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#### Research paper

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PII: DOI:	S0020-1693(17)31327-0 https://doi.org/10.1016/j.ica.2018.02.026
Reference:	ICA 18136
To appear in:	Inorganica Chimica Acta

Received Date:22 August 2017Revised Date:8 January 2018Accepted Date:20 February 2018



Please cite this article as: I. Gönül, A.Y. Burak, S. Karaca, O. Şahin, S. Serin, Novel copper(II) complexes of two tridentate ONN type ligands: Synthesis, characterization, electrical conductivity and luminescence properties, *Inorganica Chimica Acta* (2018), doi: https://doi.org/10.1016/j.ica.2018.02.026

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# Novel copper(II) complexes of two tridentate ONN type ligands: Synthesis, characterization, electrical conductivity and luminescence properties

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#### Abstract

Herein, we describe the synthesis and characterization of two novel tridentate ONN donor ligands, namely, (E)-2-(((2-(dimethylamino)ethyl))mino)methyl)-6-methoxyphenol (**HL**<sup>1</sup>) and (E)-2-(((2-(dimethylamino)ethyl))mino)methyl)-6-ethoxyphenol (**HL**<sup>2</sup>), and their copper(II) complexes,  $[Cu_2(L^1)_2(CH_3COO)_2]$  (1),  $[Cu(L^2)(CH_3COO)].2H_2O$  (2). They have been synthesized under conventional methods and characterized by elemental analysis, FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, ICP-OES, TGA, DSC and GC/MS analysis. For the morphological analysis field emission scanning electron microscopy (FESEM) was used. The geometry of the Cu(II) complexes was determined by single crystal X-ray diffraction analysis. The Cu(II) ions are in distorted square-pyramidal coordination environments. 1 crystallizes in orthorhombic space group, Pbca, while 2 crystallizes in monoclinic space group,  $P2_1/c$ . Effects of different solvents and concentrations on the photoluminescence properties of the 1-2 were investigated. The emission bands bathochromically shifted due to increase of the dipole moments of EtOH to H<sub>2</sub>O and CHCl<sub>3</sub> to DMSO, respectively. As a result of the dynamic quenching, the intensity of 1 was decreased with increasing the concentration in the water. The electrical conductivity complexes 1-2 have been also investigated.

**Keywords:** Soluble Schiff base metal complexes, Copper (II) complexes, Luminescence, Electrical conductivity, Single crystal X-ray

#### 1. Introduction

Imine groups (-C=N-) are formed by condensation of primary amines with aldehydes and known as Schiff Bases [1]. They are one of the most widely used ligands due to the their facile synthesis. These ligands coordinate metal atom via the imine nitrogen and other groups

such as carbonyl oxygen, hydroxyl or amine. The most common ones are polyfunctional ligands and they have chelating properties. Asymmetric and symmetric Schiff base ligands can provide suitable donor sets to acceptor metal ions. Especially, asymmetric ligands can be used to obtain linear complexes with some control over the position of the metals [2, 3]. The versatility of these ligands that can be coordinated to all type of metals (Lanthanides or row transition metals) makes them very widely used to obtain coordination complexes. Metal complexes of unsymmetrical Schiff base ligands have been rigorously studied and used in different fields including magnetic materials [4, 5], catalysis [6], chemical analysis, bioinorganic and medical chemistry [7-10].

In this study, we report the synthesis and characterization of new unsymmetrical tridentate ONN Schiff base ligands and their copper (II) complexes (1-2). The ligands obtained from N',N'-dimethylethane-1,2-diamine and 2-hydroxy-3-methoxy benzaldeyhde ( $HL^{1}$ ), N',N'-dimethylethane-1,2-diamine and 3-ethoxy-2-hydroxy benzaldeyhde ( $HL^{2}$ ) (Scheme 1). The synthesized compounds fully characterized by elemental analysis, thermal analysis, FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, mass spectra, ICP-OES and single crystal X-ray analysis. Solubility test were performed for the 1 and 2. The test showed that synthesized metal complexes are extremely soluble in all common organic and inorganic solvents except hexane (Table S1). Due to the this feature, luminescence properties of the compounds were investigated in different concentrations ( $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-7}$  M) and solvents. The electrical conductivity properties of the complexes have been also investigated.

### 2. Experimental

### 2.1. Materials and methods

All chemicals and solvents were purchased from commercial sources and used without further purification. Perkin-Elmer RX-1 FT-IR with KBr pellets spectrometer in the range of 4000-400 cm<sup>-1</sup> was used for the IR analysis of the compounds. Thermo Flash 2000 CHNS analyzer was used for the elemental analysis. Avance III HD Ascend<sup>TM</sup> 600 MHz ULH High Resolution Fluid NMR Spectrometer was used for the <sup>1</sup>H-NMR and <sup>13</sup>C-NMR analyses of the ligands. The melting points of the metal complexes were determined using a Gallenkamp MPD 350 BM 2.5 capillary melting point apparatus. Quantitative metal analyses were performed with Perkin-Elmer Optima 2100DV ICP-OES instrument. Perkin Elmer Pyris Diamond TG/DTA equipment was used for the TG analyses. Differential scanning

calorimeter (DSC) studies were made on Perkin Elmer DSC 4000. Mass spectrometry (MS) analysis of the ligands was measured by Thermo Scientific ISQ Single Quadrupole GC-MS with TR5MS capillary columns. The FESEM images of the compounds were recorded using Carl Zeiss, SUPRA-55. The electrical conductivity properties of compounds were determined by four-point probe method with an Electrometer Entek Electronic FPP-470. Solid pellets were prepared by Graseby SPECAC Laboratory Manual Hydraulic press under 15 tons pressure. Perkin-Elmer LS 55 Luminescence Spectrometer was used for the solid and liquid state phosphorescence excitation and emission spectra. LEICA EZ4W stereo microscope was used for the high definition views of the complexes.

### 2.2. Synthesis of $HL^{1}$

N',N'-dimethylethane-1,2-diamine (0.088 mmol) and 2-hydroxy-3-methoxy g, 1.0 benzaldeyhde (0.152 g, 1.0 mmol) were dissolved by heating in 40 mL and 20 mL of MeOH separately. Then, aldehyde solution was added dropwise to the hot amine solution and the mixture was boiled under reflux for 3 hours. The resulting viscous yellow liquid was cooled to room temperature. The obtained organic ligand dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The yellow liquid ligand HL<sup>1</sup> (Scheme 1-i) was obtained in high yield (98.85%, based on GC-MS analysis). FT-IR data (cm<sup>-1</sup>): 3425(m), 2942(m), 2827(m), 2773(m), 1632(s), 1466(s), 1255(s), 1081(m), 966(m), 840(w), 781(w), 737(m). <sup>1</sup>H NMR (DMSO, ppm, 600 MHz) δ: 8.51 (s, 1H, CH=N), 6.74-7.00 (m, 3H), 13.84 (s, 1H, C–OH), 2.18 (s, 3H, N–CH<sub>3</sub>), 3.77, (s, 3H, O–CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO, ppm, 600 MHz) δ: 153.3 (C– OH), 166.7 (CH=N), 45.7 (CH<sub>3</sub>-N), 56.5 (O-CH<sub>3</sub>), 115.0-148.8 (Aromatic Carbons). The detailed NMR spectra of the HL<sup>1</sup> are shown in Figs. S1-S7. MS (70eV): m/z 222 [M<sup>+</sup>], 179  $[C_{10}H_{13}NO_2^{2+}]$ , 136  $[C_8H_9O_2^{+}]$ , 73  $[H_2C-CH_2-NH-CH_3-CH_3]^{2+}$ , 58.04  $[CH_2=N-CH_3-CH_3]^{+}$ .

### 2.3. Synthesis of $HL^2$

N',N'-dimethylethane-1,2-diamine (0.088 g, 1.0 mmol) and 3-ethoxy-2-hydroxy benzaldeyhde (0.166 g, 1.0 mmol) were dissolved by heating in 40 mL and 20 mL of MeOH separately. Then, aldehyde solution was added dropwise to the hot amine solution and the mixture was boiled under reflux for 3 hours. The resulting viscous light brown liquid was cooled to room temperature. The obtained organic ligand dried over anhydrous  $Na_2SO_4$  and concentrated in vacuo. The liquid ligand  $HL^2$  (Scheme 1-ii) was obtained in high yield (97.43%, based on GC-MS analysis). FT-IR data (cm<sup>-1</sup>): 3440(m), 2977(m), 2935(w), 2817(s), 2784(s), 1633(s),

1466(s), 1251(s), 1078(m), 897(w), 781(w), 738(m). <sup>1</sup>H NMR (DMSO, ppm, 600 MHz)  $\delta$ : 8.50 (s, 1H, CH=N), 13.85 (s, 1H, C–OH), 6.73-6.99 (m, 3H), 2.18 (s, 3H, N–CH<sub>3</sub>), 3.98-4.10, (q, 2H, O–CH<sub>2</sub>–CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO, ppm, 600 MHz)  $\delta$ : 153.4 (C–OH), 166.8 (CH=N), 45.7 (CH<sub>3</sub>–N), 15.3 (O–CH<sub>2</sub>CH<sub>3</sub>), 116.5-147.8 (Aromatic Carbons). The detailed NMR spectra of the HL<sup>2</sup> are shown in Figs. S8-S14. MS (70eV): *m/z* 236 [M<sup>+</sup>], 193 [C<sub>11</sub>H<sub>15</sub>NO<sub>2</sub><sup>2+</sup>], 123 [C<sub>7</sub>H<sub>7</sub>O<sub>2</sub><sup>+</sup>], 72 [C<sub>4</sub>H<sub>10</sub>N<sup>+</sup>], 58.01 [CH<sub>2</sub>=N-CH<sub>3</sub>-CH<sub>3</sub>]<sup>+</sup>.



Scheme 1. Synthesis of tridentate ONN donor ligands.

### 2.4. Synthesis of $[Cu_2(L^1)_2(CH_3COO)_2](1)$

The synthesized HL<sup>1</sup> ligand (0.445 g, 2.0 mmol) was dissolved in hot MeOH (30 mL). A MeOH solution (20 mL) of anhydrous copper(II) acetate (0.363 g, 2.0 mmol) was added to the reaction medium and the mixture was boiled under reflux for 3 hours. After on cooling to room temperature, the solution was left to crystallize for one month. Obtained green single crystals suitable for X-ray diffraction (Scheme 2a). Anal. Calcd. for  $C_{28}H_{40}N_4O_8Cu_2$ : C, 48.90; H, 5.86; N, 8.15. Found: C, 48.48; H, 5.80; N, 7.76%. The ICP-OES analysis (%) showed that **1** contained Cu: 17.10; Calcd.: Cu: 18.48. FT-IR data (cm<sup>-1</sup>): 3345(m), 3040(m), 2983(m), 2927(s), 2828(s), 1624(s), 1604(s), 1470(s), 1447(s), 1376(s), 1327(s), 1220(s), 1068(w), 850(w), 780(w), 732(s), 676(w), 576(w), 460(w), 431(w).

### 2.5. Synthesis of $[Cu(L^2)(CH_3COO)].2H_2O(2)$

The synthesized  $HL^2$  ligand (0.236 g, 1.0 mmol) was dissolved in hot MeOH (30 mL). A MeOH solution (20 mL) of anhydrous copper(II) acetate (0.182 g, 1.0 mmol) was added to the reaction medium and the mixture was boiled under reflux for 3 hours. After on cooling to room temperature, the solution was left to crystallize for one month. Obtained green single crystals suitable for X-ray diffraction (Scheme 2b). Anal. Calcd. for  $C_{16}H_{30}N_2O_6Cu$ : C, 46.88; H, 7.38; N, 6.83. Found: C, 47.53; H, 7.21; N, 6.13%. The ICP-OES analysis (%) showed that **2** contained Cu: 14.83; Calcd.: Cu: 15.50. FT-IR data (cm<sup>-1</sup>): 3552(m), 3465(m), 3394(m), 2983(m), 2920(m), 2873(m), 1635(s), 1586(m), 1468(s), 1442(s), 1384(s), 1238(m), 1217(s), 1074(m), 1019(m), 907(s), 785(m), 725(s), 679(s), 534(m), 463(m).



Scheme 2. High definition microscope views of the 1 (a) and 2 (b).

### 2.6. X-ray diffraction analysis

Suitable crystals of 1-2 were selected for data collection which was performed on a D8-QUEST diffractometer equipped with a graphite-monochromatic Mo- $K_{\alpha}$  radiation at 296 K. The structures were solved by direct methods using SHELXS-97 [11] and refined by full-

matrix least-squares methods on F<sup>2</sup> using SHELXL-2013 [12]. All non-hydrogen atoms were refined with anisotropic parameters. The H atoms of C atoms were located from different maps and then treated as riding atoms with C-H distances of 0.93-0.97 Å. The water H atoms were located in a difference map refined subject to a DFIX restraint. The following procedures were implemented in our analysis: data collection: Bruker APEX2 [13]; absorption effects using the multi-scan method (SADABS) [13a]; the frames were integrated with the Bruker SAINT software package [13b] using a narrow-frame algorithm; program used for molecular graphics were as follow: MERCURY programs [14]; software used to prepare material for publication: WinGX [15]. Details of data collection and crystal structure determinations are given in Table 1. The selected bond lengths and bond angles are given in Table 2.

#### 3. Results and discussion

#### 3.1. Descriptions of crystal structures

The molecular structure of **1**, with the atom numbering scheme, is shown in Fig. 1. The asymmetric unit of the complex **1** consists of one Cu(II) ion, one acetate molecule and one  $HL^1$  ligand. The Cu(II) ion is coordinated by two nitrogen and one oxygen atoms (N1, N2 and O2) from  $HL^1$  ligand and two bridging oxygen atoms (O3 and O3<sup>i</sup>) from acetate molecules [(i) -x+1, -y+1, -z+1]. The Cu(II) ion is in a distorted square-pyramidal coordination environment. The two bridging oxygen atoms are quite different, the equatorial oxygen atom exhibits a Cu1-O3 distance of 1.967(2) Å, while that of the axial oxygen atom is much longer with 2.409(2) Å. In addition, the Cu<sup>...</sup>Cu separation is about 3.455 Å. A dimer of two monomeric units bridged by two acetate ions reveals an inversion centre in the middle of the molecules.

NAT



Figure 1. The molecular structure of 1 showing the atom numbering scheme.

The bond distances of Cu1-N1 and Cu1-N2 are 1.963(3) and 2.092(3) Å and the other Cu1-O2 bond length is 1.927(3) Å, respectively. Molecules of **1** are linked into sheets by a combination of C-H···O hydrogen bonds (Table 3). The combination of C-H···O hydrogen bonds produce C(7) chain running which is parallel to the [110] direction (Fig. 2). The asymmetric unit of **2** consists of one Cu(II) ion, one **HL**<sup>2</sup> ligand, one acetate molecule and two non-coordinated water molecules (Fig. 3).



Figure 2. An infinite 1D layer in 1.



Figure 3. The molecular structure of 2 showing the atom numbering scheme. [(i) x, 1/2-y, z-1/2].



Figure 4. An infinite 1D layer in 2.

The Cu(II) ion is coordinated by two nitrogen and one oxygen atoms (N1, N2 and O1) [Cu1-N1= 1.951(2) Å, Cu1-N2= 2.104(2) Å and Cu1-O1= 1.9364(16) Å] from **HL**<sup>2</sup> ligand and two oxygen atoms (O3 and O4<sup>i</sup>) [Cu1-O3= 1.9856(16) Å and Cu1-O4<sup>i</sup>= 2.3293(17) Å] from acetate molecules, thus showing a distorted square-pyramidal coordination geometry [(i) x, - y+1/2, z-1/2]. The Cu(II) ions and acetate molecules generate 1D coordination polymer

running parallel to the [001] direction (Fig. 4). The Cu(II)…Cu(II) separation is 4.929 Å. Adjacent 1D coordination polymers are further joined by O-H…O and C-H…O hydrogen bonds, generating a 2D supramolecular network (Fig. 5).

### Table 1

Crystal data and structure refinement parameters for complexes 1-2.

Crystal data	1	2
Empirical formula	$C_{28}H_{40}N_4O_8Cu_2\\$	$C_{15}H_{26}N_2O_6Cu$
Formula weight	687.72	393.92
Temperature	296(2) K	296(2) K
Crystal system	Orthorhombic	Monoclinic
Space group	Pbca	$P2_1/c$
<i>a</i> (Å)	8.440 (4)	9.214 (2)
<i>b</i> (Å)	17.021 (7)	21.826 (7)
<i>c</i> (Å)	21.338 (12)	9.790 (3)
β(°)	90.00	109.282 (9)
$V(\text{\AA}^3)$	3065.0 (3)	1858.4 (9)
Z	4	4
$D_{\rm c}$ (g cm <sup>-3</sup> )	1.490	1.408
$\mu$ (mm <sup>-1</sup> )	1.44	1.21
θ range (°)	3.1-27.6	3.0-28.0
Measured refls.	25353	48674
Independent refls.	3866	4799
R <sub>int</sub>	0.088	0.060
S	1.09	1.23
R1/wR2	0.051/0.181	0.042/0.108
$\Delta \rho_{max} / \Delta \rho_{min} (e \text{\AA}^{-3})$	0.56/-0.75	0.55/-0.59



Figure 5. An infinite 2D layer in 2.

### Table 2

Selected bond lengths [Å] and angles [°] for 1-2.

Complex 1			
N1-Cu1	1.963(3)	Cu1-O3-Cu1 <sup>i</sup>	103.82(10)
N2-Cu1	2.092(3)	C11-N2-Cu1	110.4(2)
O2-Cu1	1.927(3)	O3 <sup>i</sup> -Cu1-N1	112.65(11)
O3-Cu1	1.967(2)	O2-Cu1-O3	90.38(10)
O2-Cu1	2.409(2)	N1-Cu1-O3	171.08(12)
C11-N2	1.476(5)	N2-Cu1-O2	173.10(10)
		N1-Cu1-N2	83.19 (13)
Complex 2			
Cu1-O3	1.9856(16)	O3-Cu1-O1	91.79(7)
Cu1-O1	1.9364 (16)	O1-Cu1-N2	173.15(7)
Cu1-N2	2.104(2)	N2-Cu1-N1	83.74(9)
Cu1-N1	1.951(2)	Cu1-O3-C14	112.38(14)
Cu1-O4 <sup>i</sup>	2.3293(17)	Cu1-N2-C12	110.86(16)
N2-C11	1.488(3)	N1-Cu1-O4 <sup>i</sup>	89.64(8)
		C14-O4-Cu1 <sup>ii</sup>	139.88(16)

### Table 3

D-H· · ·A	D-H	H···A	D····A	D-H···A
1				
C8—H8····O4 <sup>ii</sup>	0.93	2.30	3.196 (4)	161
C11—H11C…O1 <sup>i</sup>	0.96	2.60	3.228 (5)	124
C11—H11C····O2 <sup>i</sup>	0.96	2.45	3.348 (4)	156
C12—H12B…O4	0.96	2.58	3.266 (6)	128
2				
C13—H13B $\cdots$ O4 <sup>i</sup>	0.96	2.56	3.196 (3)	124
$C13$ — $H13B\cdots O1^{i}$	0.96	2.56	3.422 (3)	149
C10—H10A…O6	0.97	2.49	3.400 (4)	155
С9—Н9…Об	0.93	2.54	3.405 (4)	155
O5—H5B…O3	0.82 (2)	2.26 (2)	3.035 (3)	159
O5—H5A…O1	0.81 (2)	2.44 (3)	2.933 (3)	120
O5—H5A…O2	0.81 (2)	2.08 (2)	2.862 (3)	162
O6—H6B····O3 <sup>iii</sup>	0.82 (2)	2.09 (2)	2.902 (3)	170
O6—H6A…O5 <sup>iv</sup>	0.81 (2)	2.04 (2)	2.849 (3)	173

Hydrogen-bond parameters for 1-2 (Å, °).

Symmetry codes: (i) -x+1, -y+1, -z+1; (ii) x-1/2, -y+3/2, -z+1 for 1;

(i) x, -y+1/2, z-1/2; (iii) x-1, -y+1/2, z-1/2; (iv) x-1, y, z-1 for **2**.

### 3.2. GC-MS analysis

GC/MS analysis was used to characterization of the synthesized liquid ligands by using TR5MS column. Helium was used as a carrier gas at a flow rate of 1.0 mL/min. The ion source temperature was set to 250 °C. The 1  $\mu$ l **HL**<sup>1</sup> and **HL**<sup>2</sup> were injected in pulsed split mode ratio 100. Injector temperature was set at 240 °C and throughout the process temperature flow was set at the speed of increasing 15 °C/min. The oven temperature program was as follows: Initial temperature 80 °C held for 1 min, 15 °C/min till 280 °C held for 10 min. Mass spectra were detected on a ISQ detector (temperature trap 250 °C) in a range of m/z 50-600. Ionization mode was internal EI (energy of electrons 70 eV); sample volume, 1  $\mu$ L; solvent, DCM.

### 3.3. Mass Spectral interpretation and identification of ligands

The synthesized ligands were also characterized by using GC/MS analysis. Since the ligands were obtained as pure, single chromatograms were obtained (Figs. S15 and S17). All

fragments of  $HL^1$  and  $HL^2$  were fully characterized in Figs. S16 and S18 according to the their mass  $(\mathbf{m})$  to charge  $(\mathbf{z})$  ratios  $(\mathbf{m}/\mathbf{z})$ . In this section, only the spectrums seen as important are explained. The mass spectrums indicated molecular weight of 222 (m/z: 223 MH<sup>+</sup> ion) which is consistent with the molecular weight of the ligand. The m/z: 58.04 ion was observed in  $HL^1$  as highest abundance. This peak is base peak and most stable ion in the structure (m/z: 58.07,  $[CH_2=N-CH_3-CH_3]^+$ ). The line at m/z: 136 is typical of an C<sub>8</sub>H<sub>9</sub>O<sub>2</sub><sup>+</sup>. The m/z: 179 fragment ion corresponds to the loss of  $C_{10}H_{13}NO_2^{2+}$  from MH<sup>+</sup>. The m/z: 73 ion due to the [H<sub>2</sub>C-CH<sub>2</sub>-NH-CH<sub>3</sub>-CH<sub>3</sub>]<sup>2+</sup> from MH<sup>+</sup>. Similarly, only the spectrums seen as important are explained for HL<sup>2</sup>. The mass spectrums indicated molecular weight of 236 (m/z: 237 MH<sup>+</sup> ion) which is consistent with the molecular weight of the ligand. The m/z: 58.01 ion was also observed in HL<sup>2</sup> as highest abundance. This peak is base peak and most stable ion in the structure (m/z: 58.07, [CH<sub>2</sub>=N-CH<sub>3</sub>-CH<sub>3</sub>]<sup>+</sup>). The line at m/z: 123 is typical of an C<sub>7</sub>H<sub>7</sub>O<sub>2</sub><sup>+</sup>. The m/z: 193 fragment ion corresponds to the loss of  $C_{11}H_{15}NO_2^{2+}$  from MH<sup>+</sup>. The m/z: 72 ion due to the  $C_4H_{10}N^+$  from MH<sup>+</sup>. These mass spectra results were supported the structure of the ligands and in agreement with the data from the single crystal X-ray analysis of the complexes.

### 3.4. FT-IR spectra

The infrared spectra of the synthesized ligands and their copper(II) complexes are presented in Figs. S19-S22. In **HL**<sup>1</sup> and **HL**<sup>2</sup> ligands, phenolic OH groups appears at 3425 and 3440 cm<sup>-1</sup>, respectively. Medium intensity bands in the range of 2945-2770 cm<sup>-1</sup> and 2980-2780 cm<sup>-1</sup> due to aliphatic C-H stretching of ligands. The azomethine bonds v(CH=N) of the ligands were appeared at 1632 and 1633 cm<sup>-1</sup>, respectively. The v(C-OH) bands were observed at 1466 cm<sup>-1</sup> for both ligands [16]. The strong bands observed at 1255 cm<sup>-1</sup> (For HL<sup>1</sup>) and 1251 cm<sup>-1</sup> (For HL<sup>2</sup>) assigned to v(C-O) stretching vibrations. In copper(II) complexes, aliphatic v(C-H) stretching groups were appeared between 3000-2800 cm<sup>-1</sup>. The IR spectra of **2**, broad band in the range 3390-3550 cm<sup>-1</sup> assignable to v(O-H) of the uncoordinated water molecules. After the coordination, imine bonds were shifted at 1624 cm<sup>-1</sup> (for 1) and 1635 cm<sup>-1</sup> (for 2). Asymmetric  $v_{as}(COO<sup>-</sup>)$  and symmetric  $v_s(COO<sup>-</sup>)$  stretching bands of the acetate groups were observed in the ranges 1447-1470 and 1220-1244 cm<sup>-1</sup> for 1, 1468-1442 and 1217-1238 cm<sup>-1</sup> for **2** [17]. The new bands were seen at 576-534 and 460-463 cm<sup>-1</sup> due to the v(Cu-O) and v(Cu-N) vibrations, respectively [18, 19].

### 3.5. TG and DSC Analysis

To determine the thermal behavior of the synthesized complexes, TG analysis were performed in the temperature range from 25 to 800 °C under N2 atmosphere with a heating rate of 10 °C.min<sup>-1</sup>. The synthesized ligands were as liquid phase so we could not performed TG analysis for them. TG and TG/DTG curves of the 1 and 2 are shown in Figs. S23-S24. The compound 1 is thermally stable up to 200 °C. Above this temperature, the TGA curve of 1 only showed one weight loss step from 201 to 320 °C, corresponding to the completely decomposition of the complex. In the TG curve of complex 2, two weight losses were observed in contrast to complex 1. The first weight loss in the temperatures 25-90 °C, which correspond to loss of solvated methanol molecules. The last weight loss of in the temperature range of 140-345 °C corresponds to the decomposition of organic ligands in the structure. The remained residuals are attributed to the final product of CuO moieties. DSC analysis were carried out between 25 and 400 °C under a nitrogen atmosphere. DSC thermograms of 1 and 2 shown in Figs. S25-S26. The DSC curve of 1 exhibited an endothermic peak at 212.5 °C corresponding to the melting point of **1**. The second curve at 256.5 °C was corresponding to its thermal decomposition. DSC curve of the 2 exhibited three endothermic peaks. DSC spectrum of 2 showed a small endothermic peak between 80-100 °C that may attribute to evaporation of water content. Second endothermic peak at 176.8 °C corresponding to the melting point of 2. The last curve at 257.5 °C was corresponding to the thermal decomposition of compound 2.

### 3.6. Morphologies of the complexes

The FESEM images provided direct information about the shape and size of the synthesized compounds. The FESEM images of **1-2** are shown in Fig. 6. The morphologies of the compounds were investigated by FESEM images in different magnifications. The images of the **1** displayed a smooth and mottled image in the cluster-like crystallized specimen. The sizes of the mottled range from 122 to 366 nm. The image of **2** is found to be more relatively smooth and homogeneous compared to **1**. The image of **2** showed much less smooth with sharp and rough structure. Their morphologies were found in different shapes and sizes vary from 200 nm to 20  $\mu$ m for **1** and 100 nm to 10  $\mu$ m for **2** due to the using different ligands.



Figure 6. FESEM images of single crystals of 1 (a-d) and 2 (e-h).

#### 3.7. Photoluminescence properties

Photoluminescence properties of the synthesized ligands and their copper(II) complexes were investigated in H<sub>2</sub>O using 1.0 x 10<sup>-5</sup> M concentration. As shown in Fig. 7, it was obtained sharp and narrow emission spectra in all compounds. The free **HL**<sup>1</sup> and **HL**<sup>2</sup> ligands exhibited sharp emission bands at  $\lambda_{max}$ : 529 and 532 nm when excited at 330 and 325 nm, respectively. The observed emission bands may be attributed to the ligand centered  $\pi^* \rightarrow \pi$  transitions in the organic molecules. 1 and 2 showed single emission bands at  $\lambda_{max}$ : 618 and 617 nm upon excitation with wavelengths of 326 and 335 nm, respectively. The wavelength of maximum emission peaks of 1 and 2 were red shift as 89 and 85 nm compared with that of **HL**<sup>1</sup> and **HL**<sup>2</sup> ligands. It is showed that electron donating groups in the structures can lead to red-shift of the emission spectra of the ligands and their metal complexes.





Figure 7. Emission spectra of the free ligands and their copper(II) complexes.

#### 3.8. The effect of different solvents on the photoluminescence properties of the 1-2

The photoluminescence properties of the copper(II) complexes were investigated in EtOH, DMSO, CHCl<sub>3</sub> and H<sub>2</sub>O solvents using 1.0 x 10<sup>-5</sup> M concentrations at 298 K and obtained data are given in Table 4. The emission spectra of the complexes gave one emission bands with high intensities for all solvents in different wavelengths (Fig. 8). The using four different solvents not only have different polarity (Polarity:  $H_2O > EtOH > DMSO > CHCl_3$ ), but also present important differences that water and ethanol are protic solvents while the dimethyl sulfoxide and chloroform are aprotic. The emission bands were observed 446, 495, 507 and 617 nm for 1 and 414, 433, 445 and 616 nm for 2 in CHCl<sub>3</sub>, DMSO, EtOH and  $H_2O$ , respectively. The emission of complexes 1 and 2 were observed to shift from 446 to 617 nm and 414 to 616 nm with increasing in the solvents polarity from  $CHCl_3$  to  $H_2O$ , corresponding to the specific solute/solvent interactions [19a]. H<sub>2</sub>O and EtOH are polar protic solvents, which are hydrogen bond donor with strong polarity, they have very strong interaction with solute through hydrogen bond. DMSO and CHCl<sub>3</sub> are polar aprotic solvents, and these kind of solvents cannot be used as hydrogen bond donor [20]. As a result, there has been a slight red shift to longer wavelength in polar aprotic solvents (446 nm in CHCl<sub>3</sub> to 495 nm in DMSO for 1, 414 nm in CHCl<sub>3</sub> to 495 nm in DMSO for 2). The emission bands changed really strong and huge red shifted to 507 nm (EtOH) to 617 nm (H<sub>2</sub>O) for 1, 445 nm (EtOH) to 616 nm

(H<sub>2</sub>O) for **2** using polar protic solvents. The emission bands bathochromically shift may be due to increase of the dipole moments of EtOH to  $H_2O$  and CHCl<sub>3</sub> to DMSO, respectively.



Figure 8. Normalized emission spectra of 1 (a) and 2 (b) in  $H_2O$ , EtOH, DMSO and CHCl<sub>3</sub> solvents (Concentrations:  $1.0 \times 10^{-5}$  M).

### Table 4

Emission data of the 1-2 in different solvents.

Solvent	Complex 1	Complex 2	
	Wavelength (nm)	Wavelength (nm)	
CHCl <sub>3</sub>	446	414	
DMSO	495	433	
EtOH	507	445	
$H_2O$	617	616	
2 -	0 - 7		

**Solvent concentrations:**  $1.0 \ge 10^{-5}$  M,  $\lambda_{ex}$ : 320 nm.

#### 3.9. The effect of concentrations on the photoluminescence properties of the 1-2

To determine the concentration effect of the complexes in water, samples were prepared in different molar concentrations. EtOH, DMSO and CHCl<sub>3</sub> solvents gave very same emission bands in 1.0 x  $10^{-4}$  - 1.0 x  $10^{-7}$  M so we investigated only in water with different concentrations. The obtained data are given in Table 5. The photoluminescence spectra of the 1 and 2 are shown in Fig. 9. The emission spectra of the 1, maximum intensity was obtained at  $\lambda_{em}$ :573 nm (Int: 507) in the 1.0 x 10<sup>-7</sup> M concentration when excited at 310 nm. The emission spectra of the 1 great red-shifted ( $\lambda_{em}$  :641 nm for 1.0 x 10<sup>-4</sup> M) and their intensities decreased (Int:507 to 150) from 1.0 x 10<sup>-7</sup> to 1.0 x 10<sup>-4</sup> M concentration. On the other hand, maximum intensity (Int:332) and emission value ( $\lambda_{em}$  :625 nm) were obtained in 1.0 x 10<sup>-4</sup> M for the complex 2 ( $\lambda_{ex}$  : 315 nm). The emission spectra of the 2 great red-shifted ( $\lambda$  :596 nm for  $1.0 \times 10^{-7}$  M) and their intensities increased (Int: 95 to 332) from  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-4}$  M concentration. It was observed that both complexes showed red shift with increasing of the concentration. Interestingly, the intensity of 1 was decreased while the intensity of 2 was increased with increasing the concentration of the solvents. This situation is due to the presence of ethoxy group in complex 2. The increasing the number of electron-donating groups has led to increase the intensity. Weak hydrogen bonds were observed between molecules in complex 1. On the other hand, coordinated acetate bridges were linked each other between molecules in complex 2. In complex 1, hydrogen bonds energy transfer absorbed by each molecules cause dynamic quenching [20a]. As a result of the dynamic quenching, the intensity of 1 was decreased with increasing the concentration in the water. It was not observed any differences in the intensities or wavelegnths of the complexes by using EtOH, DMSO and CHCl<sub>3</sub> as solvents. When used water as a solvent, dynamic quenching was observed in complex 1 due to the hydrogen bonds. Fluorescence quenching refers to any process that decreases the fluorescence intensity of a sample. A variety of molecular interactions can result in quenching. These include excited-state reactions, molecular rearrangements, energy transfer, ground-state complex formation, and collisional quenching [20b].



Figure 9. The photoluminescence emission spectra of the 1-(a) and 2-(b) in different concentrations.

### Table 5

Emission and intensity data of 1 and 2 in different concentrations.

Complex 1			Complex 2		
Concentration (M)	Wavelength (nm)	Intensity (a.u.)	Concentration (M)	Wavelength (nm)	Intensity (a.u.)
$1.0 \times 10^{-4}$	641	150	$1.0 \times 10^{-4}$	625	332
1.0 x 10 <sup>-5</sup>	618	272	$1.0 \ge 10^{-5}$	617	245
1.0 x 10 <sup>-6</sup>	596	392	1.0 x 10 <sup>-6</sup>	609	172
1.0 x 10 <sup>-7</sup>	573	507	$1.0 \ge 10^{-7}$	596	95

**Solvent:** H<sub>2</sub>O,  $\lambda_{ex}$ : 310 nm for **1**, 315 nm for **2**.

### Electrical conductivity

Solid conductors have been proposed as alternative to liquid based electrolytes, where inorganic solid conductors and solid polymer conductors are included. Among them, solid phase materials have attracted interest in devices because of its easier processability, mechanical properties and thermal stability [21, 22]. In line with this target, the crystal samples (0.05 g) were weighed and pelleted under pressure (15 tons) as a solid phase. Their thickness (0.291 mm for 1; 0.323 mm for 2) and diameters (1.0 cm) were measured. Electrical conductivity values of the copper(II) complexes were measured by four-point probe method. Average conductivity values were calculated by taking five parallel measurements. The highest electrical conductivity was exhibited by  $[Cu_2(L^1)_2(CH_3COO)_2]$  with 1.2 x 10<sup>-3</sup> S.cm<sup>-1</sup> at 25 °C. The sample [Cu(L<sup>2</sup>)(CH<sub>3</sub>COO)].2H<sub>2</sub>O showed the maximum conductivity of 9.1 x  $10^{-4}$  S/cm at ambient temperature. Due to the dimeric copper(II) structure of the 1 and having methoxy groups, it was observed to show more conductivity than complex 2. The obtained results are similar to those reported previously for conducting and semiconducting studies as ionic conductivity and solid phase conductivity [23, 24]. As shown in Fig. 10, Kaur et al.'s reported conductivity range of materials and their conductivity values [25]. In our study, obtained compounds showed conductivity values between 10<sup>-4</sup> and 10<sup>-2</sup> S.cm<sup>-1</sup>. Given the reported ranges, the synthesized compounds can be used as semiconducting material as solid phase.



Figure 10. Conductivity range of conducting and semiconducting materials [25].

#### 4. Conclusions

In summary, the asymmetric Schiff base ligand  $HL^1$  and  $HL^2$  were synthesized in conventional method. They were characterized by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, mass spectra. The copper(II) complexes of  $HL^1 / HL^2$  were also synthesized and characterized by elemental analysis, FT-IR, TGA, ICP-OES and single crystal X-ray diffraction analysis. The metal complexes exhibited distorted square-pyramidal geometrical arrangements. **1** and **2** showed excellent electrical conductivity values of  $1.2 \times 10^{-3}$  and  $9.1 \times 10^{-4}$  S.cm<sup>-1</sup> at room temperature, respectively. Luminescence properties of the complexes were also investigated in different polar solvents such as H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH, CHCl<sub>3</sub> and DMSO with increased concentration. It was not observed any emission differences by using C<sub>2</sub>H<sub>5</sub>OH, CHCl<sub>3</sub> and DMSO as solvent except H<sub>2</sub>O. It has been observed that there is an increase in emission values with increasing concentration in water.

#### Acknowledgements

The authors gratefully acknowledge financial support from the Research Unit of Çukurova University (Grant No. FBA-2017-7794), and Scientific and Technological Research Application and Research Center, Sinop University, Turkey, for the use of the Bruker D8 QUEST diffractometer.

### Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1546599 for **1** and 1546600 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: <u>deposit@ccdc.cam.ac.uk</u> or www: http://www.ccdc.cam.ac.uk).

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Figure 6.







Figure 10.

### **Figure Captions**

- Figure 1. The molecular structure of 1 showing the atom numbering scheme.
- Figure 2. An infinite 1D layer in 1.
- Figure 3. The molecular structure of 2 showing the atom numbering scheme. [(i) x, 1/2-y, z-

1/2].

- Figure 4. An infinite 1D layer in 2.
- Figure 5. An infinite 2D layer in 2.

CCE

- Figure 6. FESEM images of single crystals of 1 (a-d) and 2 (e-h).
- Figure 7. Emission spectra of the free ligands and their copper(II) complexes.
- Figure 8. Normalized emission spectra of 1 (a) and 2 (b) in  $H_2O$ , EtOH, DMSO and CHCl<sub>3</sub> solvents (Concentrations:  $1.0 \times 10^{-5}$  M).
- Figure 9. The photoluminescence emission spectra of the 1-(a) and 2-(b) in different concentrations.
- Figure 10. Conductivity range of conducting and semiconducting materials [25].

### **Highlights**

- Copper(II) transition metal complexes based on tridentate ONN donor ligands have • been synthesized.
- Luminescence properties of the synthesized compounds were investigated both in ٠ solution and solid state.
- The synthesized 1-2 can be used as semiconducting material as solid phase.

. solid p.

### **Graphical Abstract**

Two novel tridentate ONN donor ligands,  $HL^1$  and  $HL^2$ , and their copper(II) complexes,  $[Cu_2(L1)_2(CH_3COO)_2]$  (1),  $[Cu(L_2)(CH_3COO)].2H_2O$  (2) have been synthesized and fully characterized. Luminescence properties of the compounds were investigated both in solution and solid state. The electrical conductivities of the 1-2 have been also investigated.

