – y, 1 – z

**Table 4.** Putative hydrogen bonding interactions (Å, °) for the Cu<sup>II</sup> complex.

The intramolecular and intermolecular interactions of molecular crystal of the Cu<sup>II</sup> complex were explored further by surface analysis using the Crystal Explorer program [14]. The interactions in molecular crystal can be clearly observed. In the Hirshfeld surface, the existence of strong interactions showed up as red spots [74], while the blue regions were related to weak contacts. The Hirshfeld surface analysis of the Cu<sup>II</sup> complex is as depicted in Figure 4a–e.



**Figure 3.** (a) View of intramolecular hydrogen bonding of the Cu<sup>II</sup> complex; (b) View of intermolecular hydrogen bondings of the CuII complex.



**Figure 4.** Hirshfeld surface analysis of the Cu<sup>II</sup> complex: (a) Curvedness; (b) Shape-Index; (c)  $d_{\text{norm}}$ ; (d)  $d_e$ ; (e)  $d_i$ .

The short-range interaction distribution of the Cu<sup>II</sup> complex was calculated by Hirshfeld surface two-dimensional (2D) fingerprint [75]. The grey represented all regions of the fingerprint, and the blue region was used to quantify the interaction between molecules, as depicted in Figure 5. The proportions were as follows: C–H/H–C, O–H/H–O, H–H/ H–H, and Cl–H/H–Cl interactions, incorporating 8.4%, 6.8%, 14.7%, and 48.0%, respectively, of the total Hirshfeld surfaces for every molecule of the Cu<sup>II</sup> complex. It was clear from the above results that the intermolecular forces on the whole surface of Hirshfeld mainly came from Cl–H/H–Cl interaction. This is different from the previously reported salamo-like complexes [55,56], as the main interaction between them was from H–H/H–H interaction. In the Cu<sup>II</sup> complex, Cl–H/H–Cl was the main interaction, which was consistent with the formation of supramolecular structure.



**Figure 5.** Fingerprint plot of the Cu<sup>II</sup> complex: full and resolved into C–H, O–H, H–H, and Cl–H contacts exhibiting the percentages of contacts contributing to the total Hirshfeld surface area of the molecule.

## 3.5. Fluorescence Properties

The fluorescence properties of HL<sup>1</sup> and the Cu<sup>II</sup> complex were studied in ethanol solution  $(5.0 \times 10^{-5} \text{ M})$  at room temperature at ca. 390 nm excitation wavelength, as shown in Figure 6. The strong fluorescence of the ligand HL<sup>1</sup> at ca. 460 nm can be attributed to the  $\pi$ - $\pi$ \* transition. The fluorescence quenching of the Cu<sup>II</sup> complex at 460 nm can be observed at the same excitation wavelength, indicating the strong coordination of Cu<sup>II</sup> ions with nitrogen and oxygen atoms of the ligand H<sub>2</sub>L<sup>2</sup> [76,77]. The binding affinity between Cu<sup>II</sup> ions and HL<sup>1</sup> was determined further by fluorescence titration. With the increase of Cu<sup>II</sup> ions (c =  $1.0 \times 10^{-3}$  M), the fluorescence intensities decreased linearly. When the concentration of Cu<sup>II</sup> ions increased to 1.0 equivalent, the fluorescence completely quenched and reached the end of titration. Through the determination of a job curve (illustration), it was found to be consistent with the titration result. Furthermore, according to the corrected Benesi–Hildebrand formula, the bonding constant of the Cu<sup>II</sup> ions to the ligand HL<sup>1</sup> calculated in the Supplementary Materials was estimated to be  $5.09 \times 10^{10}$  M<sup>-1</sup> [37].



**Figure 6.** (a) Emission spectra of HL<sup>1</sup> and the Cu<sup>II</sup> complex (c =  $5.0 \times 10^{-5}$  M,  $\lambda_{ex} = 390$  nm, ex slit: 5.0 nm, em slit: 5.0 nm). (b) Fluorescence titration spectra of HL<sup>1</sup> (c =  $5.0 \times 10^{-5}$  M) with Cu<sup>II</sup> ions (c =  $1.0 \times 10^{-3}$  M,  $\lambda_{ex} = 390$  nm, ex slit: 5.0 nm, em slit: 5.0 nm).

#### 4. Conclusions

In this work, we have designed and synthesized an unprecedented dinuclear  $Cu^{II}$  complex  $[Cu_2(L^2)_2]$ , and a series of characterizations were made in detail. The crystal structure analysis of the  $Cu^{II}$  complex indicated that the penta-coordinated Cu1 ion possessed a slightly twisted square pyramidal geometry, and the tetra-coordinated Cu2 ion had a twisted square planar one. The Cu<sup>II</sup> complex was self-assembled by intermolecular C–H…O hydrogen-bonding interactions to form a 2D layered supramolecular network. Interestingly, one oxime oxygen atom participated in the coordination reported previously in the salamo-like metal complexes. The Cu<sup>II</sup> complex possessed the characteristic of fluorescence quenching.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4352/9/12/607/s1, Figure S1: The infrared spectra of the ligand HL<sup>1</sup> and the Cu<sup>II</sup> complex.

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