

TRANSITION METAL COMPLEXES OF HETEROCYCLIC SCHIFF BASE

Biological activity, spectroscopic and thermal characterization

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Metal complexes of Schiff base derived from 2-furancarboxaldehyde and 2-aminobenzoic acid (HL) are reported and characterized based on elemental analyses, IR, ^1H NMR, UV-Vis, solid reflectance, magnetic moment, molar conductance and thermal analysis. The ligand dissociation as well as the metal-ligand stability constants have been calculated pH-metrically at 25°C and ionic strength $\mu=0.1$ (1 M NaCl). The complexes are found to have the formulae $[\text{M}(\text{HL})_2](\text{X})_n \cdot y\text{H}_2\text{O}$ (where $\text{M}=\text{Fe}(\text{III})$ ($\text{X}=\text{Cl}$, $n=3$, $y=4$), $\text{Co}(\text{II})$ ($\text{X}=\text{Cl}$, $n=y=2$), $\text{Ni}(\text{II})$ ($\text{X}=\text{Cl}$, $n=y=2$), $\text{Cu}(\text{II})$ ($\text{X}=\text{Cl}$, $n=y=2$) and $\text{Zn}(\text{II})$ ($\text{X}=\text{AcO}$, $n=y=2$)) and $[\text{UO}_2(\text{L})_2] \cdot 2\text{H}_2\text{O}$. The thermal behaviour of these chelates is studied and the activation thermodynamic parameters are calculated using Coats-Redfern method. The ligand and its metal complexes show a biological activity against some bacterial species.

Keywords: biological activity, metal complexes, spectroscopic studies, stability constants, thermal analysis

Introduction

Many Schiff bases and their complexes have been widely studied because of their industrial applications [1]. Some Schiff bases are tested for fungicidal activity, which is related to their chemical structure [2]. Schiff base compounds containing an imine group ($-\text{RC}=\text{N}-$), are usually formed by the condensation of a primary amine with an active carbonyl. The interest in Schiff base compounds as analytical reagents is increasing, since they enable simple and unexpensive determinations of different organic and inorganic substances [3].

The present study describes the chelation behaviour of Schiff base derived from the condensation of anthranilic acid with 2-furan carboxaldehyde (HL) towards some d-block elements, which may help in more understanding of the mode of chelation of HL towards metals. For this purpose the complexes of Fe(III), Co(II), Ni(II), Cu(II), Zn(II), and $\text{UO}_2(\text{II})$ with HL are studied in solution and in the solid state. The stability constants are evaluated and structure of the studied complexes is elucidated using IR, magnetic, UV-vis diffuse reflectance, mass spectral, and ^1H NMR measurements, and thermogravimetric analysis.

Experimental

Materials

All chemicals used were of the analytical reagent grade (AR). Metal solutions were standardized by recommended procedures [4].

Synthesis of Schiff base (HL)

Hot solution (60°C) of 2-aminobenzoic acid (2.74 g, 10 mmol) in 25 mL ethanol was mixed with hot solution (60°C) of 2-furancarboxaldehyde (1.92 g, 10 mmol) in the same solvent and the reaction mixture was left under reflux for 2 h. The formed solid products were separated by filtration, purified by crystallization from ethanol, washed with diethyl ether and dried in a vacuum over anhydrous calcium chloride. The yellow Schiff base product; HL, is produced in 80% yield.

Synthesis of metal complexes

Hot solution (60°C) of the appropriate metal chloride, nitrate or acetate (1 mmol) in an ethanol-water mixture (1:1, 25 mL) was added to the hot solution (60°C) of the HL Schiff base (0.215 g, 2 mmol) in the same solvent (25 mL). The resulting mixture was stirred under reflux for one hour whereupon the complexes precipitated. They were collected by filtration, washed with a 1:1 ethanol:water mixture and diethyl ether. The analytical data for C, H and N were repeated twice.

Biological activity

0.5 mL spore suspension (10^{-6} – 10^{-7} spore mL^{-1}) of each of the investigated organisms was added to a sterile agar medium just before solidification, then poured into sterile petri dishes (9 cm in diameter) and left to solidify. Using sterile cork borer (6 mm in diameter), three holes (wells) were made in each dish,

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then 0.1 mL of the tested compounds dissolved in DMF ($100 \mu\text{g mL}^{-1}$) were poured into these holes. Finally, the dishes were incubated at 37°C for 48 h where clear or inhibition zones were detected around each hole. 0.1 mL DMF alone was used as a control under the same condition for each organism and by subtracting the diameter of inhibition zone resulting with DMF from that obtained in each case, both antibacterial activities can be calculated as a mean of three replicates [7].

Instrumental methods

The spectrophotometric measurements in solution were carried out using automated spectrophotometer UV-vis Perkin-Elmer Model Lambda 20 ranged from 200 to 900 nm. pH measurements were carried out using 716 DMS Titrino Metrohm connected with 728 Metrohm Stirrer. The molar conductance of solid complexes in DMF was measured using Sybron-Barnstead conductometer (Meter-PM.6, $E=3406$). Elemental microanalyses of the ligand and the separated solid chelates for C, H, N and S were performed in the Microanalytical Center, Cairo University using Perkin-Elmer 2400 CHN Elemental Analyzer. The PE 2400 CHN uses a combustion method to convert the sample elements to simple gases (CO_2 , H_2O and N_2), which are measured as a function of thermal conductivity. Metal (II) contents were determined by standard complexometric titration [4]. Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in the wavenumber region $4000\text{--}200 \text{ cm}^{-1}$. The UV-Vis diffuse reflectance spectra were measured on a Shimadzu 3101 pc spectrophotometer. The molar magnetic susceptibil-

ity was measured on powdered samples using the Faraday method [5]. The diamagnetic corrections were made by Pascal's constant and $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a calibrant.

The thermogravimetric analysis (TG and DTG) was carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of $10^\circ\text{C min}^{-1}$ using Shimadzu TGA-50 H thermal analyzer. The mass spectra were recorded by the EI technique at 70 eV using MS-5988 GS-MS Hewlett-Packard instrument in the Microanalytical Center, Cairo University. The ^1H NMR spectra were recorded on a JEOL FX90 Q NMR Spectrometer at 25°C .

The potentiometric measurements were carried out at 25°C and ionic strength $\mu=0.1$ by addition of appropriate amounts of 1 M sodium chloride solution. The ionization constants of the Schiff base (HL) and the stability constants of its metal chelates with Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and $\text{UO}_2(\text{II})$ ions were determined potentiometrically using the technique of Sarin and Munshi [6].

Results and discussion

The results of elemental analyses (C, H, N) with molecular formula and the melting point of the Schiff base; HL, are presented in Table 1. The results obtained are in good agreement with that calculated for the suggested formula and the melting point is sharp indicating the purity of the prepared Schiff base. The structure of the Schiff base under study is given in Fig. 1.

The mass spectrum of HL and the possible molecular ion peaks with their respective relative intensities are shown in Scheme 1. The different pathways

Table 1 Analytical and physical data of HL and its complexes

Compound	Colour/ (yield%)	M.p./ $^\circ\text{C}$	Found (calcd)/%				μ_{eff} (B.M.)	$\Delta m/$ $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$
			C	H	N	M		
HL $\text{C}_{12}\text{H}_9\text{NO}_3$	yellow (80)	180 ± 2	66.73 (66.98)	4.53 (4.19)	6.32 (6.51)	—	—	—
$[\text{Fe}(\text{HL})_2]\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ $\text{C}_{24}\text{H}_{26}\text{Cl}_3\text{FeN}_2\text{O}_{10}$	Black (68)	>300	43.75 (43.34)	3.68 (3.91)	4.05 (4.21)	8.12 (8.43)	5.82	332
$[\text{Co}(\text{HL})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ $\text{C}_{24}\text{H}_{22}\text{Cl}_2\text{CoN}_2\text{O}_8$	Brown (63)	>300	48.48 (48.32)	3.43 (3.69)	4.83 (4.70)	9.57 (9.90)	5.73	205
$[\text{Ni}(\text{HL})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ $\text{C}_{24}\text{H}_{22}\text{Cl}_2\text{NiN}_2\text{O}_8$	Brown (73)	>300	48.6 (48.32)	3.39 (3.69)	4.83 (4.70)	10.05 (9.90)	4.02	215
$[\text{Cu}(\text{HL})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ $\text{C}_{24}\text{H}_{22}\text{Cl}_2\text{CuN}_2\text{O}_8$	Deep green (65)	>300	47.72 (47.96)	3.90 (3.66)	4.42 (4.66)	10.33 (10.57)	1.93	200
$[\text{Zn}(\text{HL})_2](\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_{12}\text{Zn}$	Brown (72)	>300	51.96 (51.96)	3.54 (3.39)	4.74 (4.31)	9.65 (10.01)	Diam.	178
$[\text{UO}_2(\text{L})_2] \cdot 2\text{H}_2\text{O}$ $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_7\text{U}$	Brown (77)	>300	38.84 (39.24)	2.50 (2.30)	3.57 (3.81)	—	Diam.	32.50

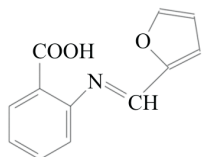


Fig. 1 Structure of Schiff base

of the fragments of the parent molecular ion peaks are also given in Scheme 1. Fragments at $m/z = 119$ (R. I.=100%, base peak) may be due to C_7H_4NO ion. The other molecular ion peaks appeared in the mass spectrum (abundance range from 2–100%) are attributed to the fragmentation of HL molecule obtained from the rupture of different bonds inside the molecule as shown below in Scheme 1.

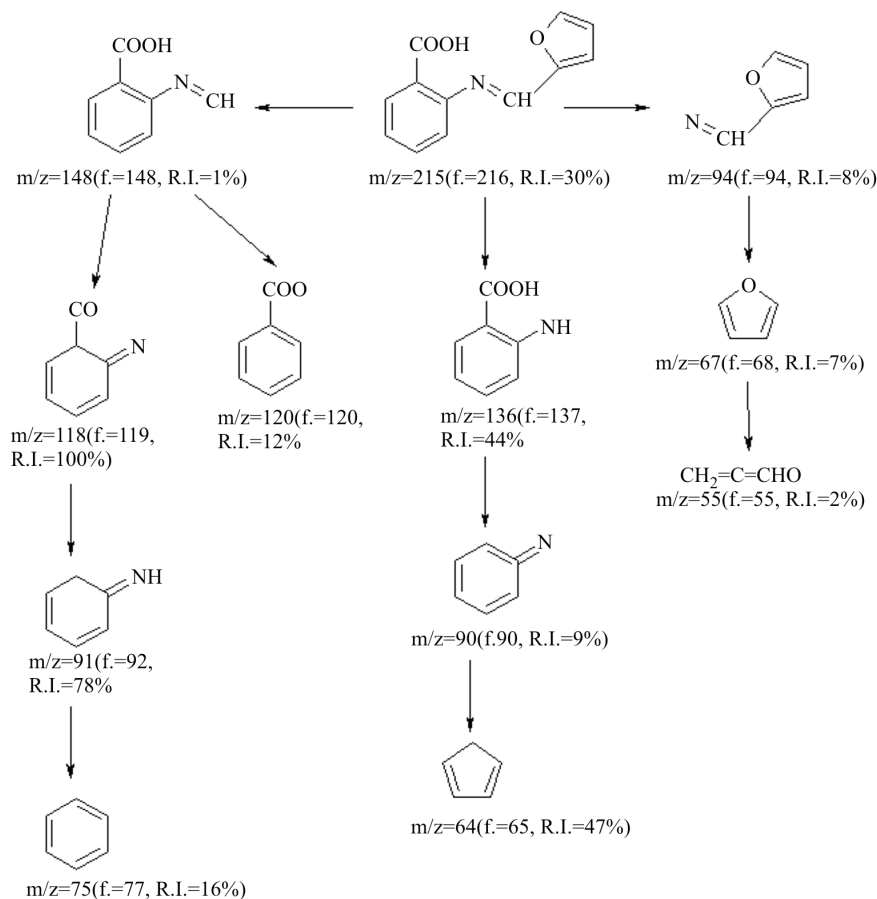
UV-Vis spectra for $2.5 \cdot 10^{-3}$ M solution of HL in absolute ethanol show three bands (Fig. 2) at 222, 229 and 240 nm beside a broad band at 331 nm with molar absorptivities (ϵ) $4.25 \cdot 10^3$, $4.15 \cdot 10^3$, $4.30 \cdot 10^3$ and $0.10 \cdot 10^3$ L mol $^{-1}$ cm $^{-1}$, respectively.

Ligand dissociation and metal-ligand stability constants

The ligand dissociation constant was determined using Irving and Rossotti [8]. It is found that HL Schiff

base has a pK_a value of 6.6 which can be attributed to the deprotonation of the carboxylate group. The free energy change, ΔG° , was also calculated and found to be 37.50 kJ mole $^{-1}$. The positive value indicates the nonspontaneous character of dissociation reaction.

The stability constants of the Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and UO $_2$ (II) complexes with HL are determined potentiometrically using the method described by Sarin [6] and Bjerrum [9]. The mean $\log\beta_1$ and $\log\beta_2$ values for the complexes are listed in Table 2. Three methods are applied for computing successive stability constants [10] namely Interpolation at half values, Correction-term and Mid-point. The complex-forming abilities of the transition metal ions are frequently characterized by stability orders. The order of stability constants was found to be $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ in accordance with the Irving and Williams order [11] for divalent metal ions of the 3d series. It is clear from Table 2 that the stability of Cu(II) complex is considerably larger as compared to other metals of the 3d series. Under the influence of the ligand field, Cu(II) ($3d^9$) will receive some extra stabilization [12] due to tetragonal distortion of octahedral symmetry in their complexes. The Cu(II) complex will be further stabilized due to the Jahn-Teller effect [12]. The free energy of formation, ΔG° , ac-

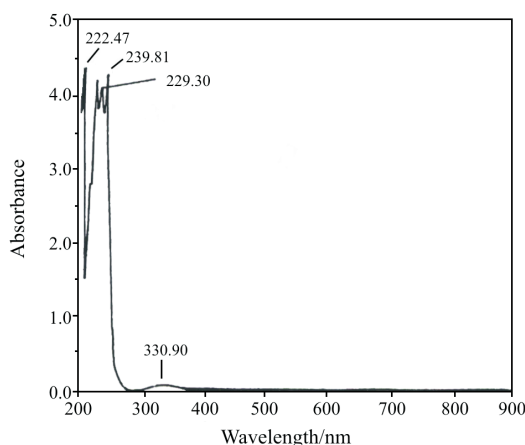


Scheme 1 Mass fragmentation pattern of HL

Table 2 $\log\beta_1$ and $\log\beta_2$ values for complexes of HL with Fe(III), UO₂(II), Co(II), Ni(II), Cu(II) and Zn(II)

Ion	$\log\beta_1$			$-\Delta G^\circ /$ kJ mol ⁻¹	$\log\beta_2$				$-\Delta G^\circ /$ kJ mol ⁻¹
	A	B	M		A	B	C	M	
Fe(III)	7.665	7.670	6.995	39.89	14.660	14.650	13.99	14.43	82.29
UO ₂ (II)	7.651	7.630	7.065	40.30	14.051	14.150	14.13	14.11	80.47
Co(II)	7.535	7.440	7.075	40.35	13.935	14.065	14.15	14.05	80.12
Ni(II)	7.600	7.575	7.175	40.92	14.050	14.250	14.35	14.21	81.04
Cu(II)	7.700	7.806	7.215	41.15	14.225	14.460	14.43	14.37	81.96
Zn(II)	7.645	7.610	7.190	41.02	14.145	14.285	14.38	14.27	81.39

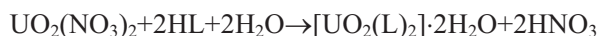
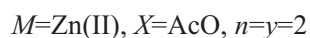
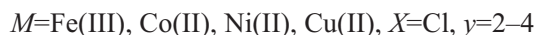
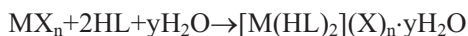
where A – interpolation at half values method; B – correction-term method; C – midpoint method; M – mean

**Fig. 2** Electronic absorption spectra of $2.5 \cdot 10^{-3}$ M HL absolute ethanol

companying the complexation reaction has been determined at 25°C. From Table 2, it is apparent that the negative values of ΔG° show that the driving tendency of the complexation reaction is from left to right and the reaction proceeds spontaneously.

Composition and structures of Schiff base complexes

The solid complexes under study were subjected to elemental analyses (C, H, N), IR, ¹H NMR, magnetic studies, molar conductance, mass spectra and thermal analysis (TG), to identify their tentative formulae in a trial to elucidate their molecular structures. The results of elemental analyses; Table 1, are in good agreement with those required by the proposed formulae. The formation of these complexes may proceed according to the following equations given below.



Molar conductivity measurements

The chelates were dissolved in DMF and the molar conductivities of 10^{-3} M of their solutions at $25 \pm 2^\circ\text{C}$ were measured. Table 1 shows the molar conductance values of the complexes. It is concluded from the results that Fe(III) chelate is found to have molar conductance value of $332 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, indicating the ionic nature of this complex. It, also, indicates the non-bonding of the chloride anions to the Fe(III). So, the Fe(III) chelate is considered as 3:1 electrolyte. On the other hand, the molar conductivity values of Zn(II), Cu(II), Co(II) and Ni(II) chelates are found to be in the range $178-215 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. It is obvious from these data that these chelates are ionic in nature and they are of the type 2:1 electrolytes. While UO₂(II) complex has $\Lambda_m = 32.50 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, which indicates the non-ionic nature of this complex, it is considered a non-electrolyte.

IR spectra and mode of bonding

The data of the IR spectra of Schiff base ligand (HL) and its complexes are listed in Table 3. The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may get involved in chelation. Upon comparison it was found that the $\nu_{(C=N)}$ stretching vibration is found in the free ligand at 1663 cm^{-1} . This band is shifted to higher (21 cm^{-1}) or lower ($7-49 \text{ cm}^{-1}$) wavenumbers in the complexes indicating the participation of the azomethine nitrogen in coordination (M—N) [13]. The $\nu_{(OH)}$, $\nu_{(C=O)}$, $\nu_{\text{asym}(\text{COO})}$ and $\nu_{\text{sym}(\text{COO})}$ stretching vibrations are observed at 3319, 1731, 1579 and 1441 cm^{-1} for HL. The participation of the carboxylate O atom in the complexes formation was evidenced from the disappearance or shift in position of these bands to $3275-3309$, $1703-1708$, $1580-1603$ and $1381-1407$ in the metal complexes [14]. A medium to sharp band due to $\nu_{(C-O-C)}$ stretching vibration of furan appeared at 1252 cm^{-1} for HL ligand [15]. This band is shifted to $1233-1293 \text{ cm}^{-1}$ in the metal complexes [15]. These shifts refer to the coordination through furan O

Table 3 IR data (4000–400 cm⁻¹) of HL and its metal complexes

Compound	ν_{OH} (carboxylic)	$\nu_{\text{C=O}}$ (carboxylic)	ν_{COO} (asym.)	ν_{COO} (sym.)	$\nu_{\text{C-N}}$	$\nu_{\text{C-O-C}}$ (furan)	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$ (furan)	$\nu_{\text{M-O}}$ (carboxylic)
HL	3391sh	1731sh	1579sh	1411sh	1663sh	1252sh	—	—	—
[Fe(HL) ₂][Cl ₃ ·4H ₂ O]	3300br	1704s	1580sh	1399sh	1618sh	1260sh	430s	482sh	563m
[Co(HL) ₂][Cl ₂ ·2H ₂ O]	3309sh	Disappear	1592sh	1407sh	1614s	1242sh	465w	516s	564s
[Ni(HL) ₂][Cl ₂ ·2H ₂ O]	3307sh	Disappear	1594sh	1407sh	1656s	1241s	425s	520s	567s
Cu(HL) ₂ Cl ₂ ·2H ₂ O	3375sh	1708s	1603sh	1381sh	1684s	1233sh	424w	483s	564s
[Zn(HL) ₂](AcO) ₂ ·2H ₂ O	3300sh	1703w	1593sh	1404sh	1656s	1293br	468s	516w	564s
[UO ₂ (L) ₂].2H ₂ O	3300br	Disappear	1601sh	1407s	1652s	1289s	425s	463s	567s

sh=sharp, *m*=medium, *br*=broad, *s*=small, *w*=weak

atom. New bands are found in the spectra of the complexes in the regions 463–520 (furan O) and 563–567 (carboxylate O), which are assigned to $\nu(\text{M}-\text{O})$ stretching vibrations for metal complexes [14, 15]. The bands at 424–468 in metal complexes, have been assigned to $\nu_{(\text{M}-\text{N})}$ mode [14, 15].

Therefore, it is concluded that HL Schiff base behaves as a neutral terdentate ligand in all the complexes except $\text{UO}_2(\text{II})$ complex, it acts as a uni-negatively coordinated to the $\text{UO}_2(\text{II})$ ion via its deprotonated carboxylated O beside the azomethine N and furan O.

¹H NMR spectra

The chemical shifts of the different types of protons in the ¹H NMR spectra of the Schiff base and its diamagnetic Zn(II) complex are listed in Table 4. Upon examination it was found that the COOH signal is found at 9.62 ppm in the spectra of HL ligand. This signal is deshielded at 8.25 ppm in case of Zn(II)-HL complex indicating the participation of the COOH group in chelation without proton displacement. Coordination through the lone pair of electrons on the O atom is expected. New signals are observed at 2.89 ppm for Zn(II) complex with HL, with an integration corresponding to six protons. The signals are assigned to two acetate molecules. Also the signals observed at 3.31 ppm with an integration corresponding to four protons in case of Zn(II) complex with HL ligand, are assigned to two water molecules.

Magnetic susceptibility and electronic spectra measurements

From the diffuse reflectance spectrum, it is observed that, the Fe(III) chelate exhibits a band at 22,026 cm^{-1} , which may be assigned to the ${}^6\text{A}_{1g} \rightarrow \text{T}_{2g}(\text{G})$ transition in octahedral geometry of the complexes [9, 12]. The ${}^6\text{A}_{1g} \rightarrow {}^5\text{T}_{1g}$ transition appears to be split into two bands at 16,313–17,636 and 12,626–13,020 cm^{-1} . The observed magnetic moment of Fe(III) complex is 5.82 B.M. Thus, the complex formed has the octahedral geometry [14]. The spec-

trum shows also a band at 25,510 cm^{-1} which may be attributed to ligand to metal charge transfer. The Ni(II) complex has a room temperature magnetic moment value of 3.02 B.M.; which is in the normal range observed for octahedral Ni(II) complexes ($\mu_{\text{eff}}=2.9\text{--}3.3$ B.M) [16]. This indicates that, the Ni(II) complex is six-coordinate and probably octahedral [13, 16]. Its electronic spectrum shows in addition the $\pi\text{--}\pi^*$ and $n\text{--}\pi^*$ bands of free ligand, display three bands, in the solid reflectance spectrum at ν_1 : 13,987 cm^{-1} : ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$; ν_2 : 16,155 cm^{-1} : ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ν_3 : 22,522 cm^{-1} : ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$. The spectrum also shows a band at 27,173 cm^{-1} which may be attributed to ligand to metal charge transfer. The electronic spectrum of the Co(II) complex gives three bands at 13,157, 16,611 and 22,123 cm^{-1} . The bands observed are assigned to the transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1), ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ (ν_2) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$ (ν_3), respectively, suggesting that there is an octahedral geometry around Co(II) ion [13, 14, 17]. The spectrum shows also a band at 27,027 cm^{-1} , which may be attributed to ligand to metal charge transfer. The magnetic susceptibility measurement, found to be 5.13 B.M. (normal range for octahedral Co(II) complexes is 4.3–5.2 B.M.), is indicative of octahedral geometry [17]. The reflectance spectrum of Cu(II) chelate consists of a broad, low intensity shoulder band centered at 16,420 and 22,026 cm^{-1} . The ${}^2\text{E}_g$ and ${}^2\text{T}_{2g}$ states of the octahedral Cu(II) ion (d^9) split under the influence of the tetragonal distortion and the distortion can therefore be such as to facilitate the three transitions ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$; ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ which remain unresolved in the spectra [17, 18]. It is concluded that, all three transitions lie within the single broad envelope observed at the same range previously mentioned [17]. The magnetic moment of 1.93 B.M. falls within the range normally observed for octahedral Cu(II) complexes [17, 18]. A moderately intense peak observed in the range 26,455 cm^{-1} is due to ligand – metal charge transfer transition.

The complexes of Zn(II) and $\text{UO}_2(\text{II})$ are diamagnetic. In analogy with those described for Zn(II) complexes containing N–O donor Schiff bases

Table 4 ¹H NMR spectral data of the Schiff base and its Zn(II) chelate

Compound	Chemical shift (δ)/ppm	Assignment
HL	9.62	(s, 1H, COOH)
	6.46–8.31	(m, 8H, 4ArH, 1 azomethine, 3 furan H)
	2.6	(CH ₃ of solvent)
[Zn(HL)](AcO) ₂ ·2H ₂ O	8.25	(s, 2H, COOH)
	7.96	(s, 2H, azomethine H)
	6.45–7.77	(m, 14H, 8ArH, 6furan H)
	3.31	(s, 4H, 2H ₂ O)
	2.89	(s, 6H, CH ₃ COO)
	2.45	(CH ₃ of solvent)

[19–21] and according to the empirical formulae of these complexes, we propose an octahedral geometry for the Zn(II) and UO₂(II) complexes.

Thermal analyses (TG)

The thermal decomposition of the complexes is used to obtain information about their properties as well as about the nature of intermediate and final products [22].

The TG curve of Schiff base HL (Fig. 3A), refers to two mass loss steps at 180–750°C. These steps involve mass losses of 100.0% (found 100.0%) decomposition. These mass losses may be due to the successive losses of C₁₂H₉NO₃ at the given temperature ranges, respectively. The curves of Fe(III) chelate (Fig.3B) shows three decomposition steps within the temperature range 25–620°C. The first two steps of decomposition within the temperature range 25–280°C correspond to the loss of water molecules of hydration, 3HCl, ½H₂ and O₂ gases with a mass loss of 26.60% (calcd. 26.86%). The energies of activation were 25.97 and 64.87 kJ mol⁻¹ for the first and second step, respectively. The subsequent step (280–620°C) corresponds to the removal of the organic part of the ligand leaving metal oxide as a residue with an activation energy of 99.05 kJ mol⁻¹. The overall mass loss amounts to 88.57% (calcd. 87.96%).

The TG curve of the Ni(II) chelate (Fig. 3C) shows three steps of decomposition within the temperature range of 30–900°C. The first steps at 30–120°C corresponds to the loss of water molecules of hydration with an activation energy of 45.45 kJ mol⁻¹. While the subsequent (2nd and 3rd) steps involve the loss of 2HCl and ligand molecules. The energies of activation were 53.97 and 195.60 kJ mol⁻¹ for the second and third steps, respectively. The overall mass loss amounts to 87.45% (calcd. 87.42%). On the other hand, [Cu(HL)₂]Cl₂·2H₂O chelate exhibits three decomposition steps. The first step in the temperature range 30–110°C (mass loss = 6.56%; calcd. for 2H₂O; 5.99%) may account for the loss of water molecules of hydration. The activation energy of this dehydration step is 66.86 kJ mol⁻¹. The mass losses of the remaining decomposition steps amount to 80.79% (calcd. 80.77%). They correspond to the removal of 2HCl and HL molecules leaving CuO as a residue with energies of activation amount to 155.7 and 254.3 kJ mol⁻¹ for the second and third steps, respectively. The TG curve of the UO₂(II) chelate(Fig. 3E) represents three decomposition steps. The first step of decomposition within the temperature range 30–120 °C corresponds to the loss of water molecules of hydration with a mass loss of 4.65% (calcd. for 2H₂O; 4.90%) and an activation energy of

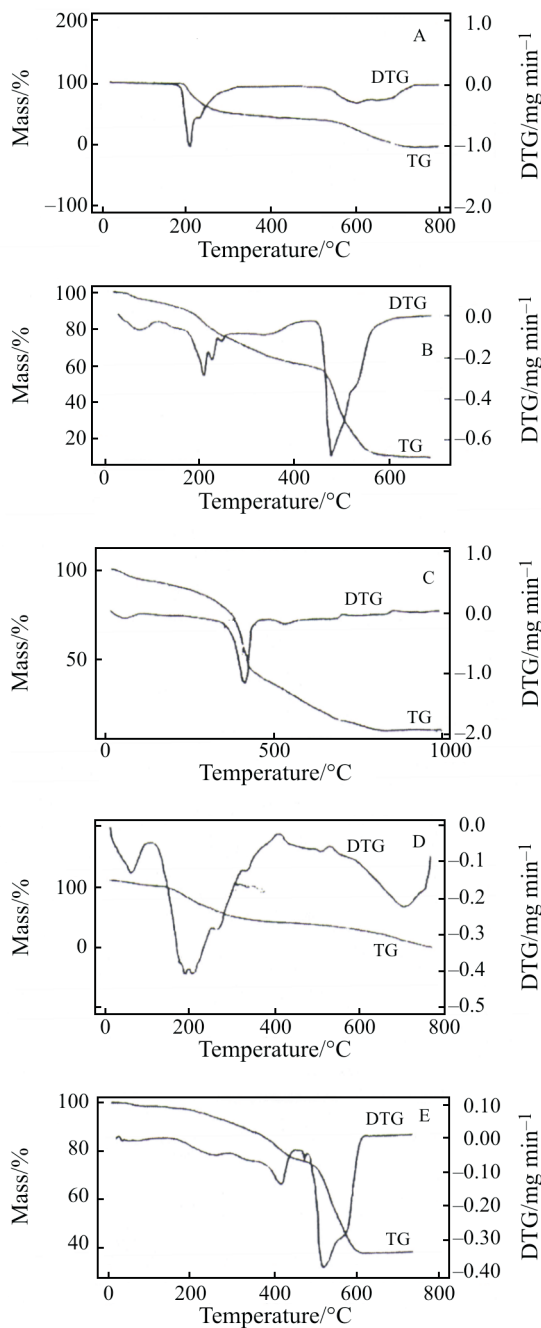


Fig. 3 Thermal analysis of HL and its complexes; where A – ligand HL, B – Fe(III), C – Ni(II), D – Cu(II), E – UO₂(II)

56.59 kJ mol⁻¹. The remaining steps of decomposition within the temperature range 120–650°C correspond to the removal of HL ligand as gases. The energies of activation were 168.7 and 242.6 kJ mol⁻¹ for the second and third steps; respectively. The overall mass losses amount to 63.18% (calcd. 63.21%). The Data are listed in Table 5.

Table 5 TG and DTG results of HL and its metal complexes

Complex	TG range/°C	DTG _{max} /°C	n*	Mass loss		Assignment	Metallic residue
				Estim. (calcd.)/%	Total mass loss		
HL	180–400	225	1	44.22 (43.72)	100.0 (100.0)	Loss of C ₅ H ₄ NO Loss of C ₇ H ₅ O ₃	–
	400–750	600	1	55.78 (56.28)			
(1)	25–280	70, 210	2	26.60 (26.86)	88.57 (87.96)	Loss of 2H ₂ O, 3HCl, 1/2H ₂ and O ₃ Loss of C ₂₄ H ₁₈ N ₂ O _{1.5}	1/2Fe ₂ O ₃
	280–620	480	1	61.97 (61.10)			
(2)	30–120	73	1	6.41 (6.04)	87.45 (87.42)	Loss of 2H ₂ O Loss of 2HCl and C ₁₂ H ₇ NO ₃ Loss of C ₁₂ H ₉ NO ₃	NiO
	120–450	400	1	48.56 (47.99)			
(3)	450–900	800	1	32.48 (33.39)	87.35 (86.76)	Loss of 2H ₂ O Loss of 2HCl and C ₂₄ H ₁₆ N ₂ O ₅	CuO
	30–110	78	1	6.56 (5.99)			
(4)	110–750	223, 600	2	80.79 (80.77)	63.18 (63.21)	Loss of 2H ₂ O Loss of C ₂₄ H ₁₆ N ₂ O ₆	UO ₂
	30–120	65	1	4.65 (4.90)			
	120–650	410, 527	2	58.53 (58.31)			

n* = number of decomposition steps

(1) [Fe(HL)₂]Cl₃·4H₂O, (2) [Ni(HL)₂]Cl₂·2H₂O, (3) [Cu(HL)₂]Cl₂·2H₂O, (4) [UO₂(L)₂]·2H₂O

Kinetic studies

The thermodynamic activation parameters of decomposition processes of dehydrated complexes namely activation energy (E^*), enthalpy (ΔH^*), entropy (ΔS^*) and Gibbs free energy change (ΔG^*) of the decomposition were evaluated graphically employing the Coats-Redfern relation [23]:

$$\log \left[\frac{\log \{W_f / (W_f - W)\}}{T^2} \right] = \log \left[\frac{AR}{\theta E^*} \left(1 - \frac{2RT}{E^*} \right) \right] - \frac{E^*}{2.303RT} \quad (1)$$

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to temperature T ; R is the gas constant, E^* is the activation energy in kJ mol^{-1} , θ is the heating rate and $(1 - (2RT/E^*)) \cong 1$. A plot of the left-hand side of Eq. (1) vs. $1/T$ gives a slope from which E^* was calculated and A (Arrhenius factor) was determined from the intercept. The entropy of activation (ΔS^*), enthalpy of activation (ΔH^*) and the free energy change of activation (ΔG^*) were calculated using the following equations:

$$\Delta S^* = 2.303[\log(Ah/kT)]R \quad (2)$$

$$\Delta H^* = E^* - RT \quad (3)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (4)$$

The data are summarized in Table 6. The activation energies of decomposition were found to be in the range 25.97–254.3 kJ mol^{-1} . The high values of the activation energy reflect the thermal stability of the complexes. The negative values of S^* indicate that the reactions are slow in nature, hence assisted by the wide range of decomposition temperature [24].

Structural interpretation

The structures of the complexes of HL Schiff base with Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and $\text{UO}_2(\text{II})$

ions were confirmed by the elemental analyses, IR, NMR, molar conductance, magnetic, solid reflectance, UV-Vis, mass and thermal analysis data. Therefore, from the IR spectra, it is concluded that HL ligand behaves as a neutral terdentate ligand in all the complexes except $\text{UO}_2(\text{II})$ complex, it acts as a uni-negatively coordinated to the $\text{UO}_2(\text{II})$ ion via its deprotonated carboxylated O beside the azomethine N and furan O. From the molar conductance data, it is found that the Fe(III) chelate is considered as 3:1 electrolyte, Co(II), Ni(II), Cu(II) and Zn(II) chelates are of the type 2:1 electrolytes, while $\text{UO}_2(\text{II})$ complex is considered as nonelectrolyte. The ^1H NMR spectra of the free ligand and its diamagnetic Zn(II) complex show that the COOH signal of HL ligand participate in chelation without proton displacement. Coordination through the lone pair of electrons on the O atom is expected. On the basis of the above observations and from the magnetic and solid diffuse reflectance measurements, octahedral geometry is suggested for the investigated complexes.

As a general conclusion, the investigated Schiff base behaves as a tridentate and its metal complex structures can be given as shown in Fig. 4.

Biological activity

All of the tested compounds showed a remarkable biological activity against different types of Gram-positive

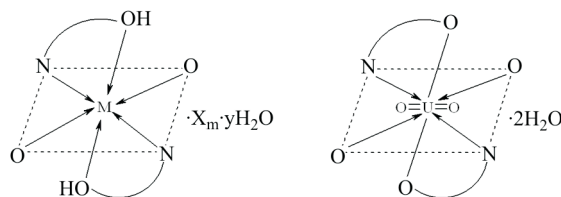


Fig. 4 Structural formulae of metal complexes $M = \text{Fe(III)}$, $X = \text{Cl}$, $m = 3$, $y = 4$. Co(II) , $X = \text{Cl}$, $m = 2$, $y = 2$. Ni(II) , $X = \text{Cl}$, $m = 2$, $y = 2$. Cu(II) , $X = \text{Cl}$, $m = 2$, $y = 2$. Zn(II) , $X = \text{AcO}$, $m = 2$, $y = 2$

Table 6 Thermodynamic data of the thermal decomposition of metal complexes of HL

Complex	Decomp. Temp./ $^{\circ}\text{C}$	$E^*/\text{kJ mol}^{-1}$	A/s^{-1}	$\Delta S^*/\text{JK}^{-1} \text{mol}^{-1}$	$\Delta H^*/\text{kJ mol}^{-1}$	$\Delta G^*/\text{kJ mol}^{-1}$
[Fe(HL) ₂]Cl ₃ ·4H ₂ O	25–110	25.97	$3.79 \cdot 10^6$	-118.2	63.98	72.25
	160–280	64.87	$4.05 \cdot 10^9$	-106.7	71.69	94.10
	450–560	99.05	$7.61 \cdot 10^{13}$	-194.6	48.99	178.40
[Ni(HL) ₂]Cl ₂ ·2H ₂ O	30–120	45.45	$2.26 \cdot 10^5$	-106.9	74.82	82.60
	330–460	53.97	$7.53 \cdot 10^7$	-148.9	91.47	151.00
	550–680	195.6	$2.09 \cdot 10^{12}$	-183.0	205.9	352.30
[Cu(HL) ₂]Cl ₂ ·2H ₂ O	30–110	66.86	$6.22 \cdot 10^{10}$	-36.83	51.23	54.10
	150–380	155.7	$4.98 \cdot 10^{11}$	-169.8	94.6	132.50
	600–750	254.3	$5.89 \cdot 10^{17}$	-204.6	152.0	287.00
[UO ₂ (L) ₂]·2H ₂ O	30–120	56.59	$3.09 \cdot 10^9$	-41.59	66.77	69.50
	180–430	168.7	$5.27 \cdot 10^{13}$	-65.64	186.3	213.20
	460–620	242.6	$3.47 \cdot 10^{12}$	-93.49	247.6	246.90

Table 7 Biological activity of HL and its metal complexes

Sample	<i>Staphylococcus pyogenes</i>			<i>Pseudomonas aeruginosa</i>			<i>Fungus (candida)</i>			<i>Escherichia coli</i>		
	5	2.5	1	5	2.5	1	5	2.5	1	5	2.5	1
HL	+	+	-	+	-	-	+	-	-	++	+	+
[Fe(HL) ₂]Cl ₃ ·4H ₂ O	++	+	-	++	+	-	+	-	-	+++	++	+
[Co(HL) ₂]Cl ₂ ·2H ₂ O	++	+	+	++	++	+	+	-	-	++	++	+
[Ni(HL) ₂]Cl ₂ ·2H ₂ O	++	+	-	+++	++	+	+	-	-	++	+	-
Cu(HL) ₂ Cl ₂ ·2H ₂ O	++	+	-	++	+	+	+	-	-	++	++	+
[Zn(HL) ₂ (AcO) ₂ ·2H ₂ O	++	++	+	+++	++	+	+	-	-	++	+	-
[UO ₂ (L) ₂]·2H ₂ O	+++	++	+	++	++	+	+	-	-	++	+	+
Traivid	++	+	-	++	+	-	-	-	-	++	+	-
Travinic	+++	++	+	+++	++	+	-	-	-	+++	++	+

The test was done using the diffusion agar technique.

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=+++

and Gram-negative bacteria. The data are listed in Table 7. On comparing the biological activity of the Schiff base and its metal complexes with the standard (Traivid and Tavinic), the following results are obtained:

The biological activity of HL is less than Tavinic and comparable with that of Traivid (standard). The biological activity of all metal complexes is higher than that of the free HL ligand, equal to that of standard Traivid and less than that of standard Tavinic. The biological activity of the complexes follow the order UO₂(II)>Zn(II)>Co(II)>Fe(III)=Cu(II)=Ni(II). Also the data in Table 7 show that *E. Coli* was inhibited by Fe(III) complex. The importance of this lies in the fact that these complexes could be applied fairly in the treatment of some common diseases caused by *E. Coli* e.g. Septicaemia, Gastroenteritis, Urinary tract infections and hospital acquired infections [25, 26]. However, Ni(II), Zn(II) and UO₂(II) complexes were specialised in inhibiting Gram-positive bacterial strains (*Staphylococcus pyogenes* and *Pseudomonas aeruginosa*). The importance of this unique property of the investigated Schiff base complexes lies in the fact that, it could be applied safely in the treatment of infections caused by any of these particular strains. In addition, all metal complexes inhibiting Fungi at high concentration (5 mg L⁻¹) more than the parent ligand and standards.

Conclusions

Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and UO₂(II) complexes of Schiff base derived from 2-aminobenzoic acid and 2-furancarboxaldehyde were prepared and characterized and the study reveals that:

- Fe(III) complex is considered as 3:1 electrolyte, Co(II), Ni(II), Cu(II) and Zn(II) complexes are ionic in nature and they are of the type 2:1 electrolytes. While UO₂(II) complex is non-ionic in nature and is considered as non-electrolyte.
- HL Schiff base behaves as a neutral terdentate ligand in all the complexes except UO₂(II) complex. It acts as a uni-negatively coordinated to the UO₂(II) ion via its deprotonated carboxylated O beside the azomethine N and furan O.
- All studied complexes have octahedral geometry.
- Thermal decomposition of complexes gave the possibility to establish the number and nature of water molecules, the composition of complexes and also the intervals of thermal stability.
- The biological activity of all complexes is higher than that of the free HL ligand and follow the order: UO₂(II)>Zn(II)>Co(II)>Fe(III)=Cu(II)=Ni(II).

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