

**Synthesis and Characterization of Cobalt(II), Nickel(II),
Copper(II) and Zn(II) complexes with N'-(phenyl (pyridin-2-yl)methylene)nicotinohydrazide**

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ABSTRACT

The Schiff base (HL), derived from 2-benzoylpyridine and nicotinic hydrazide, and its complexes with some metal transition (Co, Ni, Cu, Zn) have been synthesized. These compounds have been characterized by means of elemental analysis, ^1H and ^{13}C NMR (for HL), FTIR spectroscopy, UV-Vis spectroscopy, molar conductance and room temperature magnetic measurements. The compounds are found isostructural and are formulated as $\{[\text{Co}(\text{L})_2] \cdot 2\text{H}_2\text{O}\}$ (1), $\{[\text{Ni}(\text{L})_2] \cdot 2\text{H}_2\text{O}\}$ (2), $\{[\text{Cu}(\text{L})_2] \cdot 3\text{H}_2\text{O}\}$ (3), $\{[\text{Zn}(\text{L})_2] \cdot \text{H}_2\text{O}\}$ (4). The two ligand molecules act in their monodeprotonated form through one azomethine nitrogen atom, one pyridine nitrogen atom and one iminolate oxygen atom yielding six coordinate metal center. The complex 4 crystallizes in the monoclinic space group $\text{P}2_1$ with cell parameters of $a = 9.3429(8)$ Å, $b = 10.3034(9)$ Å, $c = 16.6349(14)$ Å, $\beta = 101.109(4)^\circ$, $V = 1571.3(2)$ Å³, $Z = 2$, $R_1 = 0.027$, $wR_2 = 0.074$. The zinc atom is six-coordinated, and the coordination polyhedron is best described as a distorted octahedral geometry. The aromatic rings of the ligand molecules are twisted each other with dihedral angle values in the range $10.168(2)^\circ$ – $74.430(1)^\circ$.

Keywords: Hydrazide, Cobalt, Nickel, Copper, Zinc, Crystal, X-ray Diffraction. –

1. INTRODUCTION

Schiff bases resulting from the condensation reaction of nicotinic hydrazide and a ketoprecursor such as ketones [1, 2] are widely used in the synthesis of organic ligands with a view to preparing lanthanide coordination complexes [3–5] and transition metals [6, 7]. These complexes are particularly interesting in various fields such as magnetism [8], catalysis [9, 10] and in medicine [11, 12], luminescence [13, 14]. The presence of phenolic nuclei suggests that these complexes can be antioxidants as reported in the literature [15, 16] but also as antibacterial agents [17–21]. In recent studies, nicotinic hydrazide complexes were prepared and showed antimicrobial-like activities [22, 23]. It is in this context that we set out to synthesize complexes at room temperature using nicotinic hydrazide and 2-benzoylpyridine in the presence of transition metal salts. Several complexes have been isolated in powder form and are characterized by different techniques.

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2. EXPERIMENTAL

2.1 Materials and Procedures

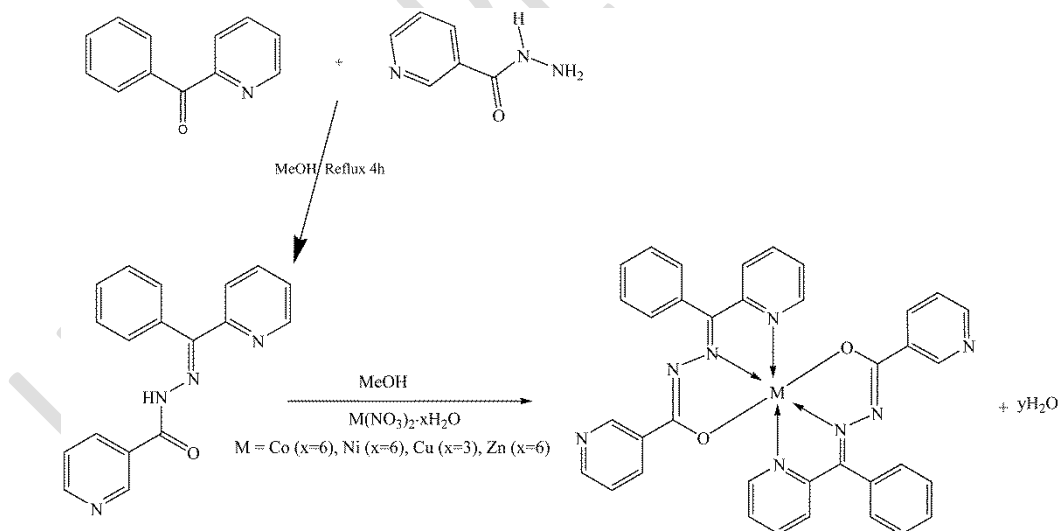
Nicotinic acid hydrazide, 2-benzoylpyridine, $M(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ($M = \text{Co(II)}$, Ni(II) , Cu(II) or Zn(II)) were commercial products (from Alfa and Aldrich) and were used without further purification. Solvents were of reagent grade and were purified by the usual methods. Elemental analyzes were performed in a Carlo- Erba EA microanalyser. Infrared spectra were recorded as KBr discs on a Bruker IFS-66V spectrophotometer. LSI-MS were recorded using a MicromassAutospec spectrometer with 3-nitrobenzyl alcohol as the matrix. The ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a BRUKER 500 MHz spectrometer at room temperature using TMS as an internal reference. The UV-Vis spectra were run on a Shimadzu UV-2501 PC Recording spectrophotometer (1000–200 nm). The molar conductance of 10^{-3} M in DMF solutions of the metal complexes was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance $\text{Hg}[\text{Co}(\text{SCN})_4]$ used as calibrant. Melting points were recorded on a Büchi apparatus and are uncorrected.

2.2 Synthesis of the HL ligand and its transition metal complexes.

2.2.1 Synthesis of the ligand N'-(phenyl (pyridin-2-yl)methylene)nicotinohydrazide (HL)

In a 250 mL round bottomed flask containing 20 mL of absolute ethanol, benzoylpyridine (2.67 g, 14.58 mmol) was added. After dissolution, nicotinic hydrazide (2.00 g, 14.58 mmol) previously dissolved in 20 mL of methanol was added. The mixture was heated under reflux for four hours. After filtration, the resulting clear brown solution was left under slow evaporation. Crystals suitable for X-ray analyze were collected after three days. IR (ν , cm^{-1}): 3062 (N–H), 3044 ($\text{C}_{\text{Ar}}\text{--H}$), 1684 (C=O), 1583 (C=N), [1541-1422] ($\text{C}_{\text{Ar}}\text{=C}_{\text{Ar}}$), 1282 (CN); 1142 (N–N); 804; 749; 699; 650; 614 ($\text{C}_{\text{Ar}}\text{--H}$). ^1H NMR (dmsO-d_6 , δ , ppm): 8.73 (s, 1H, H–C=N); [7.39-8.20] (m, 13H, H–Ar), 9.01 (s, 1H, N–H). ^{13}C NMR (dmsO-d_6 , δ , ppm): 161.46 (C=O), 152.30 (C=N), 151.68, 148.72, 138.11, 137.71, 136.78, 135.39, 135.22, 130.61, 129.23, 128.34, 124.91, 124.08, 123.76.

2.2.2 Synthesis of transition metal complexes from the ligand (HL)



Scheme 1. Synthesis procedure of the ligand HL and its Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}

The ligand HL (0.1g, 0.33mmol) was dissolved in 15 mL of methanol before adding (0.17 mmol) of transition metal nitrate $M(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ with $M = \text{Co}$, Ni , Cu and Zn . The resulting solution was stirred for two hours at room temperature, then filtered and allowed to slowly evaporate. One week later we obtain powders which are recovered by filtration then recrystallized in a methanol/DMF mixture (50/50). After three weeks suitable yellow crystals for X-ray diffraction were collected for

the Zn(II) complex. The physico-chemical data were collected using the powders or the crystals collected after the recrystallization process.

{[Co(L)₂].2H₂O} (1). Brown. IR (ν, cm⁻¹) : 3672, 3236, 2968, 2969, 2929, 1610, 1568, 1524, 1383, 1291, 1264, 1191, 1072, 1067, 1052, 1028, 969, 815, 798, 758, 696. Yield : 78%. M.P. (°C) > 260. Λ (Ω⁻¹cm² mol⁻¹) : 6 (fresh solution) and 9 (after two weeks). μ_{eff}: 3.88 μ_B. UV-visible (MeOH, λ_{max}, nm) : 325, 361, 383, 418, 465, 499. Anal. calcd. for C₃₆H₃₀CoN₈O₄ : %C, 61.98; % H, 4.33; % N, 16.06. Found % C, 61.93; % H, 4.30; % N, 16.09.

{[Ni(L)₂].2H₂O} (2). Green. IR (ν, cm⁻¹) : 3383, 2900, 2835, 1598, 1548, 1408, 1368, 1301, 1249, 1196, 1151, 1086, 1019, 825, 748, 727, 696. Yield : 80%. M.P. (°C) > 260. Λ (Ω⁻¹cm² mol⁻¹) : 10 (fresh solution) and 15 (after two weeks). μ_{eff}: 2.74 μ_B. UV-visible (MeOH, λ_{max}, nm) : 361, 419, 444, 499, 869. Anal. calcd. for C₃₆H₃₀N₈NiO₄ : % C, 62.00; % H, 4.34; % N, 16.07. Found % C, 61.90; % H, 4.30; % N, 16.09.

{[Cu(L)₂].3H₂O} (3). Green. IR (ν, cm⁻¹) : 3396, 2888, 2825, 1618, 1595, 1569, 1531, 1478, 1385 Intense, 1197, 1161, 1099, 1056, 1030, 827, 761, 696, 656. Yield : 80%. M.P. (°C) > 260, Λ (Ω⁻¹cm² mol⁻¹) : 8 (fresh solution) and 12 (after two weeks). μ_{eff}: 1.82 μ_B. UV-visible (MeOH, λ_{max}, nm) : 386, 418, 439, 459, 498, 678. Anal. calcd. for C₃₆H₃₂CuN₈O₅ : % C, 60.03; % H, 4.48; % N, 15.56. Found % C, 60.06; % H, 4.54; % N, 15.61.

{[Zn(L)₂].H₂O} (4). Yellow. IR (ν, cm⁻¹) : 3649, 2364, 1559, 1507, 1457, 1360, 1302, 1257, 1193, 1150, 1082, 1053, 1033, 1014, 918, 834, 792, 742, 697. Yield : 72%. M.P. (°C) > 260, Λ (Ω⁻¹cm² mol⁻¹) : 3 (fresh solution) and 5 (after two weeks). μ_{eff}: 0 μ_B. UV-visible 361, 419, 441, 499. Anal. calcd. for C₃₆H₂₈N₈O₃Zn : % C, 63.03; % H, 4.11; % N, 16.33. Found % C, 62.97; % H, 4.14; % N, 16.39.

2.3 Crystal structure determination

Crystals suitable for X-diffraction, of the reported compound, were grown by slow evaporation of MeOH /DMF mixture solution of the complex. Details of the X-rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using the Bruker SHELXTL diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Using the structures were solved by intrinsic phasing methods with SHELXT[24] and SHELXL [25] was used for full matrix least squares refinement. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Other H atoms were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3[26].

Table-1. Crystal data and details of the structure determination of the complex [Zn(L)₂].H₂O

Chemical Formula	C ₃₆ H ₂₆ N ₈ O ₂ Zn·H ₂ O
Shape and Color	Prism, colorless
Molar mass (g/ mol)	686.05
Crystal system,	Monoclinic,
Space group	P2 ₁
Crystal size (mm)	0.13 × 0.12 × 0.12
Temperature (K)	173
Mo Kα (Å)	0.71073
a (Å)	9.3429 (8)
b (Å)	10.3034 (9)
c (Å)	16.6349 (14)
β (°)	101.109 (4)
V (Å ³)	1571.3 (2)
Z	2
D _{calc} g/cm ³	1.450
F(000)	354
μ (mm ⁻¹)	0.83
θ (°)	2.3-27

h, k, l ranges	$-9 \leq h \leq 12, -14 \leq k \leq 14, -23 \leq l \leq 23$
Measured reflections	65719
Independent reflections	8260
Reflections [$I > 2\sigma(I)$]	7596
R_{int}	0.031
$R[I > 2\sigma(I)]$	0.027
wR_2	0.074
Goodness-of-Fit	0.99
$\Delta\rho_{max}, \Delta\rho_{min}$ ($e \text{ \AA}^{-3}$)	0.50, -0.28

3. RESULTS AND DISCUSSIONS

3.1 General study

Reaction of hydrated M(II) nitrate ($M = Co^{2+}, Ni^{2+}, Cu^{2+}$ and Zn^{2+}) and HL in 1:2 ratio in methanol produces mononuclear complexes formulated as $\{[Co(L)_2] \cdot 2H_2O\}$ (1), $\{[Ni(L)_2] \cdot 2H_2O\}$ (2), $\{[Cu(L)_2] \cdot 3H_2O\}$ (3) and $\{[Zn(L)_2] \cdot H_2O\}$ (4) (Scheme 1).

The infrared spectrum of the ligand presents two bands pointed at 3062 cm^{-1} and 3004 cm^{-1} attributed, respectively to ν_{N-H} and to $\nu_{C_{Ar}-H}$ vibrations. The $\nu_{C=O}$ vibration of the carbonyl group is located at 1684 cm^{-1} and the $\nu_{C=N}$ of the imine group is pointed at 1635 cm^{-1} [27]. The $\nu_{C_{Ar}=C_{Ar}}$ bands appear in the range $1541-1422 \text{ cm}^{-1}$. The characteristic band due to pyridine ring is pointed at 1583 cm^{-1} . The band pointed at 1282 cm^{-1} and 1142 cm^{-1} are, respectively, attributed to ν_{C-N} and ν_{N-N} vibrations. The deformation bands of the $C_{Ar}-H$ bonds are located in the range $804-614 \text{ cm}^{-1}$. 1H and carbon ^{13}C NMR spectra are carried out using dmsd- d_6 solutions. 1H NMR spectrum indicates a set of signals in the form of multiplets between 7.39 and 8.20 ppm representing the eight protons of the aromatic rings. In addition, the two appearing as singlets at 8.73 and 9.01 ppm are, respectively, due to the azomethine $H-C=N$ and to the $H-N$ protons. ^{13}C NMR spectrum indicates two characteristic signals at 160.10 and 148.91 ppm due to the carbon atoms of the $C=O$ and $H-C=N$ moieties. Signals due to aromatic carbon atoms appear in the range 151.68–123.76 ppm. The mass spectrum confirms the formation of the HL ligand with the presence of the basic peak at $m/z = 303.12$ corresponding to the molar mass of the molecular ion ($M+1$). In our previous work the crystallographic structure of HL and its antioxidant activity were reported [15].

The infrared spectra of the four complexes 1–4 indicate shift of the $\nu_{C=N}$ indicating the involvement of the azomethine nitrogen atom in the coordination. The absence of the $\nu_{C=O}$ and the ν_{N-H} indicate that iminization undergoes during the reaction. The absence of ionic and coordinating nitrate bands on the spectra of the complexes are indicative of coordination through nitrogen atoms and oxygen atoms from the ligand molecules. On the infrared spectrum of the crystal complex of $[Zn(L)_2] \cdot H_2O$, the $\nu(C=N)$ bands of imine and pyridine are located at 1558 and 1506 cm^{-1} , respectively. However, we note the iminization of the ligand which is confirmed by the disappearance of the $\nu_{C=O}$ band of the carbonyl and the appearance of new bands at 1620 and 1250 cm^{-1} attributable to $\nu(C=N)$ in the hydrazone and $\nu(CO)$ of iminole [28]. In each of the spectra of the complexes the presence of uncoordinated water molecule is attested by the presence of one strong and broad band in the range $3650-3300 \text{ cm}^{-1}$. Conductometric measurements of four complexes are carried out in a millimolar solution of Dimethylformamide (DMF). The values obtained in fresh solution and after two weeks of storage are fall in the range equal to $3-15 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$. These low values are typical of neutral electrolytes [29]. The low of the conductivity values over time show the good stability of these complexes in the DMF solution.

Table 2. UV-visible and Magnetic moments of the complexes.

Compound	UV-visible λ (nm)	μ_{eff} (μ_B)
HL	257, 275, 315, 361	
1	257, 275, 315, 325, 361, 383, 418, 465, 499	3.88
2	257, 275, 315, 361, 419, 444, 499, 869	2.74
3	257, 275, 315, 386, 418, 439, 459, 498, 678	1.82

The electronic spectra of the complexes (Table 2) which are recorded in DMF solution show absorptions in the range 257-275 nm and 315-361 nm regions. These bands are attributed, respectively, to the $\pi \rightarrow \pi^*$ transitions of the aromatic nuclei and $n \rightarrow \pi^*$ transitions of the azomethine moiety of the organic ligand molecules. The bands in the range 418-441 nm are attributed to ligand-metal charge transfers[30]. For the cobalt(II) complex (**1**), the bands pointed at 465 and 499 nm are attributable, respectively, to the transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ and ${}^2E_g \rightarrow {}^2T_{1g}(P)$. In the UV region, a band appears at 383 nm due to the transition ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$. These bands are typical of an octahedral environment around Co(II) cation[31]. For the complex (**1**), the value of the magnetic moment is $5.88 \mu_B$. On the spectrum of the Ni(II) complex (**2**), the bands are located at 444, 499 and 869 nm (table 4). They are attributed to the transitions ${}^1A_{1g} \rightarrow {}^1B_{1g}$, ${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}$ in agreement with an octahedral geometry around nickel(II)[31]. This observation is confirmed by the magnetic moment the value of $2.74 \mu_B$ corresponding to an octahedral Ni(II) cation. The spectrum of the Cu(II) complex (**3**) presents an absorption band at 678 nm (table 4) which is assigned to the transition band ${}^2E_g \rightarrow {}^2T_{2g}$ indicating an octahedral geometry around Cu(II) cation[32]. This observation is confirmed by magnetic value of $1.82 \mu_B$ which indicates the presence of a Cu^{2+} ion in octahedral environment[33]. The spectra of the Zn(II) complex (**4**) show strong absorption bands at 499 nm due to charge transfers Ligand \rightarrow Metal[34].

3.2 Structure description of the complex $C_{36}H_{26}N_8O_2Zn \cdot H_2O$

The mononuclear complex crystallizes in the monoclinic system $P2_1$. Labelled plot of the mononuclear structure of Zn(II) complex is shown in Fig. 1. Selected interatomic distances are listed in Table 3. The structure of the complex is consistent with the $[ZnL_2] \cdot H_2O$ formulation. The asymmetric unit contains one Zn^{2+} , two monoanionic organic ligand, and one water molecule. Each Schiff base molecule is its iminol form acts in tridentate fashion through one azomethine nitrogen atom, one pyridine nitrogen atom and one anionic oxygen atom resulting in two membered chelating rings ZnNCCN and ZnNNCO with bite angles of $N1-Zn1-N2 = 74.23(7)^\circ$, $O1-Zn1-N2 = 75.72(7)^\circ$, $N5-Zn1-N6 = 74.82(7)^\circ$, $O2-Zn1-N6 = 75.41(7)^\circ$. The Zn1 center is octacoordinated and is situated in a severely distorted octahedral environment. The basal plane is occupied by N1, N2, O1 and N6 atoms, the apical positions being occupied by N3 and N8 atoms. The angles in the basal plane $O1-Zn1-N2 = 75.72(7)^\circ$, $N6-Zn1-O1 = 112.98(7)^\circ$, $N1-Zn1-N6 = 97.36(7)^\circ$, $N1-Zn1-N2 = 74.23(7)^\circ$, $O1-Zn1-N1 = 149.66(7)^\circ$, $N6-Zn1-N2 = 168.73(7)^\circ$. The sum of the cisoid angles subtended by the atoms in the basal plane is 360.3° . The value of the angle between the apical atoms is $O2-Zn1-N5 = 150.21(7)^\circ$. All the angles deviate severely from the ideal angle values of 90° and 180° for octahedral geometry. These facts are indicative of a severely distorted octahedral polyhedron around the zinc(II) cation center. The aromatic rings C1/C2/C3/C4/C5/N31 and C7/C8/C9/C10/C11/C12 of one of the ligand molecule are twisted with dihedral angle of $52.55(1)^\circ$. They are respectively twisted toward the third aromatic ring C14/C15/N4/C17/C18/C19 of the ligand molecule with dihedral angle of $21.72(2)^\circ$ and $33.35(2)^\circ$. The five membered rings Zn1O1C13N3N2 and Zn1N2C6C5N1 formed by the ligand, upon coordination to the Zn(II), are not coplanar. Their mean planes form a dihedral angle of $4.04(1)^\circ$. For the second ligand molecule the mean planes of the five membered rings formed upon coordination $[Zn1O2C32N7N6$ and $Zn1N6C25C24N5]$ are quite coplanar with a dihedral angle of $1.86(1)^\circ$. The aromatic rings C20/C21/C22/C23/C24/N5 and C26/C27/C28/C29/C30/C31 of the second ligand molecule are twisted with dihedral angle of $64.792(1)^\circ$. They are respectively twisted toward the third aromatic ring C34/C33/C38/C37/C36/N8 of the ligand molecule with dihedral angle of $10.168(2)^\circ$ and $74.430(1)^\circ$.

The Zn—O bonds are $2.0710(18)$ and $2.1061(17)$ Å and are similar to those found for octahedral Zn(II) complex reported by Kane et al.[35]. The Zn— N_{imine} bond distances (Zn—N2 and Zn—N6) are observed to be $2.1004(17)$ and $2.0812(18)$ Å, respectively. They are shorter than those of the Zn— $N_{pyridine}$ bonds (Zn—N1 = $2.189(2)$ Å and Zn—N1 = $2.226(2)$ Å). These Zn—N bonds are similar to those observed for octahedral mononuclear complexes obtained with a similar ligand (E)-N'-(1-(pyridin-2-yl)ethylidene)nicotinohydrazide[36]. Intramolecular hydrogen bond involving the oxygen atom of the uncoordinated water molecule and nitrogen pyridine atom $[O3-H3A \cdots N8]$ is observed.

In the crystal, unclassical intramolecular C—H...N [C3—H3...N3,C12—H12...N3,C15—H15...N3,C19—H19...N4, C34—H34...N7] and C—H...O [C28—H28...O1, C35—H35...O3] interactions are observed in the crystal (Table 3, Figure 2).

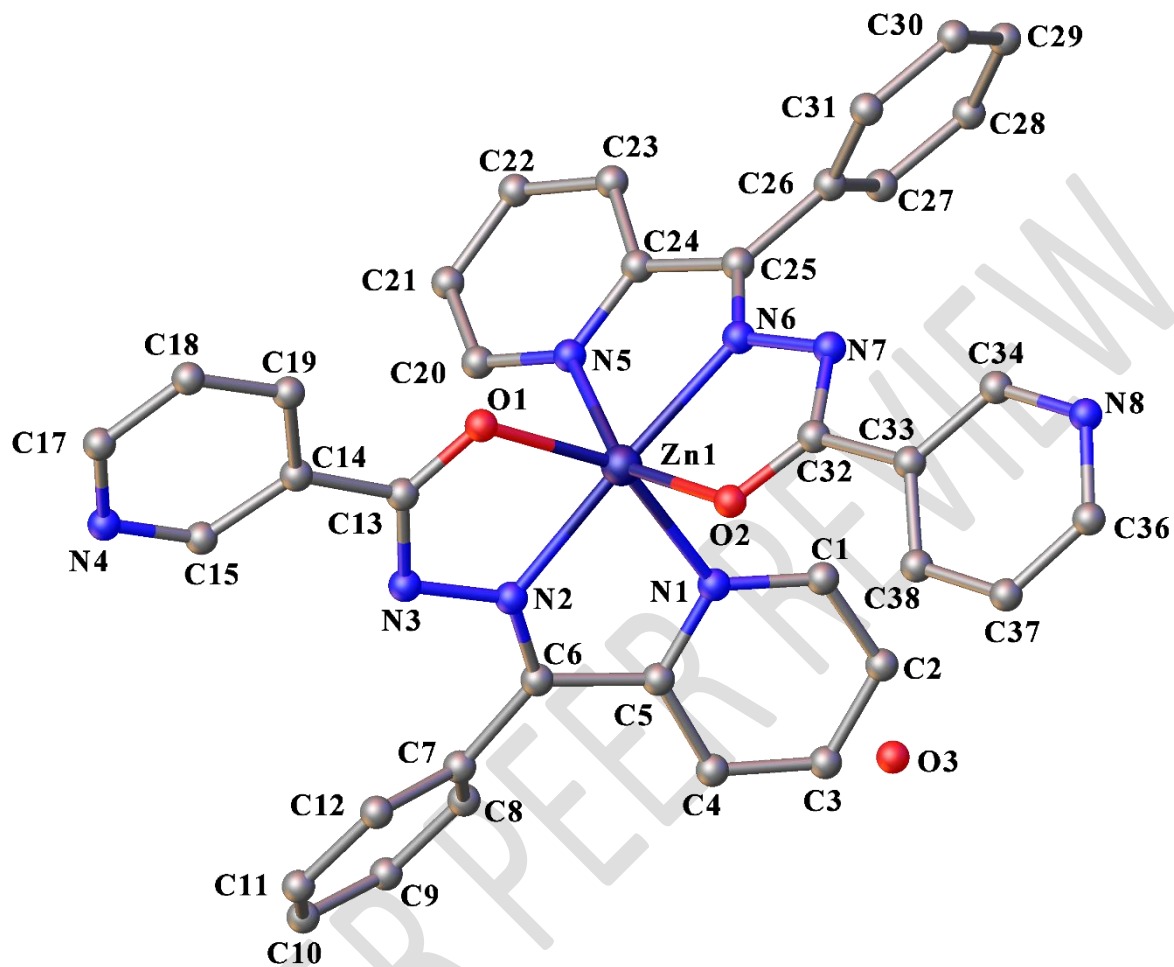


Figure 1. ORTEP plot (30% probability ellipsoids) showing the structure 4. H atoms are omitted for clarity.

Table 3. Selected interatomic bond distances and bond angles around Zn

Zn1—O1	2.0710 (18)
Zn1—N6	2.0812 (18)
Zn1—N2	2.1004 (17)
Zn1—O2	2.1061 (17)
Zn1—N1	2.189 (2)
Zn1—N5	2.227 (2)
O1—Zn1—N5	92.42 (8)
N6—Zn1—N5	74.82 (7)
N2—Zn1—N5	98.26 (7)
O2—Zn1—N5	150.21 (6)
N1—Zn1—N5	95.93 (8)
O1—Zn1—N6	112.98 (7)
O1—Zn1—N2	75.72 (7)
N6—Zn1—N2	168.73 (7)

O1—Zn1—O2	98.24 (7)
N6—Zn1—O2	75.41 (7)
N2—Zn1—O2	111.29 (7)

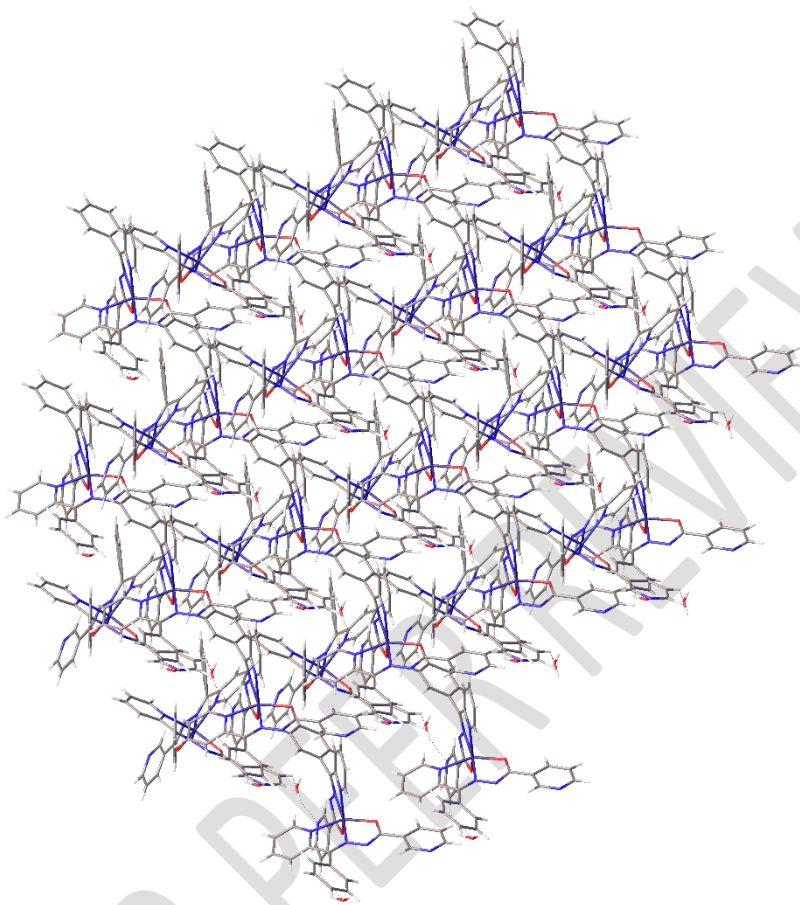


Figure 2. The packing of the compound in the crystal structure

Table 4. Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3A...N8	0.87	2.10	2.917(7)	157
C3—H3...N4	0.95	2.51	3.280(4)	138
C12—H12...N3	0.95	2.51	2.912(3)	105
C15—H15...N3	0.95	2.46	2.796(3)	101
C19—H19...N4	0.95	2.56	3.296(4)	134
C28—H28...O1	0.95	2.45	3.161(3)	132
C34—H34...N7	0.95	2.53	3.476(4)	172
C35—H35...O3	0.95	2.22	2.930(8)	131

4. CONCLUSION

This present paper describes the results of the preparation of coordination complexes of transition metal (II) nitrate salt (Co, Ni, Cu and Zn) with the ligand N'-(phenyl(pyridin-2-yl)methylene)nicotinohydrazide (HL). The ligand is characterized by elemental analyze, mass

spectroscopy, and different spectrophotometric methods such as ^1H and ^{13}C NMR, FT-IR and UV-visible. The structures of the complexes **1-4** are elucidated by element analyze, molar conductivity, room temperature magnetic measurements, FT-IR, and UV-Visible spectroscopies. X-ray crystallographic diffraction technic is used to solve the structure of complex **4**. In all the structures of the compounds, the two ligand molecules act in their iminol forms yielding six-coordinated metal ions complexes. The coordination geometry can be described as a severely distorted octahedral polyhedron.

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SUPPLEMENTARY MATERIALS

CCDC-2304399 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing

data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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