

Contents lists available at ScienceDirect

### Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

## Spectroscopic characterization of metal complexes of novel Schiff base. Synthesis, thermal and biological activity studies

### M.M. Omar\*, Gehad G. Mohamed, Amr A. Ibrahim

Chemistry Department, Faculty of Science, Cairo University, Giza 12613, Egypt

### ARTICLE INFO

Article history: Received 28 September 2008 Received in revised form 17 February 2009 Accepted 20 February 2009

Keywords:

A-Aminoantipyrine 2-Aminobenzoic acid Transition metal complexes IR Molar conductance Solid reflectance Magnetic moment Thermal analyses Biological activity

### ABSTRACT

Novel Schiff base (HL) ligand is prepared via condensation of 4-aminoantipyrine and 2-aminobenzoic acid. The ligand is characterized based on elemental analysis, mass, IR and <sup>1</sup>H NMR spectra. Metal complexes are reported and characterized based on elemental analyses, IR, <sup>1</sup>H NMR, solid reflectance, magnetic moment, molar conductance and thermal analyses (TGA, DrTGA and DTA). The molar conductance data reveal that all the metal chelates are non-electrolytes. IR spectra show that HL is coordinated to the metal ions in a uninegatively tridentate manner with NNO donor sites of the azomethine N, amino N and deprotonated caroxylic-O. From the magnetic and solid reflectance spectra, it is found that the geometrical structures of these complexes are octahedral. The thermal behaviour of these chelates shows that the hydrated complexes losses water molecules of hydration in the first step followed immediately by decomposition of the anions and ligand molecules in the subsequent steps. The activation thermodynamic parameters, such as,  $E^*$ ,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  are calculated from the DrTG curves using Coats–Redfern method. The synthesized ligands, in comparison to their metal complexes also were screened for their antibacterial activity against bacterial species, *Escherichia Coli*, *Pseudomonas aeruginosa*, *Staphylococcus Pyogones* and *Fungi* (Candida). The activity data show that the metal complexes to be more potent/antibacterial than the parent Shciff base ligand against one or more bacterial species.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

The Schiff base ligands with sulphur and nitrogen donor atoms in their structures act as good chelating agents for the transition and non-transition metal ions [1-4]. Coordination of such compounds with metal ions, such as copper, nickel and iron, often enhance their activities [5], as has been reported for pathogenic fungi [6]. There is a continuing interest in metal complexes of Schiff bases. Because of the presence of both hard nitrogen or oxygen and soft sulphur donor atoms in the backbones of these ligands, they readily coordinate with a wide range of transition metal ions yielding stable and intensely coloured metal complexes, some of which have been shown to exhibit interesting physical and chemical properties [7] and potentially useful biological activities [8]. Many reports are available for the preparation and properties of model copper complexes which mimic copper-containing metalloproteins such as hemocyanine and tyrosinase. Two noticeable properties of copper proteins are an intense absorption band [9] near 600 nm and relatively high copper(II)/copper(I) reduction potentials [7]. Attention was particularly focused on their correlation with the active site of metalloenzymes and metalloproteins containing dinuclear metallocenters in order to elucidate the factors that determine the reversible binding and activation of O2 in various natural oxygen transport systems and mono- and dioxygenases and to mimic their activity [9]. Schiff bases [10] were still regarded as one of the most potential group of chelators for facile preparations of metalloorganic hybrid materials. In the past two decades, the properties of Schiff base metal complexes stimulated much interest for their noteworthy contributions to single molecule-based magnetism, material science [11], catalysis of many reactions like carbonylation, hydroformylation, oxidation, reduction and epoxidation [12], their industrial applications [13], complexing ability towards some toxic metals [14]. The interest in Schiff base compounds as analytical reagents is increasing since they enable simple and unexpensive determinations of different organic and inorganic substances [15]. The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes.

The present study describes the chelation behaviour of Schiff base derived from the condensation of 4-aminoantipyrine with 2aminobenzoic acid (HL) towards some transition 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), UO<sub>2</sub>(II), Mn(II) and Th(IV) ions 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 elemental analyses, IR, <sup>1</sup>H NMR, solid reflectance, magnetic

<sup>\*</sup> Corresponding author. Tel.: +2 0109174425; fax: +2 0235727556. *E-mail address:* mmomar27@yahoo.com (M.M. Omar).

<sup>1386-1425/\$ -</sup> see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2009.02.043

moment, molar conductance, and thermal analyses (TGA, DrTGA and DTA) measurements. The biological activity of the parent Schiff base and its metal complexes is reported.

### 2. Experimental

### 2.1. Materials and reagents

All chemicals used were of the analytical reagent (AR) grade, and of highest purity available. They included 4-aminoantipyrine (Sigma) and 2-aminobenzoic acid (Aldrich). Cu(II)Cl<sub>2</sub>·2H<sub>2</sub>O (Sigma), Co(II)Cl<sub>2</sub>·6H<sub>2</sub>O and Ni(II)Cl<sub>2</sub>·6H<sub>2</sub>O (BDH); MnCl<sub>2</sub> (sigma), ThCl<sub>4</sub> (Aldrich), ZnCl<sub>2</sub>·2H<sub>2</sub>O (Ubichem), UO<sub>2</sub>(AcO)<sub>2</sub>·2H<sub>2</sub>O (Sigma) and FeCl<sub>3</sub>·6H<sub>2</sub>O (Prolabo) were used. Organic solvents used included absolute ethyl alcohol, diethylether and dimethylformamide (DMF). These solvents were spectroscopic pure from BDH. Hydrogen peroxide and chloride, carbonate and hydroxide salts of sodium (A.R.) were used. Hydrochloric and nitric acids (Merck) were used. De-ionized water collected from all glass equipments was usually used in all preparations.

### 2.2. Solutions

Fresh stock solution of  $5 \times 10^{-3}$  M ligand was prepared by dissolving the accurately weighed amount of 0.161 g/L in the appropriate volume of absolute ethanol.  $5 \times 10^{-3}$  M Stock solutions of the metal salts (Fe(III), 0.271 g/L; Co(II), 0.238 g/L; Ni(II), 0.238 g/L; Cu(II), 0.218 g/L; Zn(II), 0.219 g/L; UO<sub>2</sub>(II), 0.50 g/L, Mn(II), 0.170 g/L and Th(IV), 0.316 g/L) were prepared by dissolving the accurately weighed amounts of the metal salts in the appropriate volume of de-ionized water. The metal salt solutions were acidified and standardized by the recommended procedures [16].

Dilute solutions of the metal ions and Schiff base under study of  $2.5 \times 10^{-6}$  M,  $1 \times 10^{-6}$  M,  $2.5 \times 10^{-5}$  M,  $1 \times 10^{-5}$  M, and  $1 \times 10^{-4}$  M were prepared by accurate dilution. For potentiometric studies, all solutions of metal ions were prepared by dissolving the calculated amount of their salts in the least amount of water, then ethanol was added to the appropriate volume. Standard 0.1N sodium carbonate solution was prepared from dried sodium carbonate. 0.1N hydrochloric acid was prepared and standardized using sodium carbonate. 1.00 M sodium chloride solution was also prepared. A 1:1 sodium hydroxide solution was prepared from A.R. product and stored in a well steamed waxed tall glass cylinder for some days with occasional shaking to obtain a carbonate free sodium hydroxide solution. The clear solution was filtered through a sintered glass funnel G4. Solutions of the required molarity were prepared by dilution and then standardized by recommended procedure [16].

### 2.3. Instruments

pH measurements were carried out using 716 DMS Titrino Metrohm connected with 728 Metrohm Stirrer. Elemental microanalyses of the separated solid chelates for C, H and N were performed in the Microanalytical Center, Cairo University. The analyses were repeated twice to check the accuracy of the analyzed data. The molar conductance of solid chelates in DMF was measured using Sybron-Barnstead conductometer (Meter-PM.6, E=3406). Infrared spectra were recorded on a PerkinElmer FT-IR type 1650 spectrophotometer in wave number region 4000–200 cm<sup>-1</sup>. The spectra were recorded as KBr pellets. The solid reflectance spectra were measured on a Shimadzu 3101pc spectrophotometer. The molar magnetic susceptibility was measured on powdered samples using the Faraday method. The diamagnetic corrections were made by Pascal's constant and Hg[Co(SCN)<sub>4</sub>] was used as a calibrant. 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 <sup>1</sup>H NMR spectra were recorded using 300 MHz Varian-Oxford Mercury. The deuterated solvent used was dimethylsulphoxide (DMSO) and the spectra extended from 0 to 15 ppm. The thermal analyses (TGA and DTA) were carried out in dynamic nitrogen atmosphere (20 mL min<sup>-1</sup>) with a heating rate of  $10 \,^{\circ}$ C min<sup>-1</sup> using Shimadzu TGA-50H and DTA-50H thermal analyzers.

### 2.4. Procedures

### 2.4.1. Potentiometric measurements

The potentiometric measurements were carried out at 25 °C and ionic strength  $\mu$  = 0.1 M by the addition of appropriate amounts of 1 M sodium chloride solution. The pH-meter was calibrated before each titration using standard buffers. The ionization constants of the investigated Schiff base and the stability constants of their metal chelates with Fe(III), Co(II), Ni(II), Cu(II), Zn(II), UO<sub>2</sub>(II), Mn(II) and Th(IV) ions were determined potentiometrically using the technique of Sarin and Munshi [17]. For this purpose three solution mixtures of total volume 50 mL were prepared. Thus,

- (A) 3 mL of standard HCl (0.10 M) + 5 mL 1 M NaCl + 25 mL ethanol and the volume was completed up to 50 mL with distilled water.
- (B) 3 mL of 0.10 M HCl + 5 mL 1 M NaCl + 25 mL 0.001 M of ethanolic solution of the Schiff base (HL) and the volume was completed to 50 mL with distilled water.
- (C) 3 mL of 0.10 M HCl + 5 mL 1 M NaCl + 25 mL 0.001 M of ethanolic solution of the Schiff base + 5 mL 0.001 M metal ion solution and the volume was completed to 50 mL with distilled water.

The above three mixtures were titrated potentiometrically against standard sodium hydroxide solution (0.10 M). The molarities of HCl and NaOH were checked every day before the titrations. The appropriate volume of ethanol was added so as to keep the ratio 50% (v/v) ethanol/water, constant to ensure the complete solubilities of the Schiff base during the titration. The three curves obtained were referred to as: (A) acid titration curve, (B) ligand titration curve and (C) complex titration curve.

### 2.4.2. Synthesis of Schiff base (HL)

Hot solution ( $60 \,^{\circ}$ C) of 4-aminoantipyrine (5 g, 24.88 mmol) was mixed with hot solution ( $60 \,^{\circ}$ C) of 2-aminobenzoic acid (3.41 g, 24.88 mmol) in 50 mL ethanol. The resulting mixture was left under reflux for 2 h and the formed solid product was separated by filtration, purified by crystallization from ethanol, washed with diethyl ether and dried in a vacuum over anhydrous calcium chloride. The brownish yellow products were produced in 88% yield.

### 2.4.3. Synthesis of metal complexes

The metal complexes of the Schiff base, HL were prepared by the addition of hot solution ( $60 \,^{\circ}$ C) of the appropriate metal chloride or acetate (1 mmol) in an ethanol–water mixture (1:1, 25 mL) to the hot solution ( $60 \,^{\circ}$ C) of the Schiff base (0.203 g, 1 mmol) in the same solvent (25 mL). The resulting mixture was stirred under reflux for 1 h whereupon the complexes precipitated. They were collected by filtration and purified by washing with an ethanol–water mixture (1:1) and diethyl ether. The analytical data for C, H and N were repeated twice.

### 2.5. Determination of the metal content of the chelates

An accurately weighed portion of the different chelates ranged from 10 to 30 mg was placed in Kjeldahl flask. A measured volume of concentrated nitric acid ranged from 5 to 10 mL was added initially to the powdered chelates, to start the fast wet oxidation digestion. This mixture had been digested by a gradual heating with dropping of  $H_2O_2$  solution. This treatment was conducted until most of the powdered complexes were diminished and the remained solution had the colour of the corresponding metal salt. This solution was diluted up to 50 mL with bidistilled water and the metal content was determined by titration against standard EDTA solution at a suitable pH value using the suitable indicator.

### 2.6. Biological activity

5 mm disk of filter paper was transferred into 250 flasks containing 20 ml of working volume of tested solution. All flasks were autoclaved for 20 min at 121 °C.

- LB agar media surfaces were inoculated with 4 investigated bacteria (2 Gram-positive and 2 Gram-negative) then, transferred to a saturated disk with a tested solution in the center of Petri dish (agar plates).
- Finally, all these Petri dishes were incubated at 25 °C for 48 h where clear or inhibition zones were detected around each disk.
- Control flask of the experiment was designed to perform under the same condition described previously for each microorganism but with DMF solution only and by subtracting the diameter of inhibition zone resulting with DMF from that obtained in each case, so antibacterial activity could be calculated [18].
- All experiments were performed as triplicate and data plotted were the mean value.

### 3. Results and discussion

### 3.1. Characterization of Schiff base

The Schiff base is prepared as described in the experimental part, crystallized and dried under vacuum and subjected to elemental analyses, mass and IR spectral analysis. The results of elemental analyses (C, H and N) with molecular formula and the melting point are presented in Table 1. The results obtained are in good agreement with those 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 below as shown in Fig. 1.

The structure of the Schiff base is also confirmed by IR and <sup>1</sup>H NMR spectra, which will be discussed in detailed manner with metal complexes later.

### 3.1.1. Mass spectra of the Schiff base

The electron impact mass spectra of HL ligand is recorded and investigated at 70 eV of electron energy. The mass spectra of the studied Schiff base is characterized by moderate to high relative intensity molecular ions peaks at 70 eV. It is obvious that, the molecular ion peaks are in good agreement with their suggested empirical formula as indicated from elemental analyses (Table 1). The mass



Fig. 1. Structure of Schiff base.

spectrum of HL shows a well-defined parent peak at m/z=323 (M<sup>+</sup>) with a relative intensity = 1%. The parent ion and the fragments obtained by cleavage in different positions in HL molecule are shown in Scheme 1.

## 3.2. Potentiometric determination of the ionization constants of Schiff base

The ionization constants of the ionizable groups in Schiff base under investigation are determined by a method similar to that described by Sarin and Munshi [17]. The average of protons associated with the ligand ( $\bar{n}_A$ ) at different pH values is calculated utilizing acid and ligand titration curves. The pK<sub>a</sub> values can be calculated from the curves obtained by plotting  $\bar{n}_A$  versus pH. The formation curves are found between 0 and 1. This indicates that the ligand have one dissociable proton from COOH group. The pK<sub>a</sub> values can be calculated also by plotting log  $\bar{n}_A/(1 - \bar{n}_A)$  versus pH whereby a straight line is obtained intersecting the *x*-axis at the pK<sub>a</sub> value. The pK<sub>a</sub> value of 6.55 can be attributed to the ionization of -COOH proton from HL ligand. The free energy change,  $\Delta G^\circ$ , was also calculated and was found to be -45.54 kJ mol<sup>-1</sup>. The negative value indicates the spontaneous character of association reaction.

### 3.3. Potentiometric determination of the stability constants

The stability constants of the Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Th(IV) complexes with HL ligand is determined potentiometrically using the method described by Sarin [17] and Bjerrum [19]. The formation curves of the investigated complexes are obtained by plotting a graph between average number of ligands attached per metal ion ( $\bar{n}$ ) and free ligand exponent (pL), (Fig. 2). Values of  $\bar{n}$  and pL are calculated. The maximum  $\bar{n}$  values calculated for metal–ligand system are found to be not exceed two indicating the possibilities of formation of 1:1 and 1:2 (metal: ligand) complexes. The mean log  $\beta_1$  and log  $\beta_2$  values for complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Th(IV) ions and HL are listed in Table 2.

The complex-forming abilities of the transition metal ions are frequently characterized by stability orders. The order of stability constants is found to be: Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II) in accordance with Irving and Williams order [20,21] for divalent

#### Table 1

Analytical and physical data of HL ligand and its metal complexes.

Compound	Colour (yield)	M.p. (°C)	% found (calcd)	)			$\mu_{\mathrm{eff.}}$ (B.M.)	$\Lambda_{ m m}$ ( $\Omega^{-1}$ mol $^{-1}$ cm $^{2}$
			С	Н	Ν	М		
HL C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>	Yellow (88)	$78\pm2$	67.43 (67.08)	5.95 (5.59)	17.33 (17.39)	-	-	-
[Mn(L1)Cl(H2O)2]·H2O C18H23Mn Cl N4O5	Brown (75)	>300	45.99 (46.41)	4.97 (4.94)	12.21 (12.03)	11.65 (11.82)	5.35	10.11
[Fe(L1)Cl2(H2O)]·2H2O C18H23Cl2FeN4O5	Black (65)	>300	42.83 (43.04)	3.95 (3.98)	10.99 (11.15)	10.92 (11.15)	5.64	13.22
[Co(L <sup>1</sup> )Cl(H <sub>2</sub> O) <sub>2</sub> ]·H <sub>2</sub> O C <sub>18</sub> H <sub>23</sub> CoClN <sub>4</sub> O <sub>5</sub>	Green (55)	>300	45.84 (46.01)	4.87 (4.90)	11.38 (11.93)	12.86 (12.57)	5.51	10.76
[Ni(L1)Cl(H2O)2]·H2O C18H23ClNiN4O5	Yellow (73)	>300	47.13 (46.99)	4.94 (4.90)	11.56 (11.93)	12.22 (12.51)	3.95	12.95
[Cu(L <sup>1</sup> )Cl(H <sub>2</sub> O) <sub>2</sub> ]·3H <sub>2</sub> O C <sub>18</sub> H <sub>27</sub> CuClN <sub>4</sub> O <sub>7</sub>	Blue (67)	>300	42.62 (42.35)	5.31 (5.29)	10.74 (10.98)	12.74 (12.45)	2.01	9.35
$[Zn(L^1)Cl(H_2O)_2] \cdot H_2OC_{18}H_{23}ClN_4O_5Zn$	Yellow (69)	>300	45.67 (45.39)	4.73 (4.83)	11.52 (11.77)	13.96 (13.66)	Diam.	8.75
[Cd(L <sup>1</sup> )Cl(H <sub>2</sub> O) <sub>2</sub> ]·2H <sub>2</sub> O C <sub>18</sub> H <sub>25</sub> CdClN <sub>4</sub> O <sub>6</sub>	Brown (63)	>300	39.75 (39.93)	4.90 (4.62)	10.09 (10.35)	21.00 (20.71)	Diam.	7.99
[Th(L1)Cl(H2O)2]Cl2·2H2O C18H25Cl3N4O6Th	Brown (67)	>300	29.21 (29.52)	3.38 (3.42)	7.65 (7.66)	31.37 (31.72)	Diam.	162.9
$[UO_2(L^1)(CH_3COO)(H_2O)_2]\cdot 2H_2O\ C_{20}H_{28}N_4O_{10}U$	Yellow (71)	>300	31.99 (32.11)	3.90 (3.94)	7.91 (7.89)	33.35 (33.52)	Diam.	8.99



Scheme 1. Mass fragmentation pattern of HL.



Fig. 2. Formation curves of HL complexes.

metal ions of the 3d series. It is clear from Table 2 that the stability of Cu(II) complexes are larger as compared to the other metal ions of 3d series. Under influence of the ligand field, Cu(II) (3d<sup>9</sup>) will receive some extra stabilization [22] due to tetragonal distortion of octahedral symmetry in their complexes. The Cu(II) complexes will be further stabilized due to Jhan-Tellar effect [23].

One would expect a bigger difference between  $\log K_1$  and  $\log K_2$  values in such a ligand because of possible steric hindrance to the linking of the second ligand to the metal ion. The small difference may be due to trans-structure.

The free energy of formation,  $\Delta G^{\circ}$ , accompanying the complexation reaction has been determined at 25 °C. The results are given in Table 2. From the table, it is apparent that the negative values of  $\Delta G^{\circ}$  show that the driving tendency of the complexation reaction is from left to right and the reaction proceeds spontaneously.

### 3.4. Composition and structures of Schiff base complexes

The novel Schiff base ligand HL is not previously prepared and no studies concerning metals complexes are reported. Hence these complexes are prepared and completely characterized. The solid complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO<sub>2</sub>(II) and Th(IV) ions with the Schiff bases HL ligand are subjected to elemental analyses (C, H and N, metal content), IR, <sup>1</sup>H NMR, solid reflectance, magnetic studies, molar conductance and thermal analyses (TGA, DrTGA and DTA), to identify their tentative formulae in a trial to elucidate their molecular structures. The biological activity of the Schiff base ligand and its metal chelates are studied against antibacterial organisms.

#### Table 2

 $\label{eq:cumulative data of } \log \beta_1 \mbox{ and } \log \beta_2 \mbox{ values for complexes of HL ligand with } Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) \mbox{ and } Th(IV).$ 

Ion	HL								
	$\log \beta_1$ A	В	М	$-\Delta G^{\circ}$ (kJ mol <sup>-1</sup> )	$\log \beta_2$ A	В	С	М	$-\Delta G^{\circ}$ (kJ mol <sup>-1</sup> )
Mn(II)	6.88	6.75	6.82	46.5	12.76	12.53	12.58	12.62	61.4
Fe(III)	7.50	7.10	7.30	48.2	13.79	13.26	13.20	13.42	62.9
Co(II)	6.95	6.87	6.91	46.8	12.90	12.74	12.76	12.80	61.8
Ni(II)	7.00	6.89	6.95	47.0	13.24	13.07	13.04	13.12	62.4
Cu(II)	7.20	6.96	7.08	47.4	13.98	12.86	12.86	13.23	62.6
Zn(II)	7.10	6.91	7.01	47.2	13.10	13.31	12.90	13.10	62.3
Cd(II)	7.15	6.95	7.05	47.3	13.17	13.01	13.00	13.06	62.3
Th(IV)	7.40	7.06	7.23	47.9	13.66	13.58	13.08	13.44	63.0

Where (A) interpolation at half values method; (B) correction-term method; (C) mid-point method; (M) mean.

### 3.4.1. Elemental analyses of the complexes

The results of elemental analyses, Table 1 is in good agreement with those required by the proposed formulae. The formation of these complexes may proceed according to the following equations given below.

 $MX_2 + HL + 2H_2O + yH_2O \rightarrow [M(L)X(H_2O)_2] \cdot yH_2O$ 

 $M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO_2(II);$ 

y = 1-3, X = ClorAcO

 $FeCl_3 + HL + H_2O + 2H_2O \rightarrow [Fe(L)Cl_2(H_2O)] \cdot 2H_2O$ 

 $ThCl_4 + HL + 2H_2O + 2H_2O \rightarrow [Th(L)Cl(H_2O)_2]Cl_2 \cdot 2H_2O$ 

### 3.4.2. Molar conductance measurements

The chelates are dissolved in DMF and the molar conductivities of  $10^{-3}$  M of their solutions at  $25 \pm 2$  °C are measured. Table 1 shows the molar conductance values of the complexes. It is concluded from the results that the Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of HL ligand has a molar conductivity values in the range from 7.99 to  $13.22 \ \Omega^{-1} \ mol^{-1} \ cm^2$  (Table 1) which indicates the non-ionic nature of these complexes and they are considered as non-electrolytes. Th(IV) complex is found to has molar conductance value of 162.9 mol<sup>-1</sup> cm<sup>2</sup>, indicating its ionic character and that it is 2:1 electrolyte [24].

### 3.4.3. IR spectra and mode of bonding

The data of the IR spectra of Schiff base ligand (HL) and its complexes is 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 involved in chelation. There are some guide peaks, in the spectra of the ligand, which are of good help for achieving this goal. These peaks are expected to be involved in chelation such as those of OH, NH, C=O, COOH and azomethine N. The position and/or the intensities of these peaks are expected to be changed upon chelation. New peaks are also guide peaks as well as water in chelation. These guide peaks are listed in Table 3. Upon comparison it is found that:

- (1) The v(C=N) stretching vibration of the azomethine is found in the free ligand at 1638 cm<sup>-1</sup>. This band is shifted to higher or lower wavenumbers in the complexes indicating the participation of the azomethine nitrogen in coordination (M–N) [25].
- (2) The  $\upsilon$ (OH),  $\upsilon$ (C=O),  $\upsilon_{asym}$ (COO) and  $\upsilon_{sym}$ (COO) stretching vibrations are observed at 3443, 1685, 1490 and 1355 cm<sup>-1</sup> for HL, respectively. The participation of the carboxylate O atom in the complexes formation is evidenced from the disappearance or shift in position of these bands to 3424–3470, disappear–1670, 1492–1489 and 1407–1302 cm<sup>-1</sup> for HL metal complexes.
- (3) The IR spectrum of HL showed a medium broad band at (3374 and 3319) cm<sup>-1</sup> which attributed to NH<sub>2</sub> of the amino acid group. The existence of water of hydration and/or water of coordination in the spectra of the complexes render it difficult to get conclusion from the NH<sub>2</sub> group of the HL which will be overlapped by those of the water molecules. The participation of the NH<sub>2</sub> group is further confirmed by clearifying the effect of chelation on the in-plane bending,  $\delta$ (NH<sub>2</sub>) vibration. The shift of this band, from 1577 cm<sup>-1</sup> in the free HL to 1545–1599 cm<sup>-1</sup> in the complexes indicates the participation of the NH<sub>2</sub> group in complex formation [26].
- (4) New bands are found in the spectra of the complexes in the regions 566–590 (carboxylate O) which are assigned to U(M–O)

<b>Table 3</b> IR data (4000–400 cm <sup>-1</sup> ) of HL liga	nd and its metal cor	nplexes.								
Compound	v(OH) (carboxylaic)	v(C=0) (carboxylic)	$v(NH_2)$	$\delta(NH_2)$	v(C=N) (Azomethine)	<i>U</i> (COO) (sym.)	<i>v</i> (COO) (asym.)	$\upsilon(M-N)$ (Azomethine)	v(M-N) (Amino)	v(M—0)
HL	3443 sh	1685m	3374m, 3319m	1577m	1638m	1355m	1490m	I	I	I
$[Mn(L)Cl(H_2O)_2] \cdot H_2O$	3443br	Disappear	3305m	1590m	1618m	1323m	1491 m	475w	509w	572m
[Fe(L)Cl <sub>2</sub> (H <sub>2</sub> O)]·2H <sub>2</sub> O	3375br	Disappear	Within the broad	1579s	1617 m	1337sh	1494m	420w	487s	590w
			envelope of OH							
			carboxylic							
$[Co(L)Cl(H_2O)_2] \cdot H_2O$	3424br	Disappear	3307m, 3136m	1591m	1616m	1407m	1492s	419w	516s	566s
$[Ni(L)Cl(H_2O)_2] \cdot H_2O$	3388	Disappear	3305m, 3127s	1591m	16161 m	1407m	1492m	423s	520w	589s
[Cu(L)Cl(H <sub>2</sub> O) <sub>2</sub> ].3H <sub>2</sub> O	Disappear	1684m	3275s, 3172s	1551s	1597m	1385s	1494m	422w	480br	565br
[Zn(L)Cl(H <sub>2</sub> O) <sub>2</sub> ]·H <sub>2</sub> O	3448br	Disappear	3298m, 3129m	1599m	1616m	1329m	1494m	414w	464w	569s
[Cd(L)Cl(H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O	3470m	1670m	3370m, 3303m	1587m	1615sh	1302m	1489m	426w	534s	588s
$[Th(L)Cl(H_2O)_2]Cl_2 \cdot 2H_2O$	3466m	Disappear	3360m	1545m	1618m	1336s	1456m	447 s	499w	572s
[U0 <sub>2</sub> (L)(CH <sub>3</sub> CO0)(H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O	3443m	Disappear	3341br, 3145m	1569m	1617 m	1328br	1495m	425w	501s	571s
sh = sharp, m = medium, br = broad,	s = small, w = weak.									

 Table 4

 <sup>1</sup>H NMR spectral data of the Schiff base and its metal chelates.

Compound	Chemical shift ( $\delta$ ), ppm	Assignment
HL	13.30 6.481–7.693	(S, 1H, COOH) (m, 9H, 5ArH and 4 anthranilic-H)
	3.879 2.733 2.096	(br, 2H, NH <sub>2</sub> ) (S, 3H, N-CH <sub>3</sub> ) (S, 3H, C-CH <sub>3</sub> )
[Cd(L)Cl(H <sub>2</sub> O) <sub>2</sub> ]·2H <sub>2</sub> O	6.466-7.70 3.326 2.764	(m, 9H, 5ArH and 4 anthranilic-H) (br, 2H, NH <sub>2</sub> ) (S, 3H, N-CH <sub>3</sub> )
	2.108	(S, 3H, C-CH <sub>3</sub> )

stretching vibrations for HL metal complexes. The bands at 414–475 in HL metal complexes have been assigned to v(M-N) of the azomethine mode. The v(M-N) bands due to amino group are appeared at 464–520 cm<sup>-1</sup> for HL metal complexes [27].

Therefore, from the IR spectra, it is concluded that: HL behaves as a uninegatively tridentate ligand with NNO donor sites and coordinated to the metal ions via the azomethine N, deprotonated carboxylic O and amino N atoms.

### 3.4.4. <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectra of Schiff base (HL) was recorded in d<sub>6</sub>dimethylsulfoxide (DMSO) solution using tetramethylsilane (TMS) as internal standard. The chemical shifts of the different types of protons in the <sup>1</sup>H NMR spectra of the Schiff base HL and its diamagnetic Cd(II) complex are listed in Table 4. The spectra of the complex are examined in comparison with those of the parent Schiff base. Upon examinations it is found that:

- (1) The COOH signal is found at 13.30 ppm in the spectrum of HL ligand. This signal is completely disappeared in the spectrum of the Cd(II) complex indicating the involvement of the COOH group in chelation through displacement of the COOH proton.
- (2) The signals observed at 3.879 ppm for HL ligand, is assigned to NH<sub>2</sub> protons. These signal is found at 3.326 Cd(II) complex with HL. This indicates that the NH<sub>2</sub> group is coordinated to the Cd(II) ion without proton displacement.

Therefore, it is clear from these results that the data obtained from the elemental analyses, IR and <sup>1</sup>H NMR spectral measurements are in agreement with each other.

# 3.4.5. Magnetic susceptibility and electronic spectra measurements

In this part, we would like to elucidate the important role played by magnetic and electronic spectra in determining the geometrical structures of the above investigated metal chelates.

The diffuse reflectance spectrum of the Mn(II) complex shows three bands from 15,873 to 16,150 cm<sup>-1</sup> assignable to  ${}^{4}T_{1g} \rightarrow {}^{6}A_{1g}$ ,  ${}^{4}T_{2g}$  (G)  $\rightarrow {}^{6}A_{1g}$  and  ${}^{4}T_{1g}$  (D)  $\rightarrow {}^{6}A_{1g}$  transitions, respectively [28]. The magnetic moment value is found to be 5.35 B.M., which indicates the presence of Mn(II) complex in octahedral structure.

From the diffuse reflectance spectrum it is observed that, the Fe(III) chelate exhibit a band at 20,691 cm<sup>-1</sup>, which may be assigned to the  ${}^{6}A_{1g} \rightarrow T_{2g}$  (G) transition in octahedral geometry of the complexes [28]. The  ${}^{6}A_{1g} \rightarrow {}^{5}T_{1g}$  transition appears to be split into two bands at 16,135 and 12,657 cm<sup>-1</sup>. The observed magnetic moment of Fe(III) complex is found to be 5.43 B.M. Thus, the complex formed has the octahedral geometry involving d<sup>2</sup>sp<sup>3</sup> hybridization in Fe(III)

The Ni(II) complex reported herein is high spin with a room temperature magnetic moment value of 3.71 B.M.; which is in the normal range observed for octahedral Ni(II) complexes ( $\mu_{eff}$  = 2.9–3.3 B.M.) [28]. This indicates that, the complex of Ni(II) is six coordinate and probably octahedral [29]. Its electronic spectra, in addition to show the  $\pi$ - $\pi$ \* and n- $\pi$ \* bands of the free ligand, display three bands, in the solid reflectance spectra at  $\nu_1$ : 12,635 cm<sup>-1</sup>:  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ ,  $\nu_2$ : 15,595 cm<sup>-1</sup>:  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$  (F) and  $\nu_3$ : 21,172 cm<sup>-1</sup>:  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$  (P). The Racah parameters are calculated according to the following equations:

$$B = \frac{\nu_2 + \nu_3 - 3\nu_1}{15}$$
  

$$B = \frac{1}{75} \{ 3\nu_2 [25(\nu_3 - \nu_2)^2 - 16\nu_1]^2 \}^{1/2}$$
  
10 Dq =  $\nu_1$ 

The 10Dq values lie in the 12,711 cm<sup>-1</sup>, again confirming the octahedral configuration of the chelate [30]. The spectrum shows also a band at 25,651 cm<sup>-1</sup> which may attribute to ligand to metal charge transfer.

The electronic spectrum of the Co(II) complex gives three bands at 12,799, 16,771 and 20,985 cm<sup>-1</sup>. The band at 25,445 cm<sup>-1</sup> refers to the charge transfer band. The bands observed are assigned to the transitions  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)(\nu_{1})$ ,  ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)(\nu_{2})$  and  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(P)(\nu_{3})$ , respectively, suggesting that there is an octahedral geometry around Co(II) ion [31]. For calculating the Racah parameters, the following equations are used [30].

$$10 \text{ Dq} = 2\nu_1 - \nu_3 + 15B$$
  

$$B = \frac{1}{30} \left[ -(\nu_1 - \nu_3) \pm (-\nu_1^2 + \nu_3^2 + \nu_1\nu_3)^{1/2} \right]$$
  

$$10 \text{ Dq} = \frac{1}{2} (2\nu_2 - \nu_3) + 5B$$
  

$$B = \frac{1}{510} \left[ 7(\nu_3 - 2\nu_2) \pm 3[81\nu_3^2 - 16\nu_2(\nu_2 - \nu_3)^{1/2} + 16\nu_2(\nu_3 - \nu_3)^{1/2} + 16\nu_3(\nu_3 - \nu_3)^{1/2} + 16\nu_3(\nu_3 - \nu_3)^{1/2} \right]$$

From the position of the bands and the calculated Racah parameters, the chelate is octahedral with largely covalent bonds between the organic ligand and the metal ion [30]. The magnetic susceptibility measurement is found to be 5.51 B.M. (normal range for octahedral Co(II) complex is 4.3–5.2 B.M.), is an indicative of octahedral geometry [32].

The reflectance spectrum of the Cu(II) chelate consist of a broad, low intensity shoulder band centered at 14,777 and 17,493 cm<sup>-1</sup>. The  ${}^{2}E_{g}$  and  ${}^{2}T_{2g}$  states of the octahedral Cu(II) ion (d<sup>9</sup>) split under the influence of the tetragonal distortion and the distortion can be such as to cause the three transitions  ${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ ;  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  and  ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$  to remain unresolved in the spectrum [33]. It is concluded that, all three transitions lie within the single broad envelope centered at the same range previously mentioned. This assignment is in agreement with the general observation that Cu(II) d–d transitions are normally close in energy [33]. The magnetic moment of 1.97 B.M. falls within the range normally observed for octahedral Cu(II) complexes [28]. A moderately intense peak observed at 21,555 cm<sup>-1</sup> is due to ligand–metal charge transfer transition [34].

The complexes of Zn(II) and  $UO_2(II)$  are diamagnetic. In analogy with those described for Zn(II) complexes containing N–O donor Schiff bases [35,36] and according to the empirical formulae of these complexes, we proposed an octahedral geometry for the Zn(II) and  $UO_2(II)$  complexes.

### 3.4.6. Thermal analyses (TGA, DrTGA and DTA)

Thermogravimetry (TGA) is a technique in which the change in the weight of a substance is recorded as a function of temperature or time. The basic instrumental requirement for thermogravime-

Table 5

try is a precision balance with a furnace programmed for a linear rise of temperature with time. The results may be presented as (i) a thermogravimetric (TGA) curve; in which the weight change is recorded as a function of temperature or time, or (ii) as a derivative thermogravimetric (DrTGA) curve where the first derivative of the TGA curve is plotted with respect to either temperature or time.

Thermogravimetric analyses (TGA, DrTGA and DTA) of the Schiff base ligand; HL and its chelates are used to (i) get information about the thermal stability of these new complexes. (ii) decide whether the water molecules (if present) are inside or outside the inner coordination sphere of the central metal ion and (iii) suggest a general scheme for thermal decomposition of these chelates. The TGA (and DrTGA) and DTA curves are given in Fig. 3 and the data are listed in Table 5. The weight losses for each chelate are calculated within the corresponding temperature ranges.

3.4.6.1. Thermal analyses (TGA, DrTGA and DTA) of Schiff base. The TGA curve of Schiff base HL, (Fig. 3a), exhibits a first estimated mass loss of 52.02% (calcd. 51.25%) at 140–275  $^\circ\text{C},$  which may be attributed to the liberation of C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub> molecule as gases. In the 2nd and 3rd stages within the temperature range of 275–950 °C, HL losses the remaining part with an estimated mass loss of 48.76% (calcd. 48.76%) with a complete decomposition as CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, etc. gases (Table 5). These losses appear in the DTA curves as exothermic and endothermic peaks within the temperature range of decomposition from 125 to 950 °C as three endothermic peaks at 125, 450 and 950 °C and six exothermic peaks at 240, 275, 400, 440, 460 and 575 °C.

The thermogram of Fe(III) chelate shows three decomposition steps within the temperature range from 30 to 1000 °C. The first two steps of decompositions within the temperature range of 29-400 °C corresponds to the loss of water molecules of hydration, the coordinated water, HCl, two methyl groups and amino group for HL with a mass loss of 3.59% (calcd. 3.33%) and 30.89% (calcd 31.27%) for Fe(III) complex. The subsequent step (275–1000 °C) corresponds to the removal of the organic part of the ligand leaving metal oxide as a residue. The overall weight loss amounts to 84.10% (calcd. 84.34%) for Fe(III) complex. The DTA data are listed in Table 5 and represented graphically in Fig. 3b. It is clear from these data that these mass losses are accompanied by exothermic peaks at 40, 175, 350 and 475 °C and endothermic peaks at 60 and 400 °C.

The TGA curve of the Co(II) chelate is shown in Fig. 3c and listed in Table 5. It decomposes in three steps in the temperature range from 30 to 1000 °C. The first step is the loss of the hydrated water and one HCl molecules with mass loss of 3.83% (calcd. 3.29%). The 2nd and 3rd steps correspond to the removal of coordinated water, HCl molecules and the residue of ligand as gases with mass loss of 80.41% (calcd. 80.06%). These steps are accompanied by exothermic peaks at 30, 120, 225, 375, 450, 550 and 605 °C and endothermic peaks at 60, 200, 415, 475 and 900 °C.

The TGA curve of the Ni(II) chelate shows three stages of decomposition within the temperature range of 30–1000 °C. The first step corresponds to the loss of water of hydration and coordinated water while the subsequent (2nd and 3rd) stages involve the loss of HCl and ligand molecules. The overall weight loss amounts to 84.07% (calcd. 84.02%). The DTA data are listed in Table 5 and represented graphically in Fig. 3d. It is clear from these data that these mass losses are accompanied by exothermic peaks at 115, 155, 275, 450 and 550 °C and endothermic peaks at 75, 135, 325 and 510 °C.

On the other hand,  $[Cu(L)Cl(H_2O)_2] \cdot H_2O$  chelate exhibits three decomposition steps (Fig. 3e). The first step in the temperature range from 30 to 170 °C corresponds to the loss of the hydrated water with estimated mass loss = 10.59% (calcd. 10.34%). The total mass losses of the decomposition steps is found to be 84.41% (calcd. 84.63%), leaving CuO as a residue. The DTA data are listed in Table 5 and represented graphically in Fig. 3e. It is clear from these data that

Thermoa	nalytical result.	s (TGA, DrTGA	A and I	JTA) of HL ligand and its metal	complexes.			
Complex	: TG range (°C)	DrTG <sub>max</sub> (°C	c) n*	Mass loss, calcd. (found)%	Total mass loss, calcd. (found) % /	Assignment	Metallic residue	DTA
HL	140–275 275–500 500–950	225 365 600		51.25 (52.02) 28.88 (29.07) 19.88(19.69)	1 1 100.01 (100.8)	Loss of C <sub>7</sub> H <sub>5</sub> NO <sub>2</sub> , C <sub>2</sub> H <sub>6</sub> . Loss of C <sub>6</sub> H <sub>7</sub> N. Loss of C <sub>3</sub> N <sub>2</sub> .	I	125(+), 240(-), 275(-), 400(-), 440(-), 450(+), 460(-), 575(-), 950(+).
(1)	30–100 100–400 400–1000	56 217, 356 453	1 2 1	3.59 (3.33) 30.89(31.27) 49.62 (49.74)	1 1 84.10 (84.34)		1/2Fe <sub>2</sub> 0 <sub>3</sub>	40(-).60(+).175(-).350(-).400(+).475(-).
(2)	30-120	59	1	3.83 (3.29)	Π	Loss of H <sub>2</sub> O.		30(-), 60(+), 120(-), 200(+), 225(-), 375(-), 415(+), 450(-), 475(+), 550(-), 667(-), 900(+)
	120–415 415–1000	204, 371 449, 566	2 2	38.02 (37.70) 42.39 (42.36)	I 84.24 (84.00) I	Loss of HCl and C <sub>8</sub> H <sub>14</sub> O <sub>2</sub> . Loss of C <sub>10</sub> H <sub>7</sub> N <sub>4</sub> O.	CoO	
(3)	30–325 325–440 440–1000	68, 277 400 405, 548	2 1 2	11.50 (11.65) 14.17 (14.38) 58.40 (57.99)	1 1 84.07 (84.02)		NiO	75(+), 115(-), 135(+), 155(-), 275(-), 325(+), 450(-), 510(+), 550(-).
(4)	30-170	104	1	10.59(10.34)	Ι	Loss of 3H <sub>2</sub> O.		50(-), 105(+), 160(-), 170(+), 190(-), 300(-), 350(-), 410(+), 480(+), 575(-), 610(+), 640(-), 910(-)
	170–350 350–1000	251 638		29.31 (29.01) 44.51 (45.28)	1 84.41 (84.63) 1	Loss of HCl, $2H_2O$ and $C_6H_5$ . Loss of $C_{16}H_{12}N_2O$ .	CuO	
$n^* = n_{11}m$	her of decomo	sition stens	1) [ Fe/	T.)Cl <sub>2</sub> (H <sub>2</sub> O)[.2H <sub>2</sub> O (2) [Co(T.)Cl	(H, O), I.H, O (3) [Ni(L)CI(H, O), I.F	H2O (4)[Cu(1)Cl(H2O)2].3H2C	0, (+)=endo	othermic (–)=exothermic



Fig. 3. Thermal analysis of HL ligand and its complexes. (a) HL ligand, (b) Fe(III), (c) Co(II), (d) Ni(II) and (e) Cu(II) complexes.

these mass losses are accompanied by eight exothermic and five endothermic peaks at 50, 160, 190, 300, 350, 575, 640 and 910  $^{\circ}$ C and 105, 170, 410, 480 and 610  $^{\circ}$ C, respectively.

### *3.4.7. Calculation of activation thermodynamic parameters*

The thermodynamic activation parameters of decomposition processes of dehydrated complexes namely activation energy ( $E^*$ ), enthalpy ( $\Delta H^*$ ), entropy ( $\Delta S^*$ ) and Gibbs free energy change of the decomposition ( $\Delta G^*$ ) are evaluated graphically by employing the Coats–Redfern relation [37]:

$$\log\left[\frac{\log\left\{W_{\rm f}/(W_{\rm f}-W)\right\}}{T^2}\right] = \log\left[\frac{AR}{\theta E^*}\left(1-\frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303\,RT} \qquad (1)$$

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<sup>-1</sup>,  $\theta$  is the heating rate and  $(1 - (2RT/E^*)) \cong 1$ . A plot of the left-hand side of Eq. (1) against 1/T gives a slope from which  $E^*$  is calculated and A (Arrhenius factor) is determined from the intercept. The entropy of activation ( $\Delta S^*$ ), enthalpy of activation ( $\Delta H^*$ ) and the free energy change of activation ( $\Delta G^*$ ) are calculated using the following equations:

$$\Delta S^* = 2.303 \left[ \log \left( \frac{Ah}{kT} \right) R \right]$$
<sup>(2)</sup>

$$\Delta H^* = E^* - RT \tag{3}$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \tag{4}$$

The data are summarized in Table 6.

The activation energies of decomposition are found to be in the range of  $41.47-299.7 \text{ kJ} \text{ mol}^{-1}$ . The high values of the activation energies reflect the thermal stability of the complexes. The entropy of activation is found to have negative values in all the complexes which indicate that the decomposition reactions proceed with a lower rate than the normal ones.

### 3.4.8. Structural interpretation

The structures of the complexes of Schiff base; HL, with Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO<sub>2</sub>(II) and Th(IV) ions are confirmed by the elemental analyses, IR, <sup>1</sup>H NMR, molar conductance, magnetic moment, solid reflectance and thermal analyses data. Therefore, from the IR spectra, it is concluded that HL behaves as a uninegatively tridentate ligand with NNO sites and coordinated to the metal ions via the azomethine N, deprotonated carboxylic O and amino N. From the molar conductance data of the complexes ( $\Lambda_m$ ), it is concluded that the complexes are considered as non-electrolytes and Th(IV) complex is 2:1 electrolyte. The <sup>1</sup>H

3	6	6	

Table 6	
Thermodynamic data of the thermal decomposition of HL ligand and its metal complex	æs.

Complex	Decomposition temperature (°C)	$E^*$ (kJ mol <sup>-1</sup> )	$A(s^{-1})$	$\Delta S^*$ (kJ mol <sup>-1</sup> )	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$\Delta G^*$ (kJ mol <sup>-1</sup> )
HL	50-300	41.47	$3.11  imes 10^6$	-119.2	39.38	69.31
	300-500	96.48	$5.89  imes 10^6$	-117.0	93.44	136.3
	500-1000	286.30	$2.15\times10^{16}$	-61.93	281.30	244.1
(1)	30-105	48.53	$3.74\times10^{6}$	-105.8	48.03	54.42
	105-350	46.46	$4.12  imes 10^5$	-134.8	44.65	73.93
	350-600	96.14	$1.28  imes 10^7$	-110.4	93.17	132.6
	600-900	121.60	$1.29\times10^7$	-112.3	117.80	168.7
(2)	30-100	42.23	$3.02\times10^{10}$	-31.2	41.72	43.64
. ,	100-210	68.98	$3.03 imes10^6$	-117.0	67.26	91.53
	210-280	85.81	$1.22  imes 10^6$	-130.0	82.65	132.3
	2800-430	287.40	$1.03\times10^{20}$	-134.8	283.7	222.8
	430-1000	143.10	$6.57\times10^7$	-100.6	138.40	195.6
(3)	30-120	65.98	$1.40  imes 10^9$	-58.01	65.39	69.55
	120-210	144.2	$5.25 \times 10^{17}$	-100.9	143.1	129.4
	210-350	99.30	$3.09  imes 10^8$	-81.9	96.96	120.0
	350-450	171.5	$2.72\times10^{12}$	-9.3	168.1	171.9
	450-600	299.7	$1.45  imes 10^{20}$	-137.1	295.7	229.4
	600–900	230.0	$4.85\times10^{13}$	-11.98	225.4	218.8
(4)	60-110	42.30	$5.12\times10^4$	-146.0	41.42	56.79
	110-360	56.62	$1.33\times10^5$	-145.0	54.53	91.09
	360–900	113.2	$1.12\times10^{11}$	-169.1	94.2	121.4

 $(1) [Fe(L)Cl(H_2O)_2]Cl·2H_2O; (2) [Co(L)Cl(H_2O)_2] \cdot H_2O; (3) [Ni(L)Cl(H_2O)_2] \cdot H_2O; (4) [Cu(L)Cl(H_2O)_2] \cdot 3H_2O. (1) [Cu(L)Cl(H_2O)_2] \cdot 3H_2O. (2) [Cu(L)Cl(H_2O)_2] \cdot 3H_2O. (3) [Ni(L)Cl(H_2O)_2] \cdot H_2O; (4) [Cu(L)Cl(H_2O)_2] \cdot 3H_2O. (3) [Ni(L)Cl(H_2O)_2] \cdot H_2O; (4) [Cu(L)Cl(H_2O)_2] \cdot 3H_2O. (4$ 

NMR spectra of the free ligand and its diamagnetic Cd(II) complex shows that the COOH signal of HL ligand participate in chelation with proton displacement. While NH<sub>2</sub> signal of HL appeared in the spectrum of HL and its Cd(II) complex show that NH<sub>2</sub> involved in chelation without proton displacement. On the basis of the above observations and from the magnetic and solid reflectance measurements, octahedral and tetrahedral geometry is suggested for the investigated complexes.

On the basis of the above observations and from the magnetic and solid reflectance measurements, octahedral and tetrahedral geometry is suggested for the investigated complexes. The structure of the complexes are shown in Fig. 4.

### 3.5. Biological activity

The main aim of the production and synthesis of any antimicrobial compound is to inhibit the causal microbe without any side effects on the patients. In addition, it is worthy to stress here on the basic idea of applying any chemotherapeutic agent which depends essentially on the specific control of only one biological function and not multiple ones.

The chemotherapeutic agent affecting only one function has a highly sounding application in the field of treatment by anticancer, since most anticancer used in the present time affect both cancerous diseased cells and healthy ones which in turns affect



Fig. 4. Structural formulas of HL metal complexes.

the general health of the patients. Therefore, there is a real need for having a chemotherapeutic agent which controls only one function.

In testing the antibacterial activity of these compounds we used more than one test organism to increase the chance of detecting antibiotic principles in tested materials. The sensitivity of a microorganism to antibiotics and other antimicrobial agents is determined by the assay plates which incubated at 37 °C for 2 days for bacteria. All of the tested compounds show a remarkable biological activity against different types of Gram-positive (G<sup>+</sup>) and Gram-negative (G<sup>-</sup>) bacteria. The data are listed in Table 7 and shown in Fig. 5. On comparing the biological activity of the Schiff bases and their metal complexes with the standard (Cefepime), the following results are obtained:

### (a) Using *Bacillus simplex* bacteria (G<sup>+</sup>):

The data listed in Table 7 show that Cd(II) complex has the higher biological activity than that of the free HL ligand and both of them are higher than cefepime standard. The biological activity of Mn(II), Zn(II) and UO<sub>2</sub>(II) complexes is equal to that of the ligand and higher than that of the standard. Therefore, the biological activity of the complexes follow the order Cd(II) > HL = Mn(II) = Zn(II) = UO<sub>2</sub>(II) > Cu(II) > Fe(III) = Co(II) = Ni(II) = Th(IV) > cefepime.



Fig. 5. Biological activity of HL and its complexes at (a) 5 ppm, (b) 2.5 ppm and (c) 1 ppm.

Biological activity of HL and its metal complexes.

Sample	Bacillus	simplex		Exiguo	bacteriu	m acetylicum	Pseudon	nonas pu	tida	E. coli t	oacteria	
C, mg/l	5	2.5	1	5	2.5	1	5	2.5	1	5	2.5	1
HL	++	++	++	++	++	++	++	++	++	++	+	+
$[Mn(L)Cl(H_2O)_2] \cdot H_2O$	++	++	+	++	++	++	++	++	++	+	+	+
$[Fe(L)Cl(H_2O)_2]Cl\cdot 2H_2O$	++	++	+	++	++	+	++	++	+	+	+	+
$[Co(L)Cl(H_2O)_2] \cdot H_2O$	++	++	+	++	++	+	++	++	+	+	+	+
$[Ni(L)Cl(H_2O)_2] \cdot H_2O$	++	++	+	++	++	+	++	++	+	+	+	+
$[Cu(L)Cl(H_2O)_2]\cdot 3H_2O$	++	++	++	++	++	++	++	++	++	+	+	+
$[Zn(L)Cl(H_2O)_2] \cdot H_2O$	++	++	+	++	+	++	+++	++	+	+	+	+
$[Cd(L^{1})Cl(H_{2}O)_{2}]\cdot 2H_{2}O$	+++	+++	+	++	++	+	+++	++	+	+	+	+
$[Th(L)Cl(H_2O)_2]Cl_2 \cdot 2H_2O$	++	++	+	++	+	+	++	++	+	+	+	+
$[UO_2(L)(CH_3COO)(H_2O)_2] \cdot 2H_2O$	++	++	+	++	++	+	++	++	++	++	+	+
Cefepime	+	+	+	++	++	++	++	++	++	++	++	++

The test was done using the diffusion agar technique.

Inhibition values = 0.1–0.6 cm beyond control = +.

Inhibition values = 0.65-1.0 cm beyond control = ++.

Inhibition values = 1.1-1.5 cm beyond control = +++.

(b) Exiguobacterium acetylicum bacteria (G<sup>+</sup>)

The biological activity of the HL ligand is higher than that of standard cefepime and less than Cd(II) and Zn(II) complexes. All the complexes have higher activity than the standard cefepime. The biological activity of the complexes follow the order  $Cd(II) > Zn(II) > HL = Mn(II) = Ni(II) = Cu(II) = UO_2(II) > Fe(III) = Co(III) = Th(IV) = cefepime.$ 

(c) Using *Pseudomonas putida* bacteria (G<sup>-</sup>)

The biological activity of the ligand HL equals to that of the standard cefepime and Cu(II), Mn(II) and Zn(II) complexes and higher than that of the rest of complexes. The biological activity of the complexes are found to follow the order HL = cefepime = Cu(II) = Mn(II) = Zn(II) > Cd(II) > Ni(II) > Fe(III) = Co(II) = Th(IV) = UO<sub>2</sub>(II).

(d) *E. coli* bacteria (G<sup>-</sup>)

The biological activity of the free ligand HL is higher than that of cefepime and all complexes. The biological activity of the complexes follow the order HL > cefepime > UO<sub>2</sub>(II) > Mn(II) = Fe(III) = Co(II) = Ni(II) = Cu(II) = Zn(II) = Cd(II) = Th(IV).

Also the data listed in Table 7 shows that *E. Coli* is inhibited by Co(II), Cd(II) complexes and UO<sub>2</sub>(II) complexes of HL ligand. 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 [38,39].

However, Cd(II), Cu(II) and Zn(II) complexes of HL ligand were specialised in inhibiting Gram-positive and Gram-negative bacterial strains (*Bacillus simplex, Pseudomonas putida* and *Exiguobacterium acetylicum*). 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.

### 4. Conclusion

Since almost all scientists working in the field of search for new antitumours depend basically on the line of antibiotics affecting Gram-negative bacteria [40–42], and since there are certain organisms which have proved difficult to treat and most of them are Gram-negative rods. It is therefore believed that all the complexes which are biologically active against both the Gram-negative strains may has something to do with the barrier function of the envelope of these Gram-negative strains activity, acting in a way similar to that described by Nikaido and Nakae. [40] and Brown [41]. Therefore, it is claimed here that the synthesis of these complexes might be recommended and/or established a new line for search to new antitumour particularly when one knows that many workers studied the possible antitumour action of many synthetic and semisynthetic compounds, e.g., Hodnett et al. [42] and Hickman [43]. Such compounds may have a possible antitumour effect since Gram-negative bacteria are considered a quantitative microbiological method testing beneficial and important drugs in both clinical and experimental tumour chemotherapy [44].

### References

- [1] N.K. Kaushik, A.K. Mishra, Ind. J. Chem. 42A (2003) 2762.
- [2] N. Manav, N. Gandhi, N.K. Kaushik, J. Therm. Anal. Calorim. 61 (2000) 127.
- [3] A.K. Mishra, N. Manav, N.K. Kaushik, Spectrochim. Acta (Part A) 61 (2005) 3097.
   [4] M.G. Abd El, Wahed, E.M. Nour, S. Teleb, S. Fahim, J. Therm. Anal. Calorim. 76
- (2004) 343.
- [5] N.K. Singh, A. Srivastava, A. Sodhi, P. Ranjan, Trans. Met. Chem. 25 (2000) 133.
- [6] N.H. Patel, H.M. Parekh, M.N. Patel, Tans. Met. Chem. 30 (2005) 13.
- [7] Y.P. Tian, C.Y. Duan, C.Y. Zhao, X.Z. You, T.C.W. Mak, Z. Zhang, Inorg. Chem. 36 (1997) 1247.
- [8] S. Karabocek, S. Guner, N.J. Karabocek, Inorg. Biochem. 66 (1997) 57.
- [9] J. Kaizer, Z. Zsigmond, I. Ganszky, G. Speier, M. Giorgi, M. Reglier, Inorg. Chem. 46 (2007) 4660.
- [10] T. Sixt, W. Kaim, Inorg. Chim. Acta 300 (2000) 762.
- M.M.T. Khan, S.B. Halligudi, S. Shukla, Z.A. Shaikh, J. Mol. Catal. 57 (1990) 301.
   D. Bose, J. Banerjee, S.K.H. Rahaman, G. Mostafa, H.K. Fun, W.R.D. Bailey, M.J.
- Zaworotko, B.K. Ghosh, Polyhedron 23 (2004) 2045.
- [13] H.A. El-Boraey, J. Therm. Anal. Calorim. 81 (2005) 339.
- [14] A.S.M. Al-Shirif, H.M. Abdel-Fattah, J. Therm. Anal. Calorim. 71 (2003) 643.
- [15] J. Estrela dos Santos, E.R. Dockal, E.T.G. Cavalheiro, J. Therm. Anal. Calorim. 79 (2003) 243.
- [16] A.I. Vogel, Quantitative Inorganic Analysis Including Elemental and Instrumental Analysis. 2nd ed., Longmans, London, 1962.
  - [17] R. Sarin, K.N. Munshi, J. Inorg. Nucl. Chem. 34 (1972) 581.
  - [18] H. Dugas, C. Penney, Bioorganic Chemistry, Springer, New York, 1981, p. 435.
  - [19] J. Bjerrum, Kgl. Metal Amine Formation in Aqueous Solution", (Haase, openhagen), 1941.
  - [20] H. Irving, R.J.P. Williams, Nature 162 (1948) 746.
  - [21] H. Irving, R.J.P. Williams, J. Chem. Soc. (1953) 3192.
  - [22] R.D. Jones, D.A. Summerville, F. Basolo, Chem. Rev. 79 (1979) 139.
  - [23] L.E. Orgel, An Introduction to Transition Metal Chemistry Ligand Field Theory, Methuen, 1966, p. 55.
  - [24] J.A. Dean, Lange's Hand Book of Chemistry, 14th ed., Megraw-Hill, New York, 1992, p. 35.
  - [25] M. Hossain, S.K. Chattopadhyay, S. Ghosh, Polyhedron 16 (1997) 1793.
  - [26] A.A. Soliman, J. Therm. Anal. 63 (2001) 221.
  - [27] Y.M. Issa, H.M. Abdel-Fattah, M.M. Omar, A.A. Soliman, Monatsh. Chem. 126 (1995) 163.
  - [28] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, 6th ed., Wiley, New York, 1999.
  - [29] D.R. Zhu, Y. Song, Y. Xu, Y. Zhang, S.S.S. Raj, H.K. Fun, X.Z. You, Polyhedron 19 (2000) 2019.
  - [30] M.A. Ali, S.M.M.H. Majumder, R.J. Butcher, J.P. Jasinski, J.M. Jasinski, Polyhedron 16 (1997) 2749.
  - [31] N. Mondal, D.K. Dey, S. Mitra, K.M. Abdul Malik, Polyhedron 19 (2000) 2707.
  - [32] J. Kohout, M. Hvastijova, J. Kozisek, J.G. Diaz, M. Valko, L. Jager, I. Svoboda, Inorg. Chim. Acta 287 (1999) 186.
  - [33] J. Manonmani, R. Thirumurugan, M. Kandaswamy, M. Kuppayee, S.S.S. Raj, M.N. Ponnuswamy, G. Shanmugam, H.K. Fun, Polyhedron 19 (2000) 2011.

- [34] J. Sanmartin, M.R. Bermejo, A.M.G. Deibe, M. Maneiro, C. Lage, A.J.C. Filho, Polyhedron 19 (2000) 185.
- [35] V.P. Krzyminiewska, H. Litkowska, W.R. Paryzek, Monatsh. Chem. 130 (1999) 243.
- [36] K. Bertoncello, G.D. Fallon, K.S. Murray, E.R.T. Tiekink, Inorg. Chem. 30 (1991) 3562.
- [37] A.W. Coats, J.P. Redfern, Nature 20 (1964) 68.
- [38] E. Jawetz, J.I. Melnick, E.A. Adelberg, Review of Medical Microbiology, 16th ed., LangMedical Pulications, Los Anglos, CA, 1979.
- [39] W.H. Hughes, H.C. Stewart, Concise Antibiotic Treatment, Butter Worth, London, 1979.
- [40] H. Nikaido, T. Nakae, Adv. Microbiol. Physiol. 20 (1979) 163.
- [41] N.K.W. Brown, Resistance of Peseudomonas aeruginosa, 71, John Wiley, 1975.
  [42] E.M. Hodnett, A.W. Wu, F.A. French, Eur. J. Med. Chem., Chem. Therapeut. 13
- (1987) 577.
- [43] J.A. Hickman, Biochemie 60 (1987) 997.
- [44] A.M.S. El-Sharief, M.S. Ammar, Y.A. Mohammed, Egypt J. Chem. 27 (4) (1984) 535.