Syntheses, Crystal Structures and Fluorescent Studies of Cu(II) and Zn(II) Complexes Bearing 2-Acetonaphthonebenzoylhydrazone Ligand

Yueqin Li^{1,*}, Zhiwei Yang¹, Benteng Song², Hongqiang Xia², Zhuye Wang¹ ¹School of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, P. R. China ²State Key Laboratory of Magnetic Resonance and Atomic Molecular Physics, Wuhan Centre for Magnetic Resonance, Wuhan Institute of Physics and Mathematics, Chinese Academy of Science, Wuhan 430071, P. R. China

*Corresponding author. Email: yueqinli@163.com

Two new mononuclear metal-organic complexes with hydrazone ligand, namely bis(2-acetonaphthonebenzoylhydrazonato)copper and bis(2-acetonaphthonebenzoylhydrazonato)zinc have been prepared. The complexes have been characterized by physico-chemical methods and single crystal X-ray diffraction study. The Cu and Zn atoms in both complexes are coordinated by N and O donor atoms of ligand, forming a distorted tetrahedral geometry. Optical properties of the metal complexes were studied by UV–Vis absorption and photoluminescence emission spectroscopy. Geometry optimization, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels as well as the energy gap of both complexes have

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been carried out by DFT calculations.

Keywords

2-acetonaphthonebenzoylhydrazone; Cu(II) complex; Zn(II) complex; photoluminescence; DFT

calculations

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INTRODUCTION

Hydrazones are a special group of compounds in the Schiff base family. They are characterized by the presence of >C=N-N=C<. The presence of two inter-linked nitrogen atoms was separated from imines, oximes, etc. Hydrazones are considered privileged Schiff base ligands because they are easily prepared by a simple one-pot condensation reaction by using of carbonyl compound and primary amines as starting materials.^[1] Hydrazone Schiff bases of acyl, aroyl and heteroacroyl compounds have an additional donor sites like C=O, which makes them more flexible and versatile. This versatility has made hydrazones good polydentate chelating agents that can form a variety of complexes with various transition and inner transition metals and have attracted the attention of many researchers. The coordination behaviour of hydrazones is known to depend on the pH of the medium, the nature of the substituents and also on the position of the hydrazone group relative to other moieties. Moreover, deprotonation of the -NH group, which is readily achieved in the complexes ligand in particular, results in the formation of tautomeric anionic species ($-C(O)-NH-N=C \leftrightarrow -C(OH)=N-N=C \leftrightarrow -C(O)=N-N=C \leftrightarrow$), having new coordination properties.^[2, 3]

Hydrazones containing complexes play an important role as pharmaceutical chemicals, biological materials^[4] and in pharmacology,^[5] due to their sensitivity and selectivity to metal ions.^[6] On the other hand, some transition metal complexes based on hydrazone ligands are of a considerable interest. Cu(II) complexes are shown as potent inhibitor of DNA synthesis and cell

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growth,^[7] others are studied as therapeutic agents in the treatment of cancer,^[8] and some have potential for Alzheimer disease therapy.^[9] Recently, a number of attempts have been made to obtain Co(II), Ni(II), Cu(II) and Zn(II) complexes with o-amino acetophenone benzoyl hydrazone, which have been well characterized by elemental analyses and spectral data.^[10] Cu(II) and Ni(II) complexes containing anthranoylhydrazone ligands and heterocyclic coligand have been synthesized by Gup group.^[2, 3] Recently, this group have investigated the DNA binding and cleavage properties of Cu(II) complexes based on acylhydrazone ligands, and they found the copper complexes show nuclease activity.^[11, 12]

All these reported complexes were characterized using spectroscopic techniques and the structures were proposed accordingly. Yet, none was characterized unambiguously by its crystal structure. Herein, we were motivated to report the synthesis and characterization of Cu(II) and Zn(II) complex based on 2-acetonaphthonebenzoylhydrazone ligand along with the crystal structure of the obtained complexes, and to described thermogravimetric, spectroscopic and electrochemical properties of both complexes. DFT calculations were also carried out in an attempt to compare theoretical and experimental structures of such compounds with some physical aspects.

EXPERIMENTAL

Materials and Measurements

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All chemicals and solvents were obtained from commercial sources as reagent grade and used without further purification in the syntheses. Melting points were measured on a WRS-1B digital melting point apparatus. Elemental analyses for C, H and N were performed on a Perkin Elmer 240 C elemental analyzer. The FT-IR measurements (KBr pellets) were recorded in the range of 400–4000 cm⁻¹ on the instrument of Thermo Nicolet Nexus 670 infrared spectrometer. NMR spectra were recorded on a Bruker Advance 300 spectrometer at resonant frequencies of 300 MHz for ¹H and 75 MHz for ¹³C nuclei using CDCl₃ as solvent and tetramethylsilane as the reference. The UV-Vis spectra of the ligand and complexes were obtained on a Varian Cary 300 UV-Vis spectrophotometer in chloroform solution. Fluorescence emission spectra were measured with Varian Cary Eclipse Fluorescence spectrometer at room temperature.

Synthesis of 2-Acetonaphthonebenzoylhydrazone Ligand (HL)

To a solution of 2-acetonaphthone (1.360 g, 8 mmol) in anhydrous ethanol (40 mL) was added two drops of glacial acid. A solution of benzoylhydrazine (1.089 g, 8 mmol) in anhydrous ethanol (20 mL) was added dropwise over a period of 10 min with stirring. The desired benzoylhydrazone precipitated during the reaction. After refluxing the reaction mixture for 6 h, the product was filtered and washed several times with anhydrous ethanol and recrystallized from toluene, giving light yellow needle-like solid. Yield 2.12 g (92 %). M.p. = 196 - 197 °C. Anal. Calcd. for C₁₉H₁₆N₂O (FM 288.34): C 79.14, H 5.59, N 9.72; Found: C 79.34, H 5.69, N 9.96 %. ¹H NMR (ppm, 300 MHz, CDCl₃): 9.02 (s, 1 H, N–H), 7.48~7.88 (m, 11 H, Ar–H), 8.17

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(s, 1 H, 1-naphthalene ring), 2.44(s, 3 H, -CH₃); ¹³C NMR (ppm, 75 MHz, CDCl₃): 164.0, 154.9, 135.5, 134.1, 133.3, 132.7, 131.4, 128.5, 128.3, 127.9, 127.7, 127.5, 126.8, 126.4, 123.6, 14.3 ppm. FTIR data (KBr, cm⁻¹): 3348, 3060, 2966, 2926, 1666, 1583, 1521, 1489, 1379, 1269, 947, 743, 706.

Synthesis of Bis(2-acetonaphthonebenzoylhydrazonato)copper (CuL₂)

A solution of copper(II) acetate monohydrate (0.080 g, 0.4 mmol) in 10 mL of acetonitrile/ tetrahydrofuran (V/V=1:1) mixed solvent was added dropwise with stirring to a solution of 2-acetonaphthonebenzoylhydrazone (0.231 g, 0.8 mmol) in 20 mL of acetonitrile/ tetrahydrofuran (V/V=1:1) mixed solvent. The reaction mixture was stirred for 4 h at room temperature to give a dark green solution. Upon keeping the solution in air for about a week, black block-like single crystals suitable for X-ray diffraction were deposited at the bottom of the vessel. The isolated product was washed three times with cold methanol, and dried in a vacuum over night. Yield 0.153 g (60 %). M.p.: 223 – 224 °C. Anal. Calcd. for $C_{38}H_{30}O_2N_4Cu$ (FM 638.20): C 71.51, H 4.74, N 8.78 %; Found: C 71.37, H 4.43, N 9.08 %. FTIR data (KBr, cm⁻¹): 3052, 2926, 2847, 1598, 1493, 1442, 1370, 995, 750, 711, 591, 528.

Synthesis of Bis(2-acetonaphthonebenzoylhydrazonato)zinc (ZnL₂)

A solution of zinc(II) acetate dihydrate (0.088 g, 0.4 mmol) in 10 mL of methanol was added dropwise with stirring to a solution of 2-acetonaphthonebenzoylhydrazone (0.231 g, 0.8 mmol) in 20 mL of methanol. The reaction mixture was stirred for 4 h at room temperature to give a

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colorless solution. Upon keeping the solution in air for about a week, colorless needle-like single crystals suitable for X-ray diffraction were deposited at the bottom of the vessel. The isolated product was washed three times with cold methanol, and dried in a vacuum over night. Yield 0.169 g (66 %). M.p.: 263 - 264 °C. Anal. Calcd. for $C_{38}H_{30}O_2N_4Zn$ (FM 640.03): C 71.31, H 4.72, N 8.75; Found: C 71.15, H 4.77, N 8.73 %. ¹H NMR (ppm, 300 MHz, CDCl₃): 7.14~7.81 (m, 11 H, Ar–H), 8.19 (s, 1 H, 1-naphthalene ring), 1.98 (s, 3 H, -CH₃); ¹³C NMR (ppm, 75 MHz, CDCl₃): 171.5, 164.4, 135.5, 135.4, 133.7, 132.5, 130.6, 128.9, 128.2, 127.9, 127.5, 127.4, 126.8, 126.3, 123.4, 17.2. FTIR data (KBr, cm⁻¹): 3059, 2930, 2850, 1590, 1510, 1441, 1366, 996, 750, 708, 601, 531.

Crystal Structure Determination

The X-ray single-crystal data for HL, CuL₂ and ZnL₂ were recorded on a Brucker SMART Apex CCD detector diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program,^[13] and multi-scan absorption corrections were performed using the SADABS program.^[14] The structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXL-97.^[15] All non-hydrogen atoms were refined anisotropically. Experimental details for X-ray data collection of HL and both of complexes are presented in Table 1. Selected bond lengths and angles are given in Table 2. Crystallographic data for HL, CuL₂ and ZnL₂ have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1463822, 1486530 and 748315).

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RESULTS AND DISCUSSION

Synthesis of HL and the Complexes

The reaction of 2-acetonaphthone with benzoylhydrazine in anhydrous ethanol gave 2-acetonaphthonebenzoylhydrazone as a pale yellow crystalline solid. Then two metal complexes were prepared by the reaction of copper acetate monohydrate and zinc acetate dihydrate with 2-acetonaphthonebenzoylhydrazone in stoichiometry, respectively. Synthetic route for complexes are shown in Scheme 1. Complexes are very stable to moisture and oxygen. The complexes are insoluble in ethanol and methanol, whereas they are highly soluble in toluene, dichloromethane, chloroform, and *N*,*N*-dimethylformamide.

General Characterization of the Complexes

According to the literatures,^[2, 3] hydrazone ligands exist in keto or enol tautomeric form in the solid. In FTIR spectrum of the free ligand (Figure 1), the stretching vibration of v(N-H) occurred at 3349 cm⁻¹; Strong v(C=O) absorption band was observed at 1666 cm⁻¹ which indicated it was in the keto form in the solid state.^[16] The absorption peak at 1521 cm⁻¹ was assigned to the stretching vibration of C=N group. However, in the FTIR spectra of the complexes, v(C=O), v(C-N) and v(N-H) stretching vibrations disappears but two new bands are observed at 1493, 1366 cm⁻¹ of CuL₂ and 1510, 1370 cm⁻¹ of ZnL₂ due to the >C=N–N=C< and C–O stretches, respectively, suggesting that the coordination takes place in enol tautomeric form. Furthermore, HL and ZnL₂ were characterized by NMR spectroscopy (Figure 2). When compared the ¹H

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NMR spectra of ZnL₂ and that of the free ligand, the chemical shift of -CH₃ showed upfield shifting from 2.44 ppm of free ligand to 1.98 ppm. Also, chemical shifts of the aromatic protons (7.14 ~ 7.81 ppm) moved upfield comparing with those in free ligand (7.48 ~ 7.88 ppm). The disappearance of the nitrogen-bonded proton signal (9.02 ppm) also verified the successful reaction of the active hydrogen atom of HL with zinc acetate dihydrate. These data were in good agreement with previously reported for the similar compounds.^[17] Although a resolvable NMR spectrum of CuL₂ could not be measured owing to paramagnetism, the results of the elemental analysis are consistent with the required by the proposed formula. The spectroscopic data and the elemental analysis results in affair agreement with the expected structures suggest the successful preparation of HL and the target complexes.

Structure Description of the HL and the Complexes

Molecular structures of HL and complexes were depicted in Figure 3, Figure 4 and Figure 5, respectively. Selected bond distances (Å) and bond angles (°) were given in Table 2. In HL, the imine-N and carbonyl-O provides a fixed coordination mode with NO bidentates. The C(7)–O(1), N(1)–N(2), N(1)–C(3) and N(2)–C(7) bond distances of 1.2203(18), 1.3876(16), 1.2867(18) and 1.3511(19) Å, respectively, are consistent with C=O double bond, N-N single bond, C=N double bond and N-C single bond. The conjugated system of the ligand makes its planar molecular structure. In both complexes, the ligand coordinated to either Cu or Zn atom in enol tautomeric form. The ligand acts as bidentate monobasic bonding through azomethine nitrogen atoms (N1,

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N2) and deprotonated enolate groups (O1, O2) forming a distorted tetrahedral geometry around metal atoms.

Specifically, as for CuL₂, it crystallizes in the space group $P2_1/c$. The bond lengths for Cu(1)–O(1), Cu(1)–O(2), Cu(1)–N(2) and Cu(1)–N(4) are 1.907 (3), 1.897(3), 1.942(4) and 1.967(4) Å, respectively. The variation in Cu(1)-N(2) and Cu(1)-N(4) indicates the different strength of the bond formed by each of the coordination nitrogen atoms. The single bond of N(1)-C(7) and N(3)-C(26) are 1.294(6) and 1.303(6) Å, respectively, which are shorter than that of N(2)-C(7) (1.3511(19) Å) in the free ligand. These bond lengths are in agreement with that of other acylhydrazone complexes in which the acylhydrazone ligand takes enolic form.^[18] However, the C(7)–O(1) and C(26)–O(2) bond length of 1.284(6) and 1.285(6) nm are longer than that of C(7)–O(1) (1.2203(18) Å) in HL. These data approach the value of 1.282(6) Å expected for an enolic form of the acylhydrazone ligand.^[19] The bond angles of O(2)–Cu(1)–N(4) $(81.12(15)^{\circ})$, N(2)–Cu(1)–N(4) (110.05(16)^{\circ}) and O(2)–Cu(1)–O(1) (104.20(14)^{\circ}) indicate distortion perfect The dihedral from tetrahedron angle. angle between O(1)-C(7)-N(1)-N(2)-Cu(1) plane (plane 1) and O(2)-C(26)-N(3)-N(4)-Cu1 plane (plane 2) is of 47.97°.

While in ZnL_2 , the bond distances for Zn-N(1) and Zn-N(2) are 1.995(5) and 2.009(5) Å, respectively, which are comparable to the bond lengths reported for similar bis[*N*-(1-pyrenylmethyl)salicylideneaminato]zinc (2.005 Å) in the literature.^[20] The bond

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distances for Zn–O(1) and Zn–O(2) are 1.943(4) and 1.946(4) Å, respectively, which are longer than that of bis[N-(1-pyrenylmethyl)salicylideneaminato]zinc (1.912 Å).^[20] The N(1)–N(4) and N(2)-N(3) distances are 1.377(6) and 1.395(6) Å for Zn(II) complex, while the N(1)-N(2) distance of the ligand is 1.3876(16) Å. These N-N distances can be comparable with those of zinc(II) acylhydrazone complexes reported in literatures.^[21, 22] The double bond of N(3)–C(6) and N(4)–C(3) are 1.313(7) and 1.340(8) Å, respectively, which are shorter than that of N(2)-C(7) (1.3511(19) Å) in the free ligand. However, the C(6)–O(2) and C(3)–O(1) bond length of 1.293(6) and 1.292(7) Å are longer than that of C(7)-O(1) (1.2203(18) Å) in the free ligand. The angles of N(1)–Zn–O(1) and N(2)–Zn–O(2) are 81.30(19) and 81.49(18)°, respectively, which are smaller than that of the ideal tetrahedron angle. However, the angles of N(1)–Zn–N(2) and O(1)–Zn–O(2)are much larger up to 116.9(2) and 117.89(17)°, respectively. The N(1)–N(4)–C(3)–O(1)–Zn plane (plane 1) and N(2)–N(3)–C(6)–O(2)–Zn plane (plane 2) are roughly perpendicular to each other with a dihedral angle of 73.67° . The copper and zinc ions have an N₂O₂ tetrahedral coordination sphere as reported for some bis(schiff-base)zinc complexes.^[23] All these data indicate the 2-acetonaphthonebenzoylhydrazone ligand has coordinated to Cu and Zn center successfully.

Thermal Properties of Complexes

The melting point temperature (*T*m) of ZnL₂ was 263-264 °C, which is 30 °C higher than that of CuL_2 (*T*m = 223-224 °C). Thermogravimetric (TG) analysis was performed under an N₂

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atmosphere on complex samples (Figure 6). The TG curve of CuL_2 shows the first weight loss of 30 % in the temperature range from 271 to 360 °C, associated with the exclusion of two phenyl and methyl groups (calcd. 29 %); then, from 360 to 600 °C, the residual ligands are released in a featureless process. ZnL₂ started to lose weight at 268 °C and completed at 458 °C. The observed weight loss of 62% is corresponding to the loss of the phenyl and naphthyl groups (calcd. 64%). And then, the curve shows further decomposition in the temperature range 458-618 °C with an 11% weight change, corresponding to loss of the coordinated ligand parts (calcd. 12%). These results indicate that both of the complexes possess excellent thermally stability as is commonly observed for the conventional Schiff-base metal complexes.

UV-Vis Absorption and Photoluminsecence Properties

The UV-Vis spectra of the free ligand $(2 \times 10^{-4} \text{ M})$, CuL₂ and ZnL₂ $(1 \times 10^{-4} \text{ M})$ in chloroform solution were presented in Figure 7. For the free ligand, the absorption maxima appeared at 309 nm was attributed to $\pi \rightarrow \pi^*$ transition.^[24] While for the complexes, the maximum band was shifted to 318 nm and the intensity increased because of the extension of the larger conjugated system after coordination.^[25] Unfortunately the expected weak *d*-*d* transition in the visible region for the one-electron paramagnetic (meff = 1.69 and 1.64 BM) complexes cannot be detected even with concentrated solutions. It may be lost in the low energy tail of the charge transfer transition.^[2, 3, 26]

Photoluminescence emission spectra were measured at the same concentration, as shown in

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Figure 7. Under 318 nm UV light excitation, the emission spectrum for ligand shows one broad blue emission band around at 422 nm. However, CuL₂ shows relatively weak emission at 438 nm, while ZnL₂ exhibits a very strong emission band centered at 450 nm. The reason could be due to the quenching effect from the Cu(II) ion. Possible mechanism which accounts for the quenching effect is collisional quenching of the excited-state fluorophore by the Cu²⁺ quencher which may proceed via a multitude of interactions like heavy atom effect, paramagnetic interaction as well as the electron transfer process.^[27] The strong blue luminescence of ZnL₂ may be attributed to the coordination of the ligand to the zinc center, which increases the rigidity of the ligand that prevents a photo-induced electron transfer (PET) process and reduces the loss of energy via a un-radiation pathway, thus enhancing the $\pi \rightarrow \pi^*$ transition of the ligand.^[28, 29] Furthermore, the luminescence quantum yield for the ZnL₂ was determined to be $\varphi = 0.10$ with a reference solution of quinine sulfate in 0.5 mol/L sulfuric acid ($\varphi = 0.546$)^[30] and were corrected by the refractive index of the solvent at 298 K.

Energy Levels of Complexes

As is well known, theoretical calculations based on density functional theory are usually employed to rationally obtain the optimized geometries and electronic structures of organic and inorganic compounds.^[31] Herein, to better understand the geometric and spectroscopic parameters of these complexes, the molecular orbital energy levels were also studies by theoretical calculation. The ground state geometries of the Cu(II) and Zn(II) complexes were

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fully optimized at the B3LYP/6-311G(d,p) level of theory^[32] using the Gaussian09 program package.^[33] As shown in Figure 5, the calculated bond lengths of Zn-N1 and Zn-N2 in Zn(II) complex are 2.115 and 2.122 Å, respectively, and it is consistent with the X-ray data with the value of 1.995(5) and 2.009(5) Å, which proves the reliability of the calculated method used in this work. Based on the optimized structures, the energy levels and the molecular orbital distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), as well as the energy gap between HOMO-LUMO can be obtained as illustrated in Figure 9. It is obvious that the different central metal ions lead to the variation of their frontier molecular orbital energy levels. ZnL₂ has a smaller ΔE_{gap} (3.766 eV) than CuL₂ (3.834 eV). Furthermore, it is also clearly showed that both complexes have their HOMOs mainly localized on the naphthyl group and the coordinated N-N=C moiety. Meanwhile for their LUMOs, the naphthyl group has much more orbital contributions than any other moieties of the ligand. All these results can lead to an electronic transition from the ground state to the excited state due to a transfer of electrons from the HOMO to LUMO level, which is mainly a π ... π transition.^[34]

CONCLUSION

A 2-acetonaphthonebenzoylhydrazone ligand and its Cu(II) and Zn(II) complexes were synthesized and characterized by FTIR, NMR, thermogravimetric analysis, UV-Vis and emission spectroscopy. The molecular structure of HL, the Cu(II) and Zn(II) complex were further

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investigated by X-ray crystallography. These results indicate a distorted tetrahedral geometry for both complexes. The electronic structures of both complexes have been determined using DFT method. On the basis of our analysis, it has been demonstrated that the differences in the central metal ions have major influences on their spectroscopic properties and the energy levels of complexes.

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Compound	HL	CuL ₂	ZnL ₂
Formula	C ₁₉ H ₁₆ N ₂ O	$C_{38}H_{30}N_4O_2Cu$	$C_{38}H_{30}N_4O_2Zn$
FW	288.34	638.20	640.03
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / n	<i>P</i> 2 ₁ / c	<i>P</i> 2 ₁ / c
<i>a</i> (Å)	5.5829(3)	13.409(7)	13.460(3)
<i>b</i> (Å)	7.8387(4)	15.452(8)	15.673(3)
<i>c</i> (Å)	33.2247(17)	14.905(7)	14.828(3)
β (°)	90.196(2)	101.257(10)	99.74(3)
$V(\text{\AA}^3)$	1453.99(13)	3029(3)	3083.0(11)
Ζ	4	4	4
D_{calc} (g cm ⁻³)	1.31712	3029 (3)	1.379
$\mu(\text{mm}^{-1})$	0.08	0.76	0.838
F (000)	608	1324	1328
T(K)	277	296	293(2)
Goodness of fit on F^2	1.01	1.01	0.932
$R_{1}, wR_{2} \left[I > 2\sigma(I)\right]^{*}$	0.051, 0.143	0.065, 0.173	0.0758, 0.1614
$\rho_{\rm max}, \rho_{\rm min} ({\rm e} \cdot {\rm \AA}^{-3})$	0.23, -0.18	0.78, -0.57	0.36, -0.43

TABLE 1. Crystal data for HL and CuL₂ and ZnL₂

^{*} $R_1 = \sum (||F_0| - |F_c||) / \sum |F_0|; wR_2 = [\sum (w(F_0^2 - F_c^2)^2) / \sum (wF_0^2)]^{1/2}$

HL						
N1-C3	1.2867(18)	C3–C4	1.4843(19)			
N1-N2	1.3876(16)	С7–О1	1.2203(18)			
N2C7	1.3511(19)	C7–C10	1.501(2)			
N1-C3-C4	115.50(13)	C7-N2-N1	119.32(12)			
O1C7N2	123.52(14)	C3-N1-N2	116.02(12)			
CuL ₂						
Cu1–O1	1.907 (3)	N3-C26	1.303(6)1			
Cu1–O2	1.897(3)	N3-N4	1.404(5)			
Cu1–N2	1.942(4)	N4-C27	1.273(6)			
Cu1–N4	1.967(4)	N2C8	1.294(6)			
C7–O1	1.284(6)	N2N1	1.398(5)			
C7–N1	1.294(6)	O2–C26	1.285(6)			
С7–С4	1.494(7)					
O2Cu1O1	104.20(14)	C27–N4–Cu1	130.0(3)			
O2–Cu1–N2	149.54(17)	N3-N4-Cu1	112.3(3)			
O1–Cu1–N2	81.38(16)	C8-N2-N1	119.3(4)			
O2–Cu1–N4	81.12(15)	C8–N2–Cu1	128.0(4)			
O1–Cu1–N4	148.28(16)	N1–N2–Cu1	112.5(3)			
N2-Cu1-N4	110.05(16)	C26O2Cu1	111.1(3)			
O1C7N1	125.8(4)	C7-N1-N2	108.7(4)			
O1–C7–C4	116.6(5)	O2-C26-N3	125.4(4)			
N1C7C4	117.5(4)	O2–C26–C23	116.8(5)			
C7–O1–Cu1	109.6(3)	N3-C26-C23	117.8(4)			
C26-N3-N4	108.6(4)	N2	115.9(5)			
C27-N4-N3	117.6(4)	N2C8C9	122.3(5)			
ZnL ₂						
Zn-O1	1.943(4)	Zn–O2	1.946(4)			
Zn-N1	1.995(5)	Zn–N2	2.009(5)			
N2-C5	1.290(7)	C3–O1	1.292(7)			
N4–C3	1.340(8)	N4–N1	1.377(6)			

TABLE 2. Selected bond distances (Å) and bond angles (°) for HL, CuL₂ and ZnL₂

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N3-N2	1.395(6)	C2–C38	1.472(8)
C6-N3	1.313(7)	С6-О2	1.293(6)
O1–Zn–O2	117.89(17)	O1–Zn–N1	81.30(19)
O2–Zn–N1	134.6(2)	O1–Zn–N2	132.56(19)
O2–Zn–N2	81.49(18)	N1–Zn–N2	116.9(2)
C3–O1–Zn	109.8(4)	C6–O2–Zn	109.5(4)
C5–N2–Zn	129.1(4)	N3–N2–Zn	112.0(4)
C2–N1–Zn	126.7(4)	N4–N1–Zn	113.5(4)
N4C3C7	116.0(6)	O1–C3–C7	117.8(6)
O1C3N4	126.2(6)	C3-N4-N1	109.0(5)
N1C2C1	123.4(6)	N2-C5-C19	118.3(5)
N1-C2-C38	114.6(6)	N3-C6-C13	117.9(6)
O2C6C13	115.2(6)	O2-C6-N3	126.9(6)
C6-N3-N2	110.0(5)	N2-C5-C4	122.7(6)

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Figure 1. FTIR spectra of the free ligand and the complexes.

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Figure 2. ¹H NMR spectra of HL and Zn(II) complex.



Figure 3. ORTEP drawing of HL, showing 40 % probability displacement ellipsoids. The hydrogen atoms are omitted for clarity.

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Figure 4. ORTEP drawing of CuL₂, showing 40 % probability displacement ellipsoids. The hydrogen atoms are omitted for clarity.

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Figure 5. ORTEP drawing of ZnL₂, showing 40 % probability displacement ellipsoids. The hydrogen atoms are omitted for clarity.

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Figure 6. TG curves of CuL_2 and ZnL_2 at a scan rate of 10 $^{\circ}C$ min⁻¹ under nitrogen.

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Figure 7. UV-Vis absorption spectra and emission spectra of HL and complexes in dilute chloroform solution.

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Figure 8. HOMO and LUMO contours of CuL₂ and ZnL₂.

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Scheme 1. Synthetic route for HL, CuL₂ and ZnL₂.

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