

Synthesis and characterization of Zn(II), Cu(II), Co(II), Ni(II), Cd(II) and Ru(III) ions with a tridentate NNO thiazole derived Schiff base

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Abstract

Thermal reaction of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Ru(III) metal ions with a tridentate Schiff-base ligand(HL) derived from the condensation of 2-aminothiazole and 2-hydroxy-1-naphthaldehyde resulted in the formation of a series of six new metal complexes: $[Co(HL)_2Cl_2]$; **1**, $[Ni(L)(CH_3COO)(H_2O)]$; **2**, $[Cu(L)_2]$; **3**, $[Zn(L)_2]$; **4**, $[Cd(L)(CH_3COO)(H_2O)]H_2O$; **5**, $[Ru(L)_2(H_2O)_2]Cl$; **6**. The ligand and its complexes were characterized by means of elemental and thermal analyses along with molar conductance and magnetic moment measurements as well as different spectroscopic techniques. The ESR spectrum of Cu(II) complex indicated elongated and covalent character of octahedral environment.

Keywords: Spectroscopic studies; Schiff base; Transition metal complexes, Thermal studies.

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1. Introduction

Transition metal-Schiff-base complexes are of great interest in coordination chemistry. Such complexes have synthetic flexibility, sensitivity and selectivity towards a variety of metal ions [1-6]. Accordingly, this type of complexes has been subjected to be widely investigated [7, 8]. The Schiff bases derived from heterocyclic compounds and their metal complexes have been attracted to many researchers in recent years [9, 10]. The strong aromaticity of the ring system of the heterocyclic compounds, thiazoles and their derivatives, leads to interesting biological activity and greater *in vivo* stability [11-13]. Aminothiazoles have a wide spectrum of anti-tumor, anti-oxidant and anti-anoxic activities as well as inhibit lipid peroxidation and as intermediates in the synthesis of antibiotics [14-16]

In the area of bioinorganic chemistry, an unprecedented interest in Schiff base complexes lies in that they provide synthetic models for the metal containing sites in metalloproteins/enzymes because of their key role in clinical therapy, radio immunotherapy, cancer diagnosis and treatment of tumor [17]. Interest in the binding of metal complexes to nucleic acid has been motivated not only by a desire to understand the basics of these interaction modes, but also by the development of metal complexes into anti-inflammatory and anticancer agents. Hence, much attention has been targeted in the design of metal-based complexes, which can bind to DNA [18-20]. Recently, the interaction of cationic metal complexes containing multidentate aromatic ligands, as a new agent studying anticancer characteristics with DNA has gained a growing importance [21-26].

In recent years, the bioactive novel Schiff base ligands containing N,O,S donor sites with transition metal complexes have considerable attention in analytical applications [27, 28] and in the treatment of cancer cells in chemotherapeutic field [29-31]. Hence, in view of their significant usage, we have synthesized Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Ru(III) complexes with a tridentate Schiff-base ligand (HL) derived from the condensation of 2-aminothiazole and 2-hydroxy-1-naphthaldehyde. The synthesized compounds were characterized by various spectroscopic techniques, mass, elemental analysis. The DNA binding and DNA cleavage as well as antibacterial and antifungal activities were also studied.

2. Experimental

2.1. Materials and Reagents

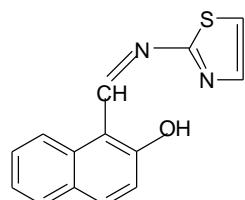
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and RuCl_3 were purchased from Fluka. The two reagents 2-aminothiazole and 2-hydroxy-1-naphthaldehyde were supplied by Aldrich. All solvents were of analytical grade and were purified by distillation before use.

2.2. Instruments

Infrared measurements using (KBr pellets) were carried out on a Unicam-Mattson 1000 FT-IR spectrometer and magnetic measurements of the complexes in the solid state (Gouy method) were recorded on a Sherwood magnetic susceptibility balance. ^1H NMR measurements were performed on a Varian-Mercury 300MHz spectrometer. Elemental analyses of carbon, hydrogen, nitrogen and sulphur (CHNS) were performed using JEOL JMS-AX500 elemental analyzer, mass spectrometry measurement of the solid complex was carried out on a JEOL JMS-AX 500 spectrometer. Thermogravimetric analyses (TG and DTG) were carried out under N_2 atmosphere with a heating rate of 10 °C/min. using a Shimadzu DT-50 thermal analyzer. All conductivity measurements were performed in DMSO (1×10^{-3} M) at 25°C, by using Jenway 4010 conductivity meter. Fluorescence measurements of all compounds were performed using a Jenway 6270 Fluorimeter. ESR spectra were recorded at Elexsys, E500, Bruker company.

2.3 Synthesis of the Schiff base ligand (HL)

A mixture of 30 mL ethanolic solution of 2-aminothiazole(1.0g, 10 mmol) and 2-hydroxy-1-naphthaldehyde (1.7g, 10 mmol) was refluxed for 3 hours. The reaction mixture attained a yellow color. The resulting solution was left to cool at room temperature overnight and concentrated by evaporation. The isolated solid yellow product was filtered off and washed several times with ethanol. The product was recrystallized from hot ethanol to give a pure compound with melting point 171°C (yield 86%). The purity of the produced Schiff base ligand was checked by TLC. The proposed molecular structure of the Schiff base ligand N-(2-hydroxy-1-naphthylidene)-2-aminothiazole (HL) is shown in **Scheme 1**.



Scheme 1. Structure of N-(2-hydroxy-1-naphthylidene)-2-aminothiazole (HL) ligand.**2.4. Synthesis of metal complexes**

The synthesis of the reported metal complexes was employed according to the general procedure [24]. An aqueous solution of the metal salt (1mmol, 10 mL) was added dropwise to an ethanolic solution of HL ligand (1mmol, 0.254 g, 25 ml) at room temperature with constant stirring for 10 minutes. The mixture solution was left to cool at room temperature. The solid complex was isolated by filtration, then washed several times with hot 3:1 ethanol-water mixture followed by ether then kept in a desiccator. **Table 1** gives the color, % yield and molar conductance of the isolated compounds.

Table 1. Physical properties of HL and its metal complexes.

Compound	Color	Yield %	Λ_m $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$
HL	Yellow	86	--
Co(II) Complex (1)	Pale brown	67	18.3
Ni(II) Complex (2)	Brown	70	7.0
Cu(II) Complex (3)	Dark brown	78	5.2
Zn(II) Complex (4)	Lemon	77	7.3
Cd(II) Complex (5)	Black	75	6.2
Ru(III) Complex (6)	Black	50	85

3. Results and discussion**3.1. Schiff base ligand characterization**

The elemental analysis data of the Schiff base ligand (HL) are represented in **Table 2**. The C, H, N, S data are in good agreement with the proposed structural formula $\text{C}_{14}\text{H}_{10}\text{N}_2\text{OS}$ of HL ligand, with molecular mass 254.306. The mass spectrum of the ligand (**Figure 1**) displayed a parent peak at $m/z = 255$ (P^+), with a relative intensity 12% confirming its structural formula.

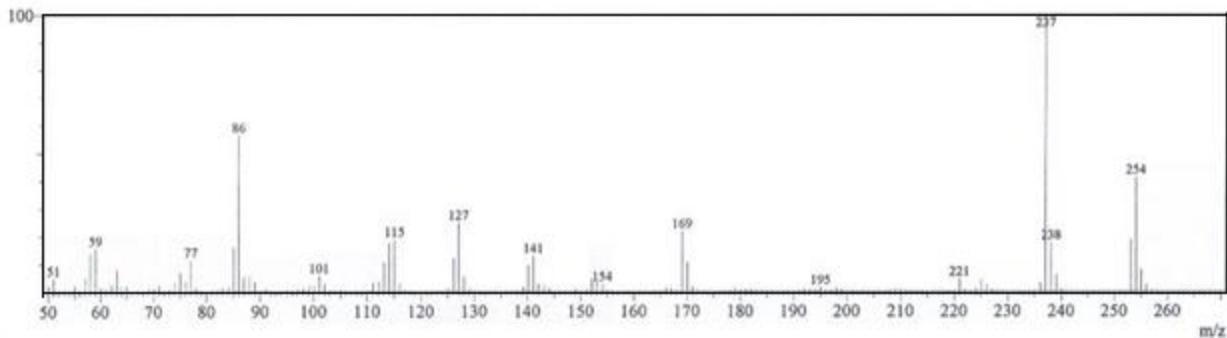
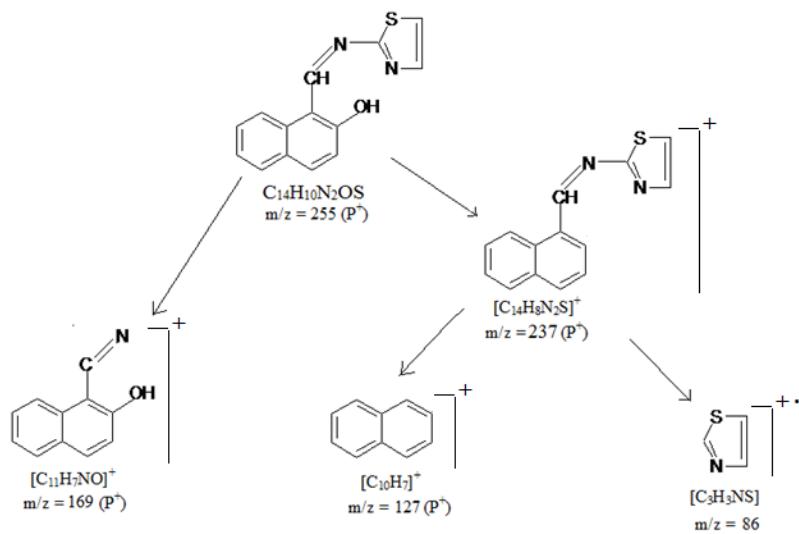


Fig. 1. The mass spectrum of the ligand HL.

The mass spectrum of the ligand showed a series of peaks at 237 u (98%), 169u (25%), 127 u (23%) and 86 u (55%) may be assigned to $[C_{14}H_8N_2S]^+$, $[C_{11}H_7NO]^+$, $[C_{10}H_7]^+$ and $[C_3H_3NS]$ fragments, respectively. The fragmentation peaks and their intensities give an idea about the stability of fragments. The fragmentation patterns of the ligand are shown in **Scheme 2**. The infrared spectrum (KBr pellets) of the solid ligand (**Figure 2 & Table 3**) showed a band at 3430 cm^{-1} referred to the stretching vibration frequency of the OH group. Furthermore, the IR spectrum of the ligand displayed two strong bands at 1619 and 1595 cm^{-1} due to $\nu(C=N)$ of thiazole ring and azomethine moiety, respectively [13, 24]. In addition, the spectrum exhibited a strong band at 1553 cm^{-1} and a medium band at 1221 cm^{-1} referred to the stretching vibration frequencies of C=C and C-O bonds, respectively. The 1H NMR spectrum of the free ligand HL in DMSO is shown in **Figure 3** and its data listed in **Table 4**. The free ligand displayed single signals at 13.82 and 9.95 ppm referred to OH and azomethine protons, respectively [32]. The multiple signals exhibited in the range 7.21-8.62 ppm were assigned to the aromatic and thiazole hydrogens.



Scheme 2. Fragmentation of the mass spectrum of the HL ligand.

Table 2. The elemental analysis data of the Schiff base ligand (HL)

Compound	%C				%H		%N		%S		Mass spectrometry	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Mol.Wt	m/z
HL	66.1	67.0	3.9	3.5	11.0	11.1	12.6	12.3	254.306	255		
Co(II) Complex (1)	52.7	52.7	3.1	2.8	8.8	8.2	10.0	9.7	638.451	639		
Ni(II) Complex (2)	49.4	49.8	3.6	3.3	7.2	7.3	8.2	7.8	389.058	389($p^+ - H$)		
Cu(II) Complex (3)	59.0	58.8	3.2	2.9	9.8	9.5	11.3	10.9	570.146	571		
Zn(II) Complex (4)	58.8	58.4	3.2	3.3	9.8	9.6	11.2	10.8	571.986	572		
Cd(II) Complex (5)	41.7	42.1	3.5	3.5	6.1	6.5	7.0	6.9	460.783	461		
Ru(III) Complex (6)	52.1	52.8	3.1	3.3	9.0	8.7	9.9	9.4	674.019	639($p^+ - Cl$)		

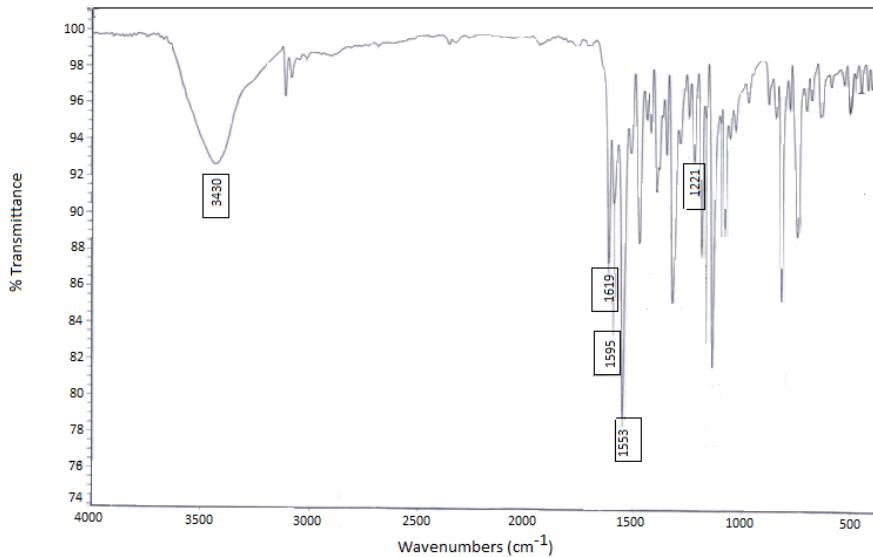


Figure 2. IR spectrum of the ligand HL.

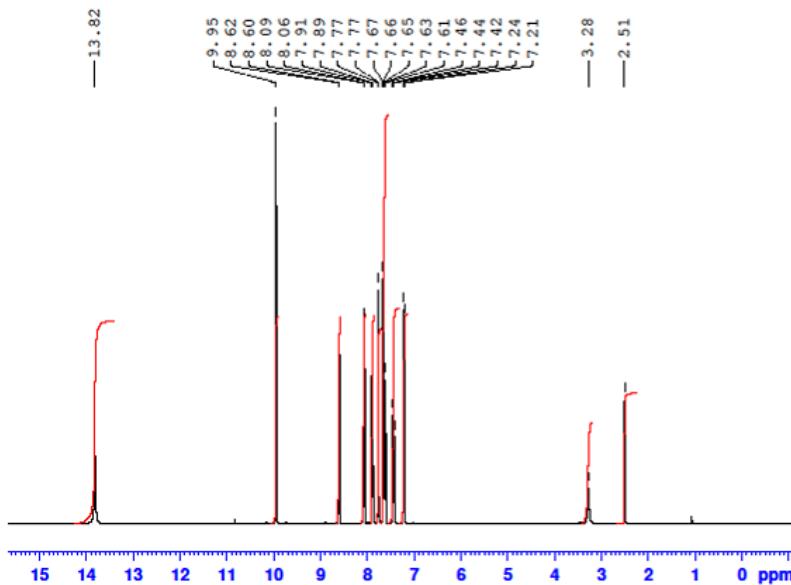


Figure 3. The ^1H NMR spectrum of the Schiff base ligand HL.

3.2. Complexes characterization

The reaction of the Schiff base ligand (**HL**) with the metal ions Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Ru(III) in EtOH produced six complexes (**1-6**). All prepared solid compounds are colored, air stable and are characterized by high melting points. The complexes are readily soluble in DMSO, but insoluble in other solvents such as ethanol, methanol, benzene, diethyl

ether and acetone. **Table 2** includes the elemental analysis and the mass spectrometry data. All data are in good agreement with the corresponding molecular formulas of the studied complexes, $\text{Co}[\text{C}_{28}\text{H}_{20}\text{N}_4\text{O}_2\text{S}_2\text{Cl}_2]$; **1**, $\text{Ni}[\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{S}]$; **2**, $\text{Cu}[\text{C}_{28}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2]$; **3**, $\text{Zn}[\text{C}_{28}\text{H}_{18}\text{N}_4\text{O}_2\text{S}_2]$; **4**, $\text{Cd}[\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_5\text{S}]$; **5** and $\text{Ru}[\text{C}_{28}\text{H}_{22}\text{N}_4\text{O}_4\text{S}_2\text{Cl}]$; **6**. The molar conductance of the complexes is measured for 10^{-3}M DMSO solution. The conductance data suggested non-electrolyte character for all complexes except ruthenium complex gave a Λ_m value of $85 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (**Table 1**) indicating 1:1 electrolyte with chloride ion [33, 34].

3.2.1. Mass spectra analysis

Mass spectrometry method is considered as a powerful structural characterization technique in coordination chemistry. It has been successfully used to confirm the molecular ion peaks of compounds. The mass spectra of the reported complexes (**1-6**) showed molecular ion peaks at m/z 639 (p^+), 389 ($\text{p}^+ \text{-H}$), 571 (p^+), 572 (p^+), 461 (p^+) and 639 ($\text{p}^+ \text{-Cl}$), respectively. These ion peaks are in good agreement with the molecular weight of the proposed molecular formulas of the studied complexes.

3.2.2. IR spectra

To determine the chelating sites coordinated to metals, a comparison between the IR spectra of the complexes and the free ligand must be concerned. The characteristic vibration bands of HL ligand show the proper shifts on complexation indicating the complex formation (**Table 3**). The IR spectra of the complexes **1**, **2**, **5** and **6** displayed broad stretching frequencies in the range $3188\text{-}3431 \text{ cm}^{-1}$ indicating the presence of OH and/or H_2O species in these complexes. On the other hand, the IR spectra of the two complexes **3** and **4** show no OH stretching bands indicating the absence of OH and H_2O species in these complexes. Furthermore, the IR spectrum of complex **1** exhibited a stretching band at 3431cm^{-1} , assigned to the presence of a free OH group in the complex without coordination to Co(II) while the IR spectra of the complexes **2-6** showed the disappearance of such OH stretching vibration of the ligand indicating the coordination of it to the metals oxidatively. Moreover, the broad IR stretching bands appeared at 3399, 3303 and 3333 cm^{-1} in the three complexes **2**, **5** and **6**, respectively, are assigned to the coordination of water molecules associated with the complexes. On the other hand, the stretching band appeared at 3188 cm^{-1} in complex **5** may be attributed to inter and/or intra hydrogen bonding of the uncoordinated water molecule. In addition, the IR spectra of the complexes (**1-5**) exhibited

$\nu(C=N)_{\text{thiazole}}$, $\nu(C=N)_{\text{azomethine}}$ and $\nu(C-O)$ bands in the ranges 1614 - 1646 cm^{-1} , 1585 - 1603 cm^{-1} and 1211 - 1228 cm^{-1} , respectively, with the proper shifts with respect to the corresponding values in the ligand [35, 36]. These results indicated the coordination of nitrogen of the thiazole ring, azomethine nitrogen and hydroxyl oxygen of the ligand to the metal ions; Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) [37]. This is ascertained by the appearance of non-ligand stretching frequency bands in the ranges 531 - 571 cm^{-1} and 451 - 510 cm^{-1} corresponding to M-O and M-N bonds, respectively (**Table 3**) [38, 39]. Moreover, the IR spectrum of ruthenium complex (**6**) exhibited strong stretching frequencies at 1620 cm^{-1} due to $\nu(C=N)$ of thiazole ring and at 1600 cm^{-1} corresponding to $\nu(CH=N)$ [40]. The stretching frequency of C=N moiety in thiazole ring (1620 cm^{-1}) showed no shift with respect to the corresponding value in the ligand (1619 cm^{-1}) indicating that thiazole nitrogen atom does not coordinate to ruthenium. Furthermore, the shifts observed in the stretching frequencies $\nu(CH=N)$ and $\nu(C-O)$ at 1600 and 1210 cm^{-1} , respectively, indicated the coordination of the azomethine nitrogen and hydroxyl oxygen of the ligand to Ru(III) (**Table 3**) [37]. Further, the IR spectra of the nickel and cadmium complexes (**2**, **5**) displayed asymmetric ($\nu_{\text{asym}}COO^-$) and symmetric ($\nu_{\text{sym}}COO^-$) stretching vibrations of the acetate groups (**Table 3**). Nickel complex displayed ($\nu_{\text{sym}}COO^-$) and $\nu_{\text{asym}}COO^-$ at 1539 and 1381 cm^{-1} , respectively, with a frequency difference $\Delta\nu$ of 158 cm^{-1} . On the other hand, cadmium complex exhibited asymmetric and symmetric stretching vibrations at 1555 and 1395 cm^{-1} , respectively, referred to the acetate group with frequency difference $\Delta\nu = 160\text{ cm}^{-1}$. These frequency difference values, 158 cm^{-1} and 160 cm^{-1} , indicated the coordination of the acetate ion to Ni(II) and Cd(II) as a bidentate chelate bonding via the two carboxylate oxygens [41-43].

3.2.3. 1H NMR spectra

The 1H NMR data of HL and the two diamagnetic zinc and cadmium complexes (**4**, **5**) are listed in **Table 4**. The 1H NMR spectra of the two complexes showed the disappearance of OH singlet of the ligand (13.82 ppm) on complexation confirming the coordination of the metal ion to ligand via the oxygen of the hydroxyl group with deprotonation. The azomethine proton of the complexes **4** and **5** showed singlets at 8.63 and 8.47 ppm with up field shift with respect to that of the ligand (9.95 ppm) confirming the coordination of azomethine nitrogen to the metals [44, 45]. The 1H NMR spectra of the two complexes exhibited signals corresponded to phenyl and thiazole moieties with the proper shifts (**Table 4**). In addition, the 1H NMR spectrum of complex

5 displayed singlets at 4.21 and 3.26 ppm corresponded to H₂O protons and a singlet at 1.89 ppm due to CH₃ protons of acetate ion [44].

Table 3. The IR data of the ligand HL and its complexes

Compound	IR						
	v(OH) and /or v(H ₂ O)	v(C=N) thiazole	v(CH=N) azomethine	v(C=C)	v(C-O)	v(M-O)	v(M-N)
HL	3430 (s)	1619(s)	1595(s)	1553(s)	1221(m)	---	---
[Co(HL) ₂ Cl ₂] Complex (1)	3431(s)	1642(s)	1589(s)	1539(s)	1220(m)	—	494(w) 456(w)
^b [Ni(L)(Ac)(H ₂ O)] Complex (2)	3399(b)	1615(s)	1603(s)	1575(s)	1214(m)	561(w)	496(w) 451(w)
Cu(L) ₂ Complex (3)	—	1614(s)	1602(s)	1536(s)	1211(m)	570(w)	507(w) 462(w)
Zn(L) ₂ Complex (4)	--	1646(s)	1590(s)	1539(s)	1219(m)	551(w)	510(w) 453(w)
^c [Cd(L)(Ac)(H ₂ O)] H ₂ O Complex (5)	3303(b,s) 3188(b,s)	1632(s)	1585(s)	1555(b,s) confused	1228(m)	571(w)	506(w) 456(w)
[Ru(L) ₂ (H ₂ O) ₂]Cl Complex (6)	3333(b,s)	1620(s)	1600(s)	1568(s)	1210(m)	531(w)	499(w)

^a s, strong; m, medium; w, weak; b, broad.

^b v_{sym}COO⁻ = 1539 cm⁻¹, v_{asym}COO⁻ = 1381 cm⁻¹, Δ(v_{asym} - v_{sym}) = 158 cm⁻¹ [bidentate COO⁻].

^c v_{sym}COO⁻ = 1555 cm⁻¹, v_{asym}COO⁻ = 1395 cm⁻¹, Δ(v_{asym} - v_{sym}) = 160 cm⁻¹ [bidentate COO⁻].

Table 4. Important ¹H NMR data of HL and its diamagnetic metal complexes.

Compound	¹ H NMR data (ppm)
HL	13.82 (s, 1H, OH), 9.95 (s, 1H, CH=N), 7.21-8.62 (m, 6H, ArH, 2 thiazole H).
Zn(L) ₂ Complex (4)	8.36 (s, 1H, CH=N), 6.80-7.80 (m, 20H, ArH, 4 thiazole H).
^c [Cd(L)(Ac)(H ₂ O)]H ₂ O Complex (5)	8.47 (s, 1H, CH=N), 8.01-6.55 (m, 6H, ArH, 2 thiazole H), 4.21 (s,b, 1H, H ₂ O), 3.26 (s, 1H, H ₂ O), 1.89 (s, 3H, CH ₃ COO).

s; singlet, m; multiplet, b; broad

3.3. Thermal analysis

In order to give more insight into the structure of the complexes, the thermal studies of metal complexes were carried out using the thermogravimetric technique (TG) and differential thermogravimetric (DTG) [46]. Thermal analyses (TG and DTG) have been used as a fundamental to verify the status of water molecules in complexes with respect to the inner coordination sphere of the metal ion as well as to provide information about the thermal stability of the complexes. The complexes were submitted to a TG analysis at ambient temperature up to 1000 °C under nitrogen atmospherewith heating rate 10 °C/min. The detailed thermal decomposition data of the reported complexes are given in Table 5. The mass losses obtained from TG curves are in a good agreement with the calculated values and consistent with the proposed structures of reported complexes (**1-6**).

The thermogram of the Co(II) complex showed three decomposition steps within the temperature range 110–897 °C. The first step of decomposition within the temperature range 110-191°C corresponded to the loss of a chlorine molecule, with a mass lossof 11.14% (Calc. 11.11%). The second step of decomposition (308-489 °C) has been assigned to the elimination of C₂₀H₁₂ON₃S₂. The third step of decomposition within the temperature range 490-897°C corresponded to the loss of 18.33% (Calc. 18.51%) and assigned to the elimination of C₈H₈N to give finally CoO as a residue.

The TGA curves of Ni(II) complex exhibited well defined three decomposition steps within the temperature range 120–1000 °C. The first step of decomposition extends from 120 °C to 178 °C referred to the loss of a water molecule with a mass loss of 4.62% (Calc. 4.63%). This temperature range indicates the coordination of a water molecule to Ni(II). The second step 179-485 °C corresponds to the loss of C₁₃H₉ON₂S with a net weight loss of 61.76% (Calc. 61.94%). The third decomposition step within the temperature range 486-1000 °C gives a mass loss of 14.41% corresponded to the loss of C₃H₃O leaving NiO as residue.

The TG plot of Cu(II) complex exhibited three decomposition steps through the temperature range 154-1000 °C. The three decomposition steps are in the ranges 154-267 °C , 268-417 °C and 418-1000 °C. These steps exhibited mass losses of 29.12, 34.45 and 22.59% corresponded to the loss of C₉H₉OS, C₁₁H₄N₂S and C₈H₅N₂ species, respectively, leaving CuO as residue.

The TG plot of Zn(II) complex offered decomposition pattern with well defined three decomposition steps. The first decomposition step is consistent with the loss of C₂H₄N species, while the second and third steps involved the removal of C₁₀H₆ON₃ and C₁₆H₁₀S₂ moieties, respectively, leaving ZnO as residue.

The thermogram of the Cd(II) complex exhibited three decomposition steps within the temperature range 45–1000 °C. The first step of decomposition (45-155 °C) referred to the loss of two water molecules with a mass loss of 7.82% (Calc. 7.82%). Generally, the temperature range 45-100 °C can be corresponded to uncoordinated water molecule while the coordinated water molecule may be eliminated in the temperature range 100-160 °C. Accordingly, it could be suggested that Cd(II) complex includes two water molecules, one of them is coordinated to Cd(II) and the other is uncoordinated one. The second step of decomposition (161-805°C) has been assigned to the elimination of C₉H₅+2NO+S while the third step (806-1000 °C) referred to the removal of C₆H₇ leaving CdO + C (30.88%) as a residue.

The three decomposition steps of Ru(III) complex are exhibited within the temperature range 120–870 °C. The first decomposition step (120 °C - 260 °C) corresponded to the loss of two water molecules with a mass loss of 5.32% (Calc. 5.35%). Within this temperature range coordinated water molecules can be eliminated, indicating the coordination of two water molecules to Ru(III) in the complex. The second decomposition step 261-375°C corresponded to the loss of C₁₆H₁₂S with a net weight loss of 34.99 % (Calc. 35.05 %). The third decomposition step within the temperature range 376-870°C exhibited mass loss of 40.71 %(Calc. 40.61 %) compatible with the loss of C₁₂H₆N₄SCl leaving RuO₂ as a residue.

3.4. Magnetic measurements

The magnetic moment of the reported complexes was measured and proved paramagnetic properties for cobalt, nickel, copper and ruthenium complexes. These complexes gave no ¹H NMR spectra. Magnetic susceptibility measurements of the four complexes at 298 K gave values corresponded to effective magnetic moment (μ_{eff}) values of 4.25 (calc.; 3.87) BM, 3.17 (calc.; 2.84) BM, 1.80 BM and 1.91 (calc.; 1.75) BM, respectively [47-49]. These magnetic moment values correspond to three unpaired electrons in cobalt complex, two unpaired electrons in nickel complex and one unpaired electron in copper and ruthenium complexes. The higher value of the measured effective magnetic moment, μ_{eff} , than the spin-only value may be due to additional

partial orbital contribution. The μ_{eff} value of the cobalt and nickel complexes indicated a high spin Co(II) d^7 and a high spin Ni(II) d^8 electronic configuration while copper and ruthenium complexes suggested a high spin Cu(II) d^9 and low-spin Ru(III), d^5 electronic configuration. These electronic configurations are in accordance with +2 formal oxidation state of cobalt, nickel and copper in their complexes and +3 formal oxidation state for ruthenium in its complex.

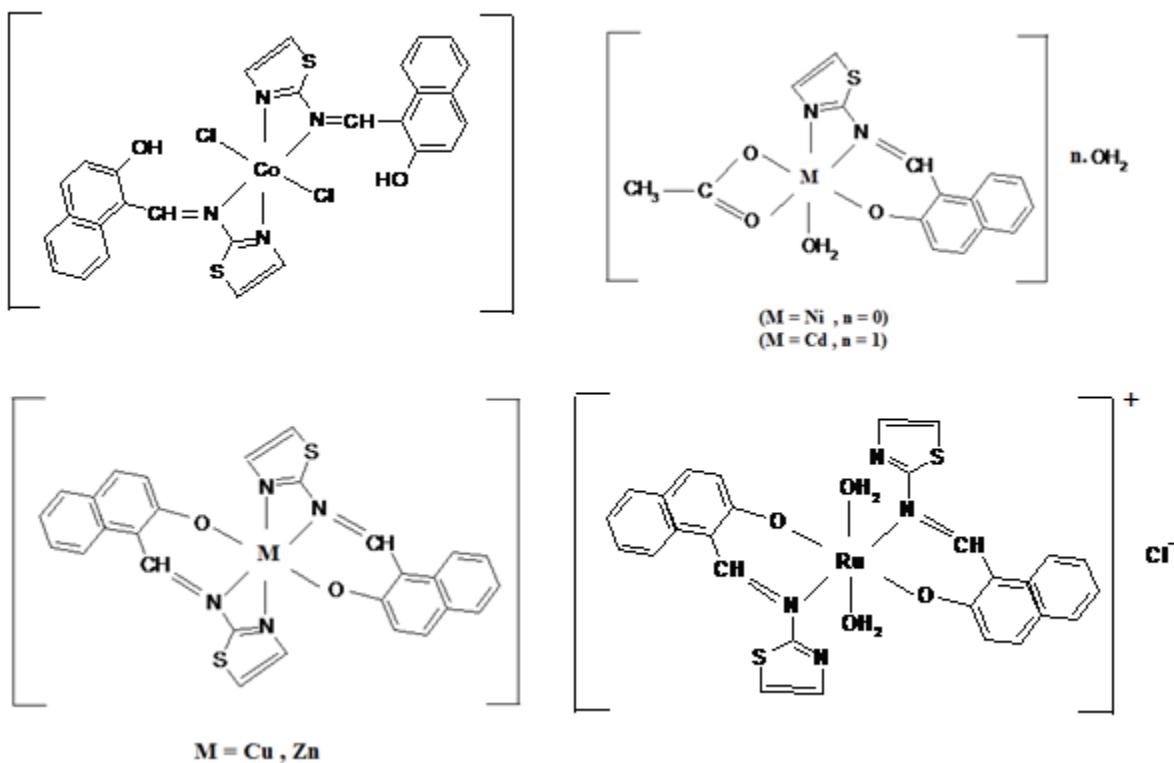
Table 5. Thermal analytical data for HL and its metal complexes.

Molecular formulas of complexes	Molecular weight	Decomposition temperature °C	% Mass Loss	Mass loss Found (Calc.) g/mol	Eliminated species	% Residual Found (Calc.)
Complex (1) Co[C ₂₈ H ₂₀ N ₄ O ₂ S ₂ Cl ₂]	638.451	110-191	11.14	71.10 (70.90)	Cl ₂	12.04 (11.11)
		308- 489	58.49	373.45 (374.32)	C ₂₀ H ₁₂ ON ₃ S ₂	CoO
		490-897	18.33	117.07 (118.15)	C ₈ H ₈ N	
Complex (2) Ni[C ₁₆ H ₁₂ N ₂ O ₄ S]	389.058	120-178	4.62	18.00 (18.02)	H ₂ O	19.10 (19.2)
		179-485	61.76	240.30 (241.00)	C ₁₃ H ₉ ON ₂ S	NiO
		486-1000	14.41	56.1 (55.06)	C ₃ H ₃ O	
Complex (3) Cu[C ₂₈ H ₁₈ N ₄ O ₂ S ₂]	570.146	154-267	29.12	166.03(165.17)	C ₉ H ₉ OS	13.81 (13.95)
		268-417	34.45	196.42(196.15)	C ₁₁ H ₄ N ₂ S	CuO
		418-1000	22.59	128.80(129.13)	C ₈ H ₅ N ₂	
Complex (4) Zn[C ₂₈ H ₁₈ N ₄ O ₂ S ₂]	574.002	125-200	7.46	42.84 (42.05)	C ₂ H ₄ N	14.18 (13.43)
		201-398	32.09	184.19 (184.16)	C ₁₀ H ₆ ON ₃	ZnO
		400-1000	46.27	265.58 (266.26)	C ₁₆ H ₁₀ S ₂	
Complex (5) Cd[C ₁₆ H ₁₆ N ₂ O ₅ S]	460.783	45-160	7.82	36.00 (36.03)	2H ₂ O	30.88 (30.47)
		161-805	44.47	204.90 (205.14)	C ₉ H ₅ +2NO+S	CdO + C
		806-1000	16.83	77.53 (79.12)	C ₆ H ₇	
Complex (6) Ru[C ₂₈ H ₂₂ N ₄ O ₄ S ₂ Cl]	674.019	120-260	5.32	35.86 (36.03)	2H ₂ O	18.98 (19.73)
		261-375	34.99	235.84 (236.27)	C ₁₆ H ₁₂ S	RuO ₂
		376-870	40.71	274.39 (273.68)	C ₁₂ H ₆ N ₄ SCl	

According to the present spectroscopic study (IR, ¹H NMR, mass) together with the analytical (elemental analysis, conductivity measurements) and thermodynamic data, the structure of the reported complexes were proposed as shown in **Scheme 3** [34, 50, 51].

3.5. ESR studies

The X-band ESR spectrum of copper complex was recorded in DMSO at room temperature (**Figure 4**). The ESR spectrum exhibited anisotropic signals in the high field region due to the tumbling motion of the molecules with $g_{||} = 2.213$ and $g_{\perp} = 2.024$. The observed trend of $g_{||} > g_{\perp} > g_e$ (2.0023) is characteristic for a d^9 system with an axial symmetry type of $d_{x^2-y^2}$ ground state [52]. In addition, exchange coupling interaction between two copper(II) ions explained by Hathaway expression $G = (g_{||} - 2)/(g_{\perp} - 2)$. If $G > 4.0$, the exchange interaction is



Scheme 3. The structure of the reported complexes

negligible, which is typically the investigated Cu (II) complex ($G= 8.875$) [53]. The most sensitive of these functions appears to be g_{\parallel} ; consequently, it will be chosen as the best

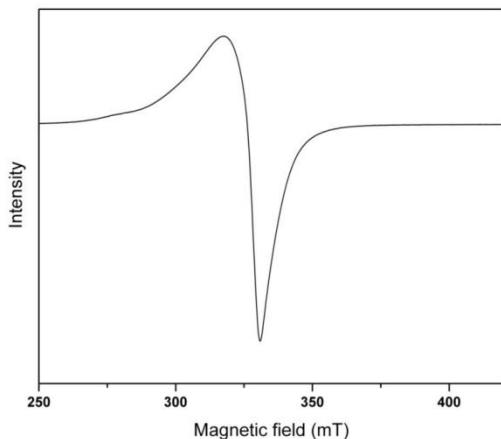


Figure 4. ESR spectrum of Cu complex at room temperature.

indication of "covalent" character. Kivelson and Neiman noted that for an ionic environment, g_{\parallel} is normally 2.3 or larger, but for covalent environment, the goal is less than 2.3, consequently the environment around the investigated copper complex is essentially covalent [54].

4. Conclusions

The tridentate Schiff-base ligand (HL) derived from the condensation of 2-aminothiazole and 2-hydroxy-1-naphthaldehyde and as well as its six transition metal complexes (**1-6**) have been synthesized. They have been characterized based on the analytical, spectral and magnetic measurements. The results of these investigations support the suggested structure of the metal complexes.

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ملخص البحث باللغة العربية

عنوان البحث:

تحضير وتوصيف متراکبات مخلبية من Zn(II), Cu(II), Co(II), Ni(II), Cd(II), Ru(III) مع قاعدة شيف ثلاثية السن مشتقة من ثيازول NNO

الملخص العربي:

نتج عن التفاعل الحراري لأيونات المعادن Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Ru(III) مع قاعدة شيف ثلاثية السن (HL) ، المستمدة من تكتيف 2 -امينوثيازول و 2-هيدروكسي-1-نفالديهيد ، تشكيل سلسلة من ستة متراکبات معدنية جديدة هي:



تم توصيف الصيغة البنائية للمانح (HL) ومتراکباته بإجراء التحليل العنصري والحراري لها مع قياسات التوصيل الكهربائي المولاري وقياسات العزم المغناطيسي فضلا عن تقنيات طيفية مختلفة مثل طيف الرنين المغزلي الإلكتروني ESR.