Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Spectrochimica Acta Part A 67 (2007) 25–38
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Mononuclear metal complexes of organic carboxylic acid derivatives: Synthesis, spectroscopic characterization, thermal investigation and antimicrobial activity

Zeinab H. Abd El-Wahab

Chemistry Department, Faculty of Science (Girl's), Al-Azhar University, Nasr City, P.O. Box 11754, Cairo, Egypt

Received 17 April 2006; accepted 5 May 2006

Abstract

Two Schiff base ligands bearing organic acid moiety, vis., *N*-(2-thienylmethylidene)-2-amino-4-chlorobenzoic acid (HL^1) and *N*-(2-hydroxybenzylidene)-2-amino-4-chlorobenzoic acid (H_2L^2) have been synthesized by the interaction of 2-thiophenecarboxaldehyde and 2-hydroxybenzaldehyde with 2-amino-4-chlorobenzoic acid. Co(II), Ni(II), Cu(II) and Zn(II) complexes of these ligands have been prepared. They are characterized on the basis of analytical data, molar conductance, IR, ^{1}H NMR, UV–vis, mass spectra, magnetic measurements, thermal analysis and X-ray powder diffraction technique. The molar conductance data reveal that these complexes are non-electrolytes. The ligands are coordinated to the metal ions in a terdentate manner with ONO/ONS donor sites of the carbonyl oxygen, azomethine nitrogen and phenolic oxygen or thiophenic sulphur. An octahedral structure is proposed for the prepared metal complexes and some ligand field parameters (D_q, B and β) in addition to CFSE were calculated. The thermal stability of the metal complexes is evaluated. The Schiff base ligands and their metal complexes have been tested against four species of bacteria as well as four species of fungi and the results have been compared with some known antibiotics.

Keywords: Schiff base ligands; Metal chelates; Spectral characterization; Thermal analysis; XRD and antimicrobial activity

1. Introduction

Schiff bases are compounds containing the azomethine group (RC=N–) and are usually formed by the condensation of a primary amine with an active carbonyl compound [1,2]. Schiff bases have been used extensively as ligands in the field of coordination chemistry, some of the reasons are that the intramolecular hydrogen bonds between the (O) and the (N) atoms which play an important role in the formation of metal complexes and that Schiff base compounds show photochromism and thermochromism in the solid state by proton transfer from the hydroxyl (O) to the imine (N) atoms [3]. A large number of Schiff bases and their complexes have been investigated for their interesting and important properties, such as their ability to reversibly bind oxygen, catalytic activity in the hydrogenation of olefins, photochromic properties and complexing ability towards some toxic metals, furthermore complexes of Schiff bases showed promising applications in biological activity and biological modeling applications [4–8].

As an extension of our work on the structural characterization of Schiff base ligands and their metal complexes [9–15], the main target of the present article is to study the coordination behavior of the two ligands, HL^1 and H_2L^2 that incorporate several binding sites towards Co(II), Ni(II), Cu(II) and Zn(II) ions, also to evaluate the relative thermal stability of the synthesized complexes and to examine their antimicrobial activity against different species of bacteria and fungi.

2. Experimental

2.1. Reagents and instruments

All chemicals used were of highest available purity. They include 2-thiophenecarboxaldehyde, 2-hydroxybenzaldehyde and 2-amino-4-chlorobenzoic acid (BDH). The metal chloride salts, namely, cobalt and nickel chloride hexahydrates (Sigma), cupric chloride dihydrate (Merck) and zinc chloride (Adwic) products. Organic solvents used included absolute ethyl alcohol, diethylether, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) were purchased from Merck or Sigma. Concentrated

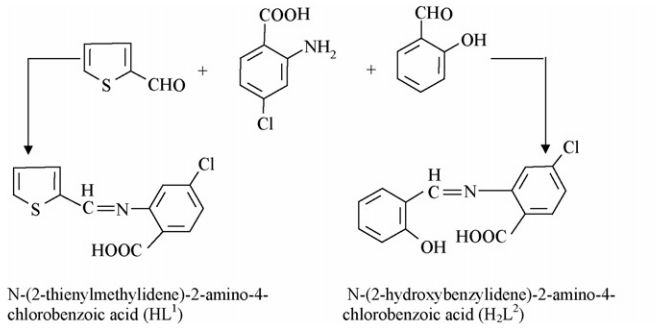
---

E-mail address: zhabdelwahab@yahoo.com.

1386-1425/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2006.05.038

nitric and perchloric acid were reagent grade and were used as supplied.

The elemental analysis was made using Perkin-Elmer 2408 CHN analyzer. Metal contents were determined by titration against standard EDTA solution after complete decomposition of the complexes with nitric and perchloric acid in kjeldahl flask several times and the chloride contents were determined gravimetrically. Melting or decomposition points were carried out on a melting point apparatus, Gallenkamp, England. IR spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer using KBr discs. ^{1}H NMR spectra were recorded using Brucker ARX-300 spectrometer using DMSO-d_6 as a solvent, chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were recorded at 70 eV and 300 °C on a MS 5988 Hewlett-Packard mass spectrometer. Electronic spectra of solutions of both ligands in DMF and the solid reflectance spectra of their metal complexes were recorded on a Jasco model V-550 UV–vis spectrophotometer. Magnetic susceptibility of the metal complexes were measured by the Gouy method at room temperature using a Johnson Matthey, Alpha products, model MKI magnetic susceptibility balance and the effective magnetic moments were calculated using the relation $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{m}}T)^{1/2}$ B.M., where χ_{m} is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds. The molar conductance measurements were measured in solutions of the metal complexes in DMF (10^{-3} M) using WTWD-812 Weilheium-Conductivity meter model LBR, fitted with a cell model LTA100. A Shimadzu TGA-50H thermal analyzer was used to record simultaneously the TG and DTG curves, the experiments were carried out in dynamic nitrogen atmosphere (20 ml min^{-1}) with a heating rate 10 °C min^{-1} in the temperature range 20–1000 °C using platinum crucibles. Highly sintered α-Al_2O_3 was used as a reference. The X-ray powder diffraction analysis of the two ligands and their Ni(II) and Cu(II) complexes were carried out by using Rigku Model ROTAFLEX Ru-200. Radiation was provided by copper target (Cu anode 2000 W) high intensity X-ray tube operated at 40 kV and 35 MA. Divergence slit and the receiving slit were 1 and 0.1, respectively. The antimicrobial activity of both ligands and their metal complexes were screened using the diffusion agar technique at the Medical Mycology Laboratory in the Regional Center for Mycology and Biotechnology at Al-Azhar University.



N-(2-thienylmethylidene)-2-amino-4-chlorobenzoic acid (HL^1)

N-(2-hydroxybenzylidene)-2-amino-4-chlorobenzoic acid (H_2L^2)

Fig. 1. Structure of Schiff base ligands used (HL^1) and (H_2L^2). *N*-(2-Thienylmethylidene)-2-amino-4-chlorobenzoic acid (HL^1), *N*-(2-hydroxybenzylidene)-2-amino-4-chlorobenzoic acid (H_2L^2).

Table 1
Analytical data and some physical properties of Schiff base ligands (HL^1) and (H_2L^2) and their metal complexes

Compound no.	Emperical formula [molecular weight found (calcd.)[a]]	Color	Λ_M[b]	mp (°C)	Elemental analysis, found (calc.) (%)					
					C	H	N	S	Cl	M
HL^1	$C_{12}H_8NSO_2Cl$ [264.00 (265.73)]	Orange	–	220	55.00 (54.24)	2.65 (3.04)	5.99 (5.27)	11.54 (12.07)	13.01 (13.34)	–
1	$[Co(L^1)_2]\cdot 2H_2O$ ($CoC_{24}H_{14}N_2S_2O_4Cl_2\cdot 2H_2O$) [622.00 (624.41)]	Buff	7	>300	46.51 (46.16)	2.74 (2.26)	4.91 (4.49)	9.95 (10.27)	11.01 (11.35)	9.96 (9.44)
2	$[Ni(L^1)_2]\cdot 2H_2O$ ($NiC_{24}H_{14}N_2S_2O_4Cl_2\cdot 2H_2O$) [623.00 (624.17)]	Pale green	12	>300	46.41 (46.18)	2.32 (2.27)	4.01 (4.49)	10.99 (10.28)	11.00 (11.36)	9.31 (9.40)
3	$[Cu(L^1)_2]$ ($CuC_{24}H_{14}N_2S_2O_4Cl_2$) [591.00 (592.99)]	Pale green	9	290	48.59 (48.61)	2.31 (2.38)	4.44 (4.73)	10.44 (10.82)	11.77 (11.96)	10.44 (10.72)
4	$[Zn(L^1)_2]\cdot H_2O$ (Zn $C_{24}H_{14}N_2S_2O_4Cl_2\cdot H_2O$) [610.00 (612.85)]	Pale brown	14	>300	47.09 (47.03)	2.43 (2.31)	4.86 (4.57)	10.79 (10.47)	12.00 (11.57)	10.85 (10.67)
H_2L^2	$C_{14}H_{10}NO_3Cl$ [277.00 (275.70)]	Reddish brown	–	208	60.08 (60.99)	3.55 (3.66)	5.41 (5.08)	–	11.92 (12.86)	–
5	$[Co(HL^2)_2]\cdot H_2O$ ($CoC_{28}H_{18}N_2O_6Cl_2\cdot H_2O$) [624.00 (626.33)]	Pale blue	11	>300	53.39 (53.69)	2.94 (2.90)	4.91 (4.47)	–	11.65 (11.32)	9.31 (9.41)
6	$[Ni(HL^2)_2]$ ($NiC_{28}H_{18}N_2O_6Cl_2$) [608.00 (608.07)]	Pale green	15	>300	55.79 (55.30)	2.71 (2.99)	4.15 (4.61)	–	11.11 (11.66)	9.28 (9.65)
7	$[Cu(HL^2)_2]$ ($CuC_{28}H_{18}N_2O_6Cl_2$) [610.00 (612.93)]	Green	17	260	54.58 (54.86)	2.98 (2.97)	4.93 (4.57)	–	11.99 (11.57)	10.18 (10.37)
8	[Zn $(HL^2)_2]\cdot 2H_2O$ ($ZnC_{28}H_{18}N_2O_6Cl_2\cdot 2H_2O$) [652.00 (650.81)]	Buff	11	240	51.21 (51.67)	2.99 (2.79)	4.23 (4.31)	–	10.70 (10.89)	9.71 (10.05)

[a] Found values obtained from mass spectra.

[b] Molar conductance (Ω^{-1} cm^2 mol^{-1}) of 1×10^{-3} M solution in DMF at room temperature.

Table 2
IR spectral assignment for schiff base ligands (HL^1) and (H_2L^2) and their metal complexes ($\upsilon_{cm^{-1}}$)

Compound no.	$\upsilon_{C=O}$ (carboxy.)	$\Delta\upsilon$ ($\upsilon_{asy.}-\upsilon_{sy.}$)	$\upsilon_{C=N}$ (azome.)	$\upsilon_{C–C}$ (thioph.)	υ_{CSC} (ring)	$\upsilon_{O–H}$ (pheno.)	$\upsilon_{C–O}$ (pheno.)	$\upsilon_{M–O}$	$\upsilon_{M–N}$	$\upsilon_{M–S}$
HL^1	1668 sh		1610 sh	1550 m	850 sh	–	–	–	–	–
1	1614, 1400	214	1584 sh	1536 w	836 sh	–	–	520 s	500 s	468 w
2	1612, 1348	264	1586 sh	1534 w	838 sh	–	–	550 w	494 w	474 w
3	1620, 1398	222	1600 sh	1530 m	840 sh	–	–	519 s	498 w	479 s
4	1632, 1400	232	1589 sh	1539 w	837 sh	–	–	553 s	502 s	444 s
H_2L^2	1668 sh		1612 sh	–	–	3288 br	1248 sh	–	–	–
5	1614, 1402	212	1576 sh	–	–	3240 br	1236 sh	520 w	–	468 s
6	1614, 1400	214	1586 sh	–	–	3149 br	1236 sh	526 w	–	474 w
7	1600, 1378	222	1592 sh	–	–	3122 br	1230 sh	526 s	–	484 s
8	1612, 1346	266	1586 sh	–	–	3250 br	1158 sh	540 w	–	446 w

sh, sharp; s, small; m, medium; br, broad; w, weak.

2.2. *Schiff base ligands synthesis*

The two Schiff base ligands, HL^1 and H_2L^2 (Fig. 1) were prepared by adding a solution of 2-thiophenecarboxaldehyde (9.35 ml, 0.1 mol) or 2-hydroxybenzaldehyde (10.66 ml, 0.1 mol) in ethanol (25 ml) to 2-amino-4-chlorobenzoic acid (17.16 g, 0.1 mol) in ethanol (50 ml) in presence of few drops of piperidine. The mixture was kept under reflux for 4 h on a water bath and then allowed to cool to room temperature. The product was filtered off, recrystallized from ethanol and dried in a desciccator over anhydrous $CaCl_2$ to give orange powder of Schiff base ligand, HL^1 in 89% yield or reddish brown powder of Schiff base ligand, H_2L^2 in 76% yield. Some physico-chemical characteristic of both ligands and their elemental analysis is collected in Table 1.

2.3. *Metal complexes synthesis*

A hot ethanolic solution of the appropriate metal chloride (0.1 mol) namely, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$ and $ZnCl_2$ was added to a hot ethanolic solution of the Schiff base ligands, HL^1 or H_2L^2 (0.2 mol). The resulting mixture was stirred under reflux for 2 h where upon the metal complexes were precipitated. The precipitated solid complexes were filtered recrystallized and dried in vacuum desiccator over anhydrous $CaCl_2$. These complexes are stable in air, soluble in DMF and DMSO, insoluble in most organic solvents and its elemental analysis are in accordance with the proposed stoichiometry and agree well with the suggested molecular formula. Their micro-analytical data are listed in Table 1.

3. Results and discussion

Condensation of the aldehydes with amine readily gives rise to the corresponding imines "Schiff base ligands, HL^1 and H_2L^2". Their reaction with the metal ions Co(II), Ni(II), Cu(II) and Zn(II), afford the metal complexes (**1–8**), the general reaction for the preparation of the metal complexes of HL^1 and H_2L^2 is shown below:

$$2HL^1 + M(Cl)_x{\cdot}nH_2O \rightarrow [M(L^1)_2]y + z \qquad (1)$$

where $M = Co(II)$: $x = 2$, $n = 6$, $y = 2H_2O$, $z = 4H_2O + 2HCl$; $M = Ni(II)$: $x = 2$, $n = 6$, $y = 2H_2O$, $z = 4H_2O + 2HCl$; $M = Cu(II)$: $x = n = 2$, $y = \text{nil}$, $z = 2H_2O + 2HCl$; $M = Zn(II)$: $x = 2$, $n = \text{nil}$, $y = H_2O$, $z = 2HCl$.

$$2H_2L^2 + M(Cl)_x{\cdot}nH_2O \rightarrow [M(HL^2)_2]y + z \qquad (2)$$

where $M = Co(II)$: $x = 2$, $n = 6$, $y = H_2O$, $z = 5H_2O + 2HCl$; $M = Ni(II)$: $x = 2$, $n = 6$, $y = \text{nil}$, $z = 6H_2O + 2HCl$; $M = Cu(II)$: $x = n = 2$, $y = \text{nil}$, $z = 2H_2O + 2HCl$; $M = Zn(II)$: $x = 2$, $n = \text{nil}$, $y = 2H_2O$, $z = 2HCl$.

3.1. *IR spectra*

The mode of binding of both Schiff base ligands to the metal ions was elucidated by recording the IR spectra of the complexes as compared with the spectra of the free ligands. The small difference between the infrared spectra of both Schiff base ligands indicates that, the ligands have a similar structure but the spectra of the free ligands differ obviously from that of their complexes as clear from Table 2. The spectra of both free ligands show two strong bands at 1610 and 1612 cm^{-1} characteristics of the $\upsilon_{C=N}$ (azomethine) stretching mode for (HL^1) and (H_2L^2), respectively [9,16,17] indicating the formation of the Schiff base products. These bands are shifted towards lower frequencies in the spectra of all metal complexes 1600–1576 cm^{-1} compared with the free Schiff base indicating the involvement of the azomethine nitrogen in chelation with the metal ions, the coordination of nitrogen to the metal ion would be expected to reduce the electron density of the azomethine link and thus cause a shift in the $\upsilon_{C=N}$ group [11]. The intense band at 1668 cm^{-1} present in the IR spectra of the free ligands may be assigned to the $\upsilon_{C=O}$ (carboxylic group), similar band was observed at the same frequency region in the IR spectra of some organic acid ligands [18,19]. However, the spectra of all complexes show the absence of this band accompanied by the appearance of two characteristic bands at 1632–1600 and 1402–1346 cm^{-1} attributed to $\upsilon_{asy.}(COO^-)$ and $\upsilon_{sy.}(COO^-)$, respectively, indicating the participation of the carboxylate oxygen atom in the complexes formation. The mode of coordination of carboxylate group (Fig. 2) has often been deduced from the magnitude of the observed separation between the $\upsilon_{asy.}(COO^-)$ and $\upsilon_{sy.}(COO^-)$,

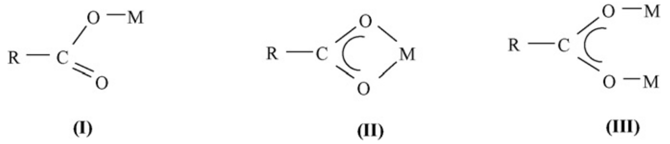


Fig. 2. Possible coordination modes of the carboxylate group.

the separation value (Δ) between $\upsilon_{asy.}(COO^-)$ and $\upsilon_{sy.}(COO^-)$ in metal complexes was more than 200 cm^{-1} (266–212 cm^{-1}) suggests the coordination of carboxylate group in all metal complexes of the two ligands in a monodentate fashion [20–23].

The Schiff base ligand (HL^1), its spectrum displays two bands at 1550 and 850 cm^{-1} ascribed to $\upsilon_{C–C}$ and $\upsilon_{C–S–C}$ (thiophene moiety) [24] which shifts to lower frequencies in the spectra of metal complexes (**1**–**4**) in the region 1539–1530 and 840–836 cm^{-1}, respectively, suggesting the coordination of metal ions through the sulphur atom of thiophene moiety supported from ^{1}H NMR data.

The observed broad band at 3288 cm^{-1} in the IR spectrum of the ligand, H_2L^2 was assigned to $\upsilon_{O–H}$ (phenolic) of aldehyde moiety [13,14,17]. The observed low value of this band is due to the intramolecular hydrogen bonding between the hydrogen atom of OH group and the azomethine nitrogen atom, O–H$\cdots$N, where the free $\upsilon_{O–H}$ is generally observed between 3650 and 3500 cm^{-1} according to the assignment made by Sonmez and Sekerci [25]. This band was shifted to lower frequencies in metal complexes (**5**–**8**) at 3250–3122 cm^{-1} suggesting the involvement of O–H group in coordination. Additionally, the IR spectrum exhibits a strong band at 1248 cm^{-1} may be referred to $\upsilon_{C–O}$ (phenolic), the same band was observed at the same frequency in the IR spectrum of salicylidene thiophenol Schiff base [6] which undergoes a shift toward lower frequencies in the region 1236–1158 cm^{-1} in the metal complexes (**5**–**8**). This shift confirms the participation of the oxygen atom of aldehyde moiety in coordination to the metal ion.

Conclusive evidence of the bonding is also shown by the observation that new bands in the spectra of all metal complexes appear in the low frequency regions at 553–519, 502–494 and 484–444 cm^{-1} characteristic to $\upsilon_{M–O}$, $\upsilon_{M–N}$ and $\upsilon_{M–S}$ stretching vibrations, respectively, that are not observed in the spectra of both free ligands [15,26]. Furthermore, the observed broad bands appear at 3452–3400 cm^{-1} in some complexes may attributed to OH stretching vibration of lattice water molecules, another bands observed at 900–844 cm^{-1} due to bending vibration of H_2O indicating that these complexes are hydrated supported from thermal analysis study [27,28].

Table 3
^{1}H NMR spectra data of Schiff base ligands (HL^1) and (H_2L^2) and their diamagnetic Zn(II) complexes (δ, ppm)

Compound no.	COOH$^{(s)}$	OH$^{(s)}$	HC=N$^{(s)}$	Aromatic (and/or) thiophene protons$^{(m)}$
HL^1	11.43	–	8.93	7.94–6.95
4	–	–	8.99	7.65–6.79
H_2L^2	11.41	10.20	8.92	7.68–6.94
8	–	10.35	8.96	7.65–6.95

s, singlet; m, multiple.

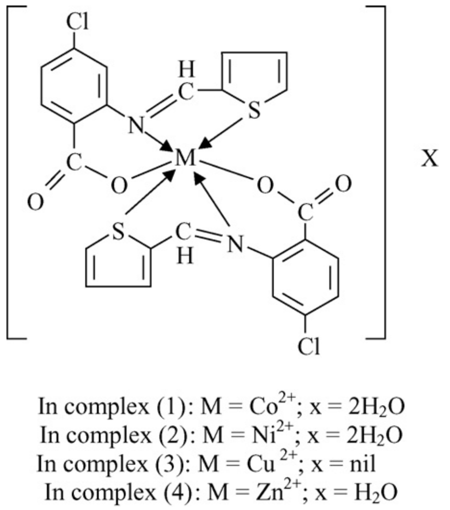


Fig. 3. Proposed molecular structure of metal complexes (**1**–**4**). In complex (**1**): M = Co^{2+}, x = 2H_2O; in complex (**2**): M = Ni^{2+}, x = 2H_2O; in complex (**3**): M = Cu^{2+}, x = nil; in complex (**4**): M = Zn^{2+}, x = H_2O.

3.2. ^{1}H NMR spectra

The NMR spectra of the free Schiff base ligands (HL^1) and (H_2L^2) and their diamagnetic Zn(II) complexes (**4** and **8**) were recorded in d_6-dimethylsulfoxide (DMSO) solution using tetramethylsilane (TMS) as internal standard. The ^{1}H NMR spectra of zinc(II) complexes are compared with those of the free ligands (Table 3). Upon complexation, the signal due to the carboxylic proton which appears in the free ligands at δ 11.43–11.41 ppm (s, 1H) [29] is completely disappeared in the spectrum of the Zn(II) complexes indicating the deprotonation of carboxylic group and its involvement in chelation through the displacement of the COOH proton. The shift to higher field of the CH=N– proton signal which appears in the free ligands

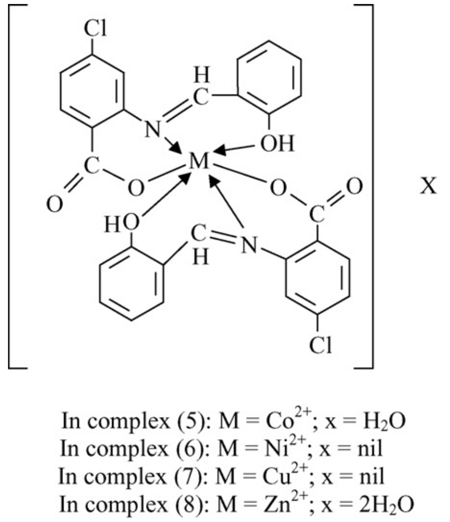


Fig. 4. Proposed molecular structure of metal complexes (**5**–**8**). In complex (**5**): M = Co^{2+}, x = H_2O; in complex (**6**): M = Ni^{2+}, x = nil; in complex (**7**): M = Cu^{2+}, x = nil; in complex (**8**): M = Zn^{2+}, x = 2H_2O.

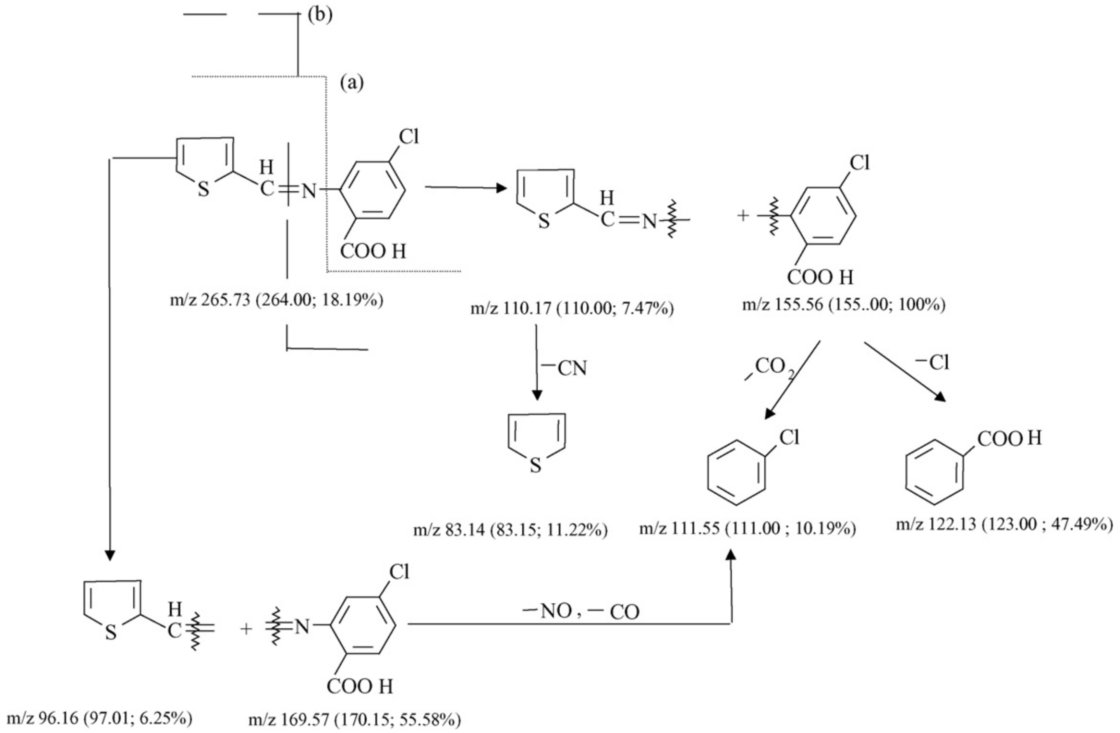


Fig. 5. Proposed fragmentation route of Schiff base ligand, HL^1.

at δ 8.93–8.92 ppm (s, 1H) [30] suggesting the coordination to the metal ions via the azomethine nitrogen. The upfield shift of the signal due to phenolic proton in zinc(II) complex (**8**) which appears in the free ligand (H_2L^2) at δ 10.20 ppm (s, 1H) [25] supports the involvement of OH group in coordination to the metal ions. The signals at δ 7.94–6.79 ppm (multiplets) are due to the aromatic and thiophenic protons [31]. The downfield shift of the thiophenic protons in zinc(II) complex (**4**) indicating that the thiophenic sulphur taking part in complexation to metal ions. Depending on the IR and ^{1}H NMR Spectra, the suggested structures of the complexes are given in Figs. 3 and 4 which are confirmed by the other techniques.

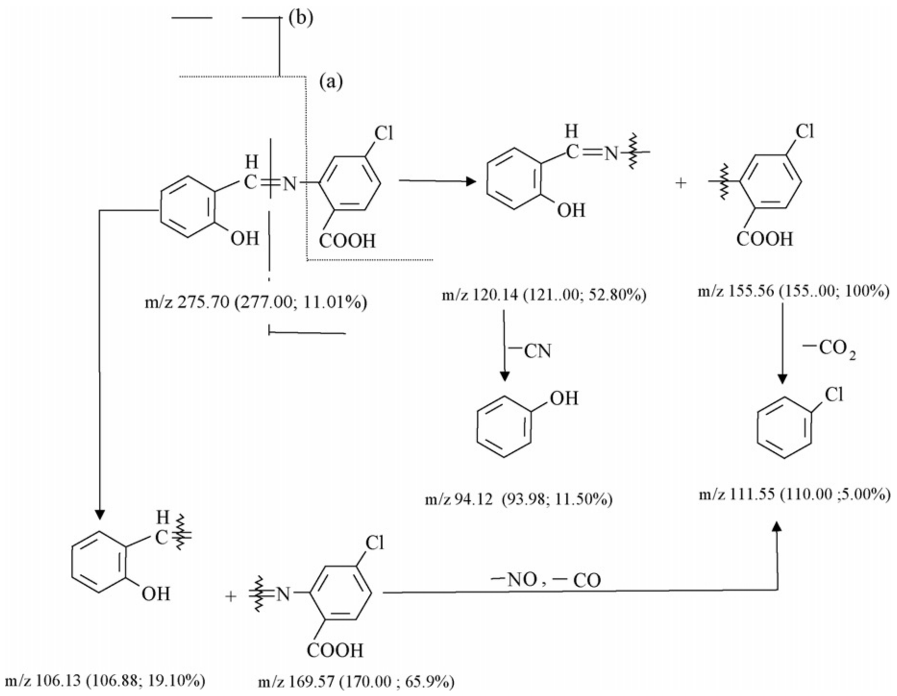


Fig. 6. Proposed fragmentation route of Schiff base ligand, H_2L^2.

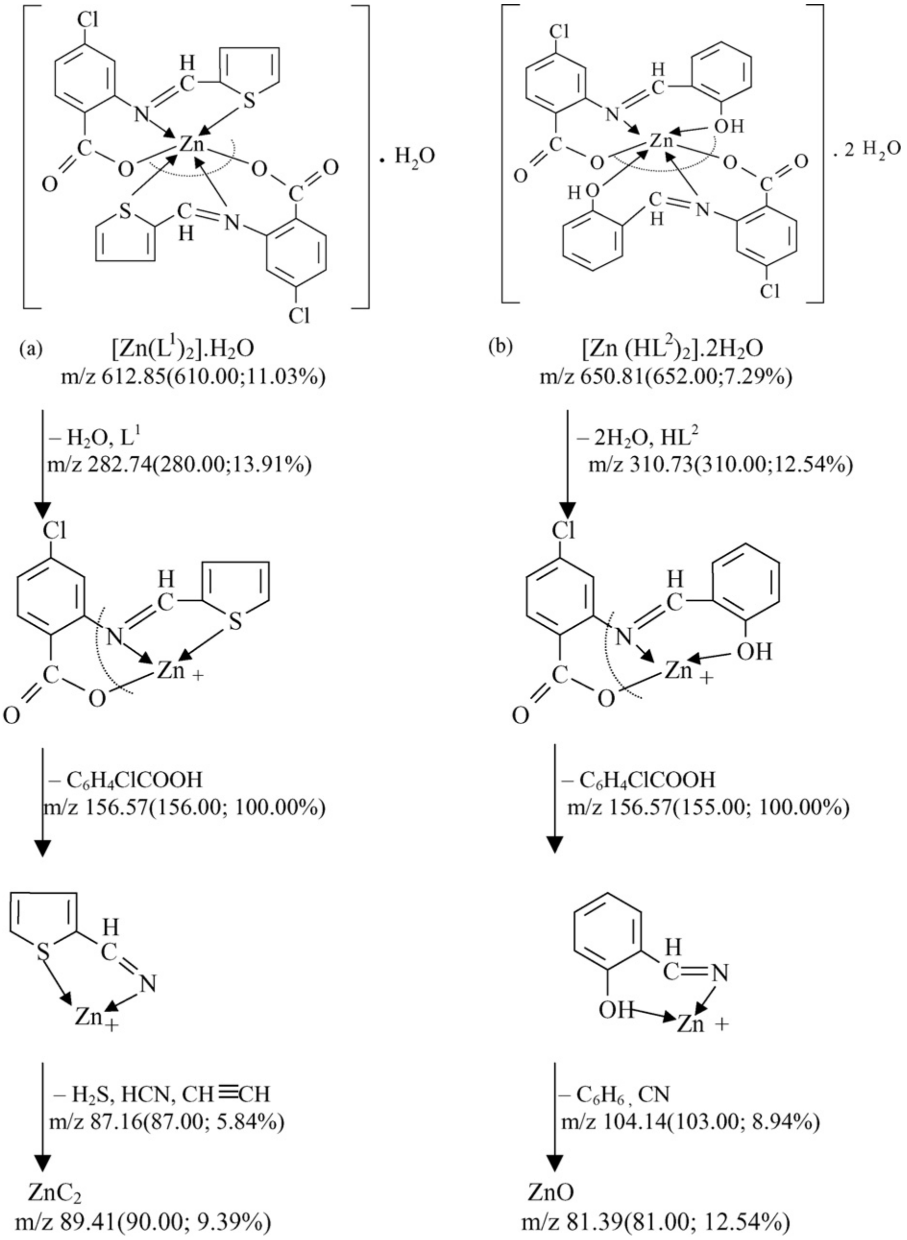


Fig. 7. Proposed fragmentation route of: (a) $[Zn(L^1)_2]\cdot H_2O$ and (b) $[Zn(HL^2)_2]\cdot 2H_2O$.

Table 4
Electronic spectral data, magnetic moment values and ligand field parameters of the paramagnetic metal complexes

Compound no.	μ_{eff} (B.M.)	Absorption bands (cm^{-1})/peak assignment			Ligand field parameters				CFSE (cm^{-1})
		υ_1	υ_2	υ_3	D_q (cm^{-1})	B (cm^{-1})	β	β (%)	
Co(II) complexes									
(**1**) $[Co(L^1)_2]\cdot 2H_2O$	4.93	13.33×10^3	15.90×10^3	18.35×10^3	2086.50	837	0.85	15.03	16.69×10^3
(**5**) $[Co(HL^2)_2]\cdot H_2O$	4.56	12.90×10^3	14.43×10^3	18.05×10^3	2022	831	0.84	15.63	16.18×10^3
		$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$					
Ni(II) complexes									
(**2**) $[Ni(L^1)_2]\cdot 2H_2O$	3.06	12.50×10^3	18.52×10^3	21.28×10^3	1250	653	0.60	39.65	15×10^3
(**6**) $[Ni(HL^2)_2]$	2.93	12.20×10^3	17.39×10^3	20.83×10^3	1220	531	0.49	50.92	14.64×10^3
		$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$					
Cu(II) complexes									
(**3**) $[Cu(L^1)_2]$	1.99	15.93×10^3	16.11×10^3	18.22×10^3					
(**7**) $[Cu(HL^2)_2]$	1.96	15.82×10^3	16.33×10^3	17.91×10^3					
		$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$	$^2B_{1g} \rightarrow {}^2A_{1g}$					

3.3. Mass spectra

The mass spectra of the ligands used, HL^1 and H_2L^2 exhibit the molecular ion peaks at *m*/*e* (264.00 and 277.00) (calculated 265.73 and 275.70) with abundance 18.19% and 11.01%, respectively. Their proposed pathway fragmentation pattern is depicted in Figs. 5 and 6. The mass spectra of the metal complexes (**1**–**8**) have been investigated in which the molecular ion peaks are detected. All metal complexes show similar fragmentation pattern and Fig. 7 shows the proposed fragmentation pattern of the zinc(II) complexes as representative example.

3.4. Molar conductance data

The metal complexes discussed herein were dissolved in DMF and the molar conductivities of 10^{-3} M of their solutions at room temperature were measured to establish the charge of the metal complexes. The conductance data, Table 1 indicate that, all the metal complexes having conductivity values in the range characteristic for the non-electrolytic nature suggesting that these complexes are neutral [32].

3.5. Magnetic susceptibility measurements and electronic absorption spectra

The electronic spectra of both free ligands under study in DMF solution were characterized mainly by two absorption bands in the region $(25.00–50.00) \times 10^3\ \mathrm{cm}^{-1}$ assigned to π–π^* and n–π^* transition, involving the molecular orbitals of the C=N and both benzene and thiophene rings [8]. In metal complexes, these transitions were found to be shifted to lower or higher energy region compared to the free ligands transitions confirming the coordination of the ligands to metal ions, in addition to d–d transitions and the intramolecular charge transfer transitions between the ligands and metal ions. The spectra data (Table 4) includes absorption regions, band assignment and magnetic susceptibility values.

At room temperature, Co(II) complexes (**1** and **5**) show magnetic moment values in the range 4.93–4.56 B.M., which higher than the spin only value (3.87) due to the orbital angular momentum contribution in d^7-system and close to the value required for an octahedral structure [11]. The magnetic moment values for the Ni(II) complexes (**2** and **6**) were found to be 3.06–2.93 B.M., which is in the normal range (2.80–3.80) for an octahedral environment [1]. Cu(II) complexes (**3** and **7**) show magnetic values of 1.99–1.96 B.M. falls within the range normally observed for octahedral Cu^{2+} complexes [15]. Zn(II) complexes (**4** and **8**) are found to be diamagnetic as expected for d^{10} configuration.

The metal ion, Co(II) (d^7) gives rise to the free ion terms ^4F, ^4P and a number of doublet states [33], the electronic spectra of Co(II) complexes (**1** and **5**) display three bands at $(13.33–12.90) \times 10^3$, $(15.90–14.43) \times 10^3$ and $(18.35–18.05) \times 10^3\ \mathrm{cm}^{-1}$ wave number regions, respectively, may assigned to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (υ_1),

Table 5
Thermal behavior of metal complexes (**1**–**8**) of the Schiff base ligands (HL^1) and (H_2L^2)

Compound no.	Temperature range (°C)	Loss in weight found (calcd.) (%)		Decomposition product loss
		Mass loss	Total mass loss	
(**1**) $[Co(L^1)_2]\cdot 2H_2O$	40–450	88.56 (88.00)		$2H_2O$ (lattice) and $2L^1$ leaving CoO residue
(**2**) $[Ni(L^1)_2]\cdot 2H_2O$	25–88	8.67 (8.57)		H_2O (lattice) and Cl
	88–234	14.43 (14.43)		H_2O (lattice), CO_2 and CO
	234–425	28.75 (28.88)		CN and biphenyl fragment
	425–600	33.64 (34.24)	85.49 (86.12)	CN, O, Cl, 2CH≡CH and thiophene fragment leaving NiS residue
(**3**) $[Cu(L^1)_2]$	50–100	8.19 (7.76)		NO_2
	100–375	41.26 (41.88)		CN, CO, CH≡CH and two thiophene fragment
	375–500	38.33 (37.96)	87.78 (87.60)	$2C_6H_5Cl$ leaving CuO residue
(**4**) $[Zn(L^1)_2]\cdot H_2O$	50–130	3.24 (2.94)		H_2O (lattice)
	130–325	30.03 (30.06)		NO and biphenyl fragment
	325–425	22.14 (22.54)		O_2, CN, CO and 2CH≡CH
	425–600	30.82 (30.53)	86.23 (86.07)	Cl_2, S and thiophene fragment leaving ZnC_2 residue
(**5**) $[Co(HL^2)_2]\cdot H_2O$	38–127	6.58 (6.23)		(1/2)H_2O (lattice) and NO
	127–265	13.91 (13.91)		(1/2)H_2O (lattice) and C_6H_6
	265–450	31.35 (31.65)		CO_2 and biphenyl fragment
	450–800	27.62 (28.13)	79.46 (79.92)	CO_2, CO, CN and C_6H_6 leaving $CoCl_2$ residue
(**6**) $[Ni(HL^2)_2]$	34–108	11.54 (11.66)		2Cl
	108–246	9.68 (9.54)		CO and NO
	246–434	29.76 (29.97)		CO and biphenyl fragment
	434–600	33.26 (35.56)	84.24 (86.73)	O_2, NO and biphenyl fragment leaving NiC_2 residue
(**7**) $[Cu(HL^2)_2]$	100–350	43.08 (43.91)		CO_2, Cl_2 and biphenyl fragment
	350–581	46.63 (46.05)	89.71 (89.96)	CO_2, O_2, 2CN and biphenyl fragment leaving Cu residue
(**8**) $[Zn(HL^2)_2]\cdot 2H_2O$	100–300	89.97 (89.95)		$2H_2O$ (lattice) and $2HL^2$
	300–596	8.93 (10.05)	98.90 (100.00)	Zn and no residue

${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (υ_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (υ_3), respectively of the d^7-system suggesting Co(II) high-spin complexes octahedral environment of donor atoms with a ground state term symbol ${}^4F$, its magnetic moment values confirm the octahedral structure [15]. The ligand field parameters (D_q, B and β) where D_q is the crystal field splitting parameter, B the Racah interelectronic repulsion parameter and β is the nephelauxtic parameter were calculated [34]. The smaller B value (837–831 cm^{-1}) compared to the free metal ion (985 cm^{-1}) is due to the strong interaction between the reactive sites of the organic compound with cobalt(II) ion which indicate a reduction of about 15.63–15.03% from the free ion value, also (β) value is less than unity (0.85–0.84) suggesting a largely covalent bond between the organic ligand and cobalt(II) ion in these complexes. Additionally, the crystal field stabilization energy (CFSE) for Co(II) in a crystal field with O_h symmetry was calculated.

The free ion terms for Ni(II) ion (d^8) are ${}^3F$, ${}^3P$, ${}^1G$, ${}^1D$ and ${}^1S$ [33]. The electronic spectra of Ni(II) complexes (**2** and **6**) exhibit three electronic spectra bands in the range (12.50–12.20) × 10^3, (18.52–17.39) × 10^3 and (21.28–20.83) × 10^3 cm^{-1} suggesting high-spin Ni(II) complexes with octahedral configuration with a ground state term symbol ${}^3F$. These bands are assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (υ_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (υ_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (υ_3) transition, respectively for an octahedral geometry [35]. The ligand field parameters (D_q, B and β) were calculated [36] and the smaller B value (653–531 cm^{-1}) compared to the free metal ion (1082 cm^{-1}) is due to the strong interaction between the reactive sites of the organic com-

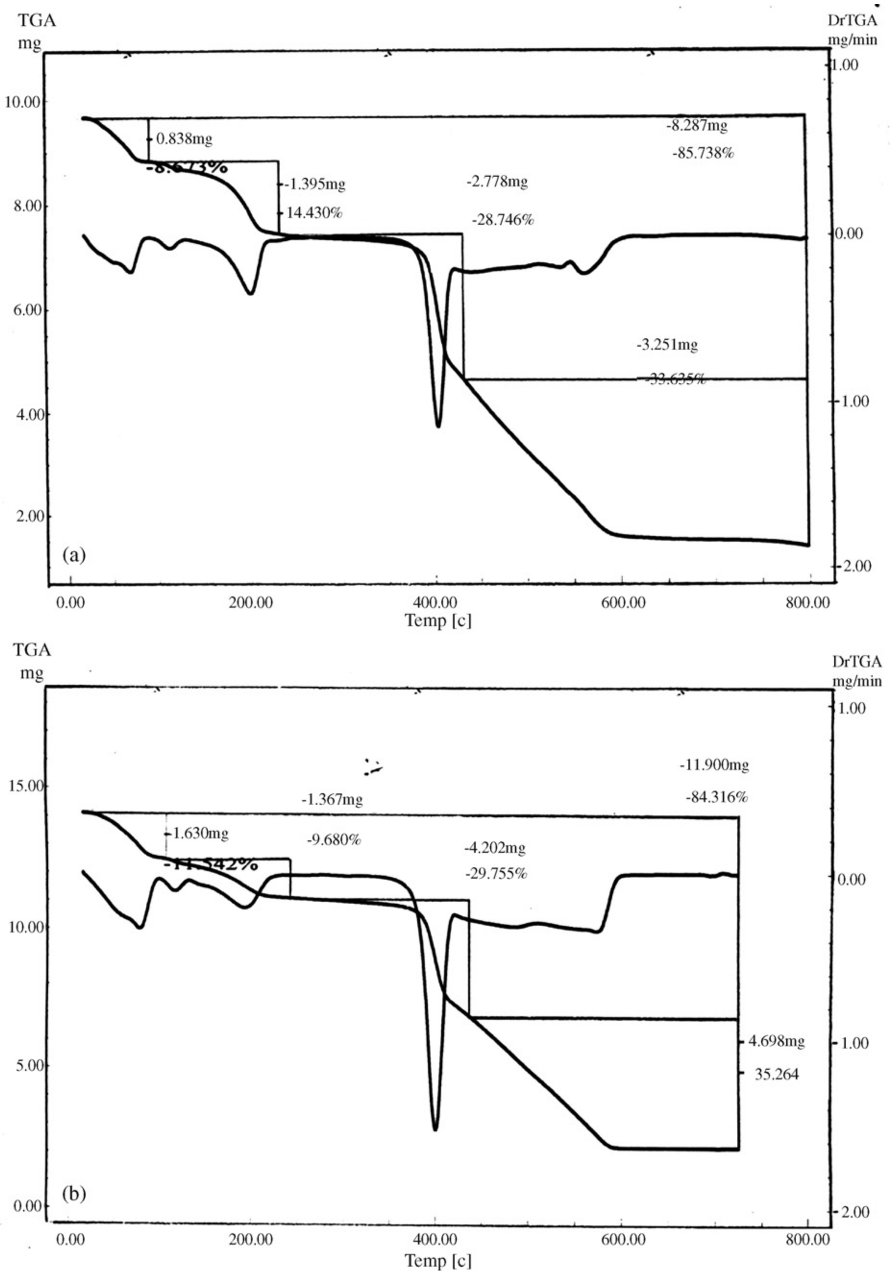


Fig. 8. TG and DTG curve of: (a) $[Ni(L^1)_2]\cdot 2H_2O$ and (b) $[Ni(HL^2)_2]$.

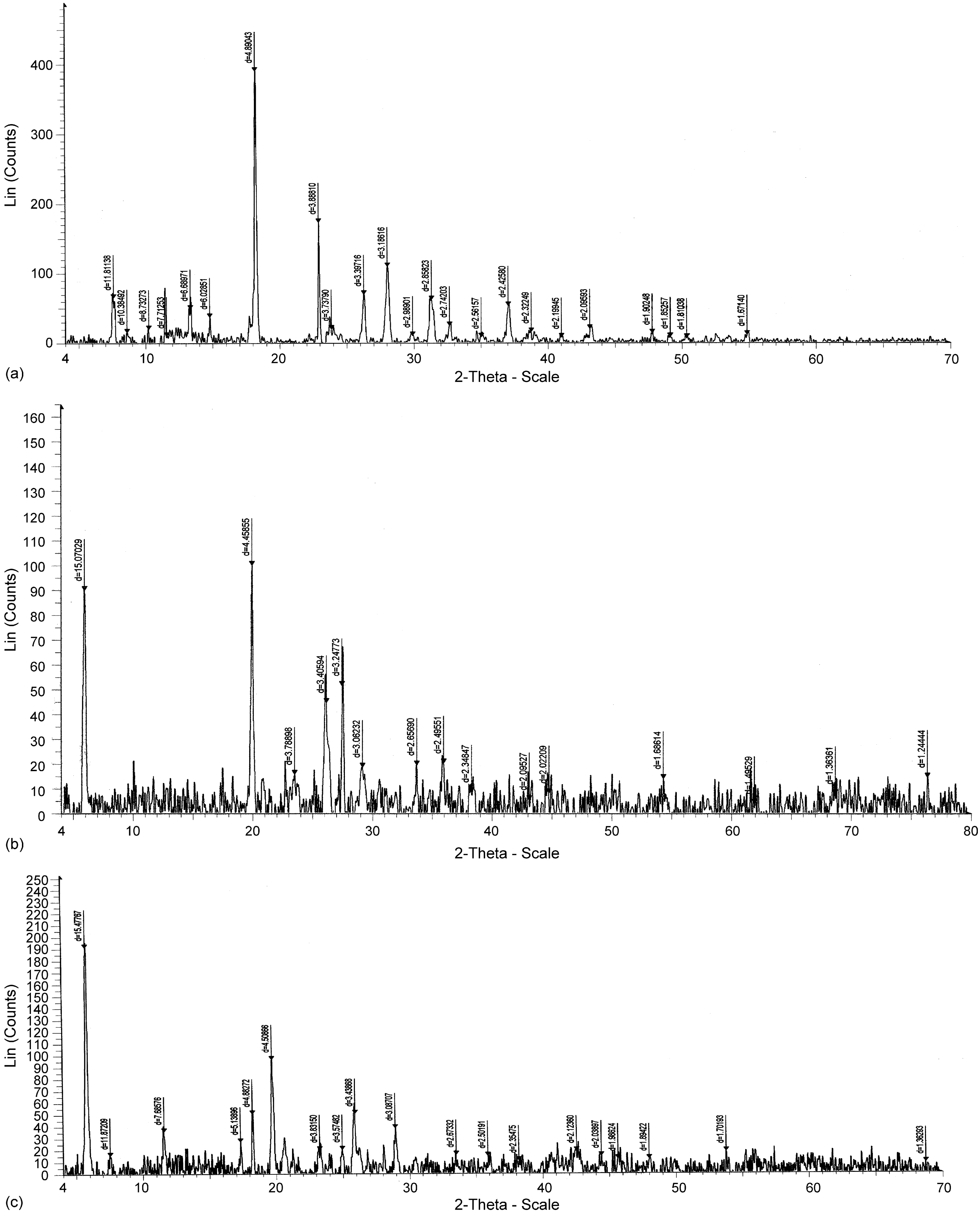


Fig. 9. X-ray diffraction pattern of: (a) Schiff base ligand, HL^1, (b) $[Ni(L^1)_2]\cdot 2H_2O$ and (c) $[Cu(L^1)_2]$.

pound with nickel(II) ion which indicate a reduction of about 50.92–39.65% from the free ion value, also (β) value is less than unity (0.60–0.49) suggesting a largely covalent bond between the organic ligand and nickel(II) ion in these complexes. Additionally, the crystal field stabilization energy (CFSE) for Ni(II) in a crystal field with O_h symmetry was calculated.

The metal complexes (**3** and **7**) for Cu(II) ion (d^9), their spectra consist of a broad, low intensity shoulder band centered

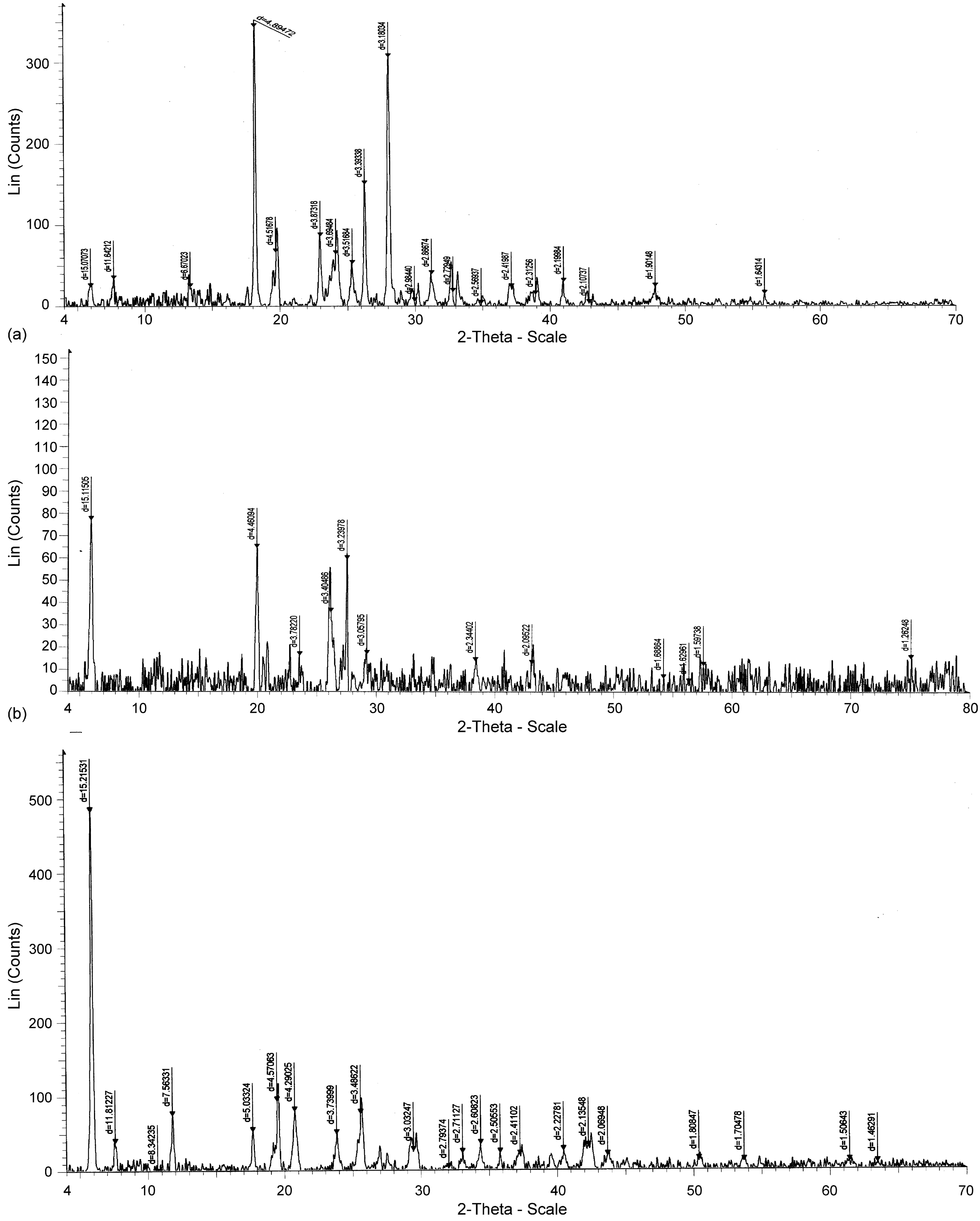


Fig. 10. X-ray diffraction pattern of: (a) Schiff base ligand, H_2L^2, (b) $[Ni(HL^2)_2]$ and (c) $[Cu(HL^2)_2]$.

Table 6
X-ray diffraction data of Schiff base ligand (HL^1) and its Ni(II) and Cu(II) complexes (**2**, **3**)

HL^1			$[Ni(L^1)_2]\cdot 2H_2O$			$[Cu(L^1)_2]$		
d (Å)	2*θ*	*I*/*I*^{0}	*d* (Å)	2*θ*	*I*/*I*^{0}	*d* (Å)	2*θ*	*I*/*I*^{0}
11.81	7.48	16.60	15.07	5.86	89.80	15.48	5.71	100.00
10.38	8.51	3.80	4.46	19.90	100.00	11.87	7.44	8.00
8.73	10.12	5.00	3.79	23.46	15.40	7.69	11.50	18.70
7.71	11.46	2.50	3.41	26.14	44.50	5.14	17.24	14.10
6.69	13.22	12.50	3.25	27.44	51.40	4.88	18.15	26.40
6.03	14.68	9.40	3.06	29.14	18.30	4.51	19.67	50.40
4.89	18.13	100.00	2.66	33.71	19.20	3.83	23.20	10.60
3.89	22.85	44.40	2.50	35.96	19.90	3.57	24.89	10.60
3.74	23.79	5.10	2.35	38.30	8.30	3.44	25.89	26.50
3.40	26.21	17.80	2.10	43.14	5.10	3.09	28.90	20.00
3.19	27.98	28.00	2.02	44.78	7.90	2.67	33.49	8.20
2.99	29.87	2.60	1.69	54.37	13.70	2.50	35.86	7.70
2.86	31.27	15.80	1.50	62.02	3.70	2.35	38.19	5.60
2.74	32.63	6.20	1.36	68.79	7.70	2.12	42.54	9.80
2.56	35.01	2.00	1.24	76.49	14.30	2.04	44.39	7.60
2.43	37.03	13.60				1.99	45.64	6.30
2.32	38.74	4.10				1.89	47.99	6.20
2.20	41.00	1.90				1.70	53.82	9.50
2.10	43.13	5.10				1.36	68.83	4.50
1.90	47.77	3.50						
1.85	49.14	2.10						
1.81		1.80						

at (18.22–15.93) × 10^3 and (17.91–15.82) × 10^3 cm^{-1}, respectively, may be assigned to the transitions $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$, respectively, corresponding to a distorted octahedral geometry of Cu(II) ion [15].

Zn(II) complexes (**4** and **8**) are diamagnetic and in analogy with the previously described Zn(II) complexes of some tridentate donor ligands [1,13,25,26,37] and according to the empirical formula of these complexes, we propose an octahedral geometry for the Zn(II) complexes. Their electronic spectra show an absorption bands at (26.32–25.00) × 10^3 cm^{-1} attributed to LMCT transition which is compatible with octahedral structure [38].

Table 7
X-ray diffraction data of Schiff base ligand (H_2L^2) and its Ni(II) and Cu(II) complexes (**6**, **7**)

H_2L^2			$[Ni(HL^2)_2]$			$[Cu(HL^2)_2]$		
d (Å)	2*θ*	*I*/*I*^{0}	*d* (Å)	2*θ*	*I*/*I*^{0}	*d* (Å)	2*θ*	*I*/*I*^{0}
15.07	5.86	6.80	15.12	5.84	100.00	15.21	5.80	100.00
11.64	7.59	9.60	4.46	19.89	83.90	11.81	7.48	7.70
6.67	13.26	6.70	3.78	23.50	21.00	8.34	10.60	0.70
4.89	18.11	100.00	3.40	26.15	46.40	7.56	11.69	15.30
4.52	19.64	19.20	3.24	27.51	77.20	5.03	17.61	10.80
3.87	22.94	24.90	3.06	29.18	21.80	4.57	19.41	19.20
3.69	24.07	18.50	2.34	38.37	17.60	4.29	20.69	16.40
3.52	25.30	15.10	2.10	43.14	16.20	3.74	23.77	10.00
3.39	26.24	43.40	1.69	54.28	7.90	3.49	25.53	15.70
3.18	28.03	89.00	1.63	56.42	5.50	3.03	29.43	5.20
2.98	29.92	1.60	1.60	57.66	15.30	2.79	32.01	0.40
2.87	31.17	11.20	1.26	75.20	19.30	2.71	33.01	4.60
2.73	32.79	5.00				2.61	34.36	7.00
2.57	34.89	0.70				2.51	35.81	4.60
2.42	37.12	6.50				2.41	37.26	4.00
2.31	38.91	4.00				2.23	40.46	5.20
2.20	40.99	8.50				2.14	42.29	6.30
2.11	42.88	0.90				2.07	43.71	3.80
1.90	47.80	6.70				1.81	50.42	2.50
1.64	55.91	4.10				1.70	53.72	2.20
						1.51	61.51	2.00
						1.46	63.55	1.60

3.6. Thermogravimetric analysis

Thermal analysis plays an important role in studying the properties of metal complexes to obtain a useful data on the metal–ligand bonds. The thermal decomposition of all metal complexes (**1**–**8**) was studied using the TG-technique. During the heating of the metal complexes, the TG-curves undergo a series of thermal changes associated with a weight loss of the samples. Analysis of the obtained TG-curves is given in Table 5 and the correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formulae of the complexes. Fig. 8 is a representative example for thermal analysis of the metal complexes under study.

3.7. X-ray diffraction study

Single crystals of the complexes under study could not be obtained because the metal complexes wear isolated as powder rather than single crystals, in addition to their insolubility in most organic solvents, thus no definitive structure can be described. X-ray diffraction patterns of both ligands, HL^1 and H_2L^2 and their Ni(II) and Cu(II) complexes (**2**, **3**, **6** and **7**) were recorded between 4° and 80° (2θ) and are given in Figs. 9 and 10. The value of (2θ), interplanar spacing d (Å) and the relative intensities (I/I^0) of the compounds under study were recorded in Tables 6 and 7. Comparing the X-ray diffraction patterns of each ligand with its corresponding metal complexes indicate that the interplanar spacing, d (Å) and the relative intensities (I/I^0) are different which could be attributed to the complex formation. Furthermore, correlation the analytical, spectroscopic and magnetic data enables us to predict the possible structure for the metal complexes.

3.8. Antimicrobial studies

The two Schiff base ligands, HL^1 and H_2L^2 and their metal complexes (**1**–**8**) have been tested against four species of bacteria; *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Escherichia coli* as well as four species of fungi; *Aspergillus fumigatus*, *Penicillium italicum*, *Syncephalastrum racemosum* and *Candida albicans*. The test was done using the diffusion agar technique [39] and both chloramphenicol and Terbinafin were used as standard antibacterial and antifungal agents, respectively. The compounds to be tested were dissolved in dimethylformamide at a different concentration 1, 2.5 and 5 mg/ml and the diameter (cm) of the inhibitation zone was measured, all data were collected in Tables 8 and 9.

On comparing the biological activity of the Schiff base ligands and their metal complexes the following results are obtained:

(1) The ligands and their metal complexes, all have the capacity of inhibiting the metabolic growth of the investigated bacteria and fungi to different extent. This inhibitory capacity is reinforced with the increment of concentration.

Table 8

Antibacterial and antifungal activity data for Schiff base ligand HL^1 and its metal complexes (**1**–**4**)

	HL^1 (free ligand)			**1**			**2**			**3**			**4**			St.		
	5 mg/ml	2.5 mg/ml	1 mg/ml	5 mg/ml	2.5 mg/ml	1 mg/ml	5 mg/ml	2.5 mg/ml	1 mg/ml	5 mg/ml	2.5 mg/ml	1 mg/ml	5 mg/ml	2.5 mg/ml	1 mg/ml	5 mg/ml	2.5 mg/ml	1 mg/ml
Staphylococcus aureus	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	++	++	++
Pseudomonas aeruginosa	0	0	0	0	0	0	+	0	0	+	+	0	+	0	0	+++	+++	++
Bacillus subtilis	+	+	+	+	0	0	+	0	0	0	0	0	0	0	0	+++	+++	++
Escherichia coli	+	0	0	+	0	0	0	0	0	0	0	0	0	0	0	++	++	++
Aspergillus fumigatus	++	+	+	+	+	+	+	+	0	0	0	0	++	++	+	+++	+++	++
Penicillium italicum	+	0	0	0	0	0	0	0	0	+	0	0	+	0	0	+++	+++	++
Syncephalastrum racemosum	++	+	+	++	++	+	++	+	+	0	0	0	+	+	+	+++	+++	+++
Candida albicans	+	0	0	+	+	0	0	0	0	+	+	+	+	0	0	++	++	++

St.: reference standard; chloramphenicol was used as a standard antibacterial agent and Terbinafin was used as a standard antifungal agent, well diameter: 0.6 cm, inhibition values = 0.1–0.5 cm beyond control = +; inhibition values = 0.6–1.0 cm beyond control = ++; inhibition values = 1.1–1.5 cm beyond control = +++; 0 = not detected.

Table 9
Antibacterial and antifungal activity data for Schiff base ligand H_2L^2 and its metal complexes (**5**–**8**)

	H_2L^2 (free ligand)			**5**			**6**			**7**			**8**			St.		
	5 mg/ml	2.5 mg/ml	1 mg/ml	5 mg/ml	2.5 mg/ml	1 mg/ml	5 mg/ml	2.5 mg/ml	1 mg/ml	5 mg/ml	2.5 mg/ml	1 mg/ml	5 mg/ml	2.5 mg/ml	1 mg/ml	5 mg/ml	2.5 mg/ml	1 mg/ml
Staphylococcus aureus	+	0	0	0	0	0	+	+	0	0	0	0	+	0	0	++	++	++
Pseudomonas aeruginosa	+	0	0	0	0	0	0	0	0	0	0	0	0	0	0	+++	+++	++
Bacillus subtilis	+	+	+	+	0	0	++	+	+	+	+	+	+	+	+	+++	+++	++
Escherichia coli	+	0	0	+	+	0	+	0	0	+	0	0	++	++	0	++	++	++
Aspergillus fumigatus	+	+	+	+	+	+	+	+	+	+	0	0	0	0	+	+++	+++	++
Penicillium italicum	+	+	+	+	+	0	+	0	0	+	+	0	++	+	+	+++	+++	++
Syncephalastrum racemosum	++	++	+	++	+	0	+	+	+	++	++	+	+	+	0	+++	+++	+++
Candida albicans	+	+	+	+	0	0	+	+	0	0	0	0	0	0	0	++	+++	++

St.: reference standard; chloramphenicol was used as a standard antibacterial agent and Terbinafin was used as a standard antifungal agent, well diameter: 0.6 cm, inhibition values = 0.1–0.5 cm beyond control = +; inhibition values = 0.6–1.0 cm beyond control = ++; inhibition values = 1.1–1.5 cm beyond control = +++; 0 = not detected.

Table 10
Antibacterial activity of some known antibiotics

Antibiotic name	*Staphylococcus aureus*	*Pseudomonas aerruginosa*	*Escherichia coli*
Amikacin	R	+++	++
Doxycllin	+++	R	R
Augmantin	+++	R	+++
Sulperazon	+++	+++	R
Unasyn	+++	R	++
Septrin	R	R	R
Cefobid	R	R	R
Ampicillin	R	++	++
Nitrofurantion	+++	R	R
Traivid	R	R	+++
Erythromycin	+++	R	R

R = resistance.

(2) The different coordinated metal ions have different influence towards the tested bacteria and fungi. This result reflects the difference of the way and mechanism that the complexes interact with bacteria and fungi due to the difference in metal ions.
(3) The inhibitation zone of the metal chelates generally is higher than that of the free ligands.
(4) The two ligands and their metal complexes were found to be more effective against the fungi than bacteria species.

Comparison of the antibacterial activity of the synthesized compounds with some known antibiotics shows some metal complexes possess remarkable antimicrobial activity equal to or higher than some possess antibiotics as clear from Table 10.

4. Concluding remarks

In this work, the coordination chemistry of the two Schiff base ligands, HL^1 and H_2L^2 and their metal complexes with cobalt(II), nickel(II), copper(II) and zinc(II) metal ions were described and characterized on the basis of analytical, magnetic and spectral data as well as thermal gravimetric studies. The two Schiff base ligands act as monobasic tridentate, coordinated to the metal ions in a terdentate manner with ONO/ONS donor sites of the carbonyl oxygen, azomethine nitrogen and phenolic oxygen or thiophenic sulphur and in both, the coordination mode of carboxylate group is the unidentate mode. Correlating the experimental data, one can suggest the octahedral structure for the prepared metal complexes. Additionally some metal complexes posses antibacterial and antifungal activity against the selected species of bacteria or fungi more than the free Schiff base ligands which is in accordance with the fact that the chelating of metal to ligands increase the biological activity of the molecule. These results were compared with some known antibiotics showing that, the free ligands or some their metal complexes possess a higher degree of antibacterial activity than the antibiotics itself. The importance of this lies in the fact that these complexes could be applied in the treatment of some common diseases.

References

[1] M. Sonmez, A. Levent, M. Sekerci, Synth. React. Inorg. Met.: Org. Chem. 33 (2003) 1747.

[2] Y.K. Vaghasiya, R. Nair, M. Soni, S. Baluja, S. Chanda, J. Serb. Chem. Soc. 69 (2004) 991.

[3] Y. Elerman, M. Kabak, A. Elmali, Z. Naturforsch. B 57 (2002) 651.

[4] M.M.H. Khalil, M.M. Aboaly, R.M. Ramadan, Spectrochim. Acta A 61 (2005) 157.

[5] N. Chantarasiri, V. Ruangpornvisuti, N. Muangsin, H. Detsen, T. Mananunsap, C. Batiya, N. Chaichit, J. Mol. Struct. 701 (2004) 93.

[6] A.A. Soliman, J. Therm. Anal. Calorim. 63 (2001) 221.

[7] A.A. Soliman, G.G. Mohamed, J. Thermochim. Acta 421 (2004) 151.

[8] E. Tas, M. Aslanoglu, M. Ulusoy, M. Guler, Polish J. Chem. 78 (2004) 903.

[9] G.G. Mohamed, Z.H. Abd El-Wahab, J. Therm. Anal. Calorim. 73 (2003) 347.

[10] Z.H. Abd El-Wahab, M.R. El-Sarrag, Spectrochim. Acta A 60 (2004) 271.

[11] Z.H. Abd El-Wahab, M.M. Mashaly, A.A. Salman, B.A. El-Shetary, A.A. Faheim, Spectrochim. Acta A 60 (2004) 2861.

[12] M.M. Mashaly, Z.H. Abd El-Wahab, A.A. Faheim, Synth. React. Inorg. Met.: Org. Chem. 34 (2004) 229.

[13] M.M. Mashaly, Z.H. Abd El-Wahab, A.A. Faheim, J. Chin. Chem. Soc. 51 (2004) 901.

[14] Z.H. Abd El-Wahab, M.M. Mashaly, A.A. Faheim, J. Chem. Pap. 59 (2005) 25.

[15] G.G. Mohamed, Z.H. Abd El-Wahab, Spectrochim. Acta A 61 (2005) 1059.

[16] P.B. Sreeja, M.R.P. Kurup, Spectrochim. Acta A 61 (2005) 331.

[17] C. Jayabalakrishnan, K. Natarajan, Trans. Met. Chem. 27 (2002) 75.

[18] W. Ference, A.W. Dziewulska, J. Therm. Anal. Calorim. 63 (2001) 865.

[19] M.L. Hu, N.W. Zhu, X.H. Li, F. Chen, Cryst. Res. Technol. 39 (2004) 505.

[20] A. Szorcsik, L. Nagy, L. Pellerito, T. Yamaguchi, K. Yoshida, J. Radioanal. Nucl. Chem. 256 (2003) 3.

[21] A. Szorcsik, L. Nagy, J. Sletten, G. Szalontai, E. Kamu, T. Fiore, L. Pellerito, E. Kalman, J. Organomet. Chem. 689 (2004) 1145.

[22] V.C. Wei, L.Y. Tuan, L.D. Zheng, Chin. J. Chem. 18 (2000) 351.

[23] B.S. Garg, D.N. Kumar, M. Sarbhai, Spectrochim. Acta A 61 (2005) 141.

[24] C. Spinu, A. Kriza, Acta Chim. Slov. 47 (2000) 179.

[25] M. Sonmez, M. Sekerci, Polish J. Chem. 76 (2002) 907.

[26] G.G. Mohamed, M.M. Omar, A.M.M. Hindy, Spectrochim. Acta A 62 (2005) 1140.

[27] A.I. El-Said, J. Therm. Anal. Calorim. 68 (2002) 917.

[28] A.S.M. Al-Shihri, H.M. Abdel-Fattah, J. Therm. Anal. Calorim. 71 (2003) 643.

[29] M.J.M. Takac, D.V. Topic, Acta Pharm. 54 (2004) 177.

[30] E. Tas, M. Aslanoglu, M. Ulusoy, H. Temel, J. Coord. Chem. 57 (2004) 677.

[31] E.A. Bakhite, A.E. Abdel-Rahman, O.S. Mohmed, E.A. Thabet, Bull. Korean Chem. Soc. 23 (2002) 1709.

[32] A. Golcu, M. Tumer, H. Demirelli, R.A. Wheatley, Inorg. Chim. Acta 358 (2005) 1785.

[33] S.F.A. Kettle, Coordination Compounds, Thomas Nelson and Sons Ltd., 1997.

[34] G.G. Mohamed, N.E.A. El-Gamel, Spectrochim. Acta A 60 (2004) 3141.

[35] P.P. Dholakiya, M.N. Patel, Synth. React. Inorg. Met.: Org. Chem. 34 (2004) 383.

[36] V.V. Pavlishchuk, S.V. Kolotilov, A.W. Addison, R.J. Butcher, E. Sinn, J. Chem. Soc. Dalton Trans. (2000) 335.

[37] M.M. Omar, G.G. Mohamed, Spectrochim. Acta A 61 (2005) 929.

[38] N. Raman, S. Ravichandran, C. Thangaraja, J. Chem. Sci. 116 (2004) 215.

[39] M.S.A. El-Gaby, Chin. Chem. Soc. 51 (2004) 125.