

## Study of Binary and Ternary Complexes of Co(II), Ni(II), Cd(II), Fe(III), and UO<sub>2</sub>(II) Complexes of Amino Carboxylic Acid Derivatives and Pyridine, Synthesis, Spectroscopic Characterization, Thermal Investigation and Biological Activity

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**T**WO Schiff base ligands of organic acid moiety, viz., N-(2-carboxyphenyl) salicylideneimine, (H<sub>2</sub>L<sup>1</sup>) and N-(2-carboxyphenyl) thiopheneimine, (HL<sup>2</sup>) have been synthesized by the interaction of salicylaldehyde and 2-thiophenecarboxaldehyde with 2-amino benzoic acid. Co (II), Ni (II), Cd (II), Fe (III) and UO<sub>2</sub> (II) complexes of these ligands have been prepared. Also, the ternary complexes were prepared by using pyridine (Py) as a secondary ligand. All synthesized compounds were identified and confirmed by elemental analysis, molar conductance, IR, <sup>1</sup>HNMR, UV-Vis, mass spectra, magnetic measurements, and thermal analysis. The molar conductance data reveal that these complexes are non-electrolytic, 1:1 and 1:2 electrolytic nature of the metal complexes. The ligands are coordinated to the metal ions in a terdentate manner with ONO/ONS donor sites of the carbonyl oxygen, azomethine nitrogen and phenolic oxygen or thiophenic sulphur. An octahedral structure is proposed for the prepared metal complexes. The thermal stability of the metal complexes is evaluated. The synthesized ligands, in a comparison to their metal complexes also were screened for their antibacterial activity against bacterial species, *Bacillus cereus*, *Bacillus subtilis* and *Escherichia coli*. The activity data show that some metal complexes to be more potent / antibacterial than the parent organic ligands against one or more bacterial species.

**Keywords:** Schiff base ligands, Binary and ternary complexes, Thermal studies, Biological activity and Chelation theory.

Schiff bases are compounds containing the azomethine group (R-CH=N-) and are usually formed by the condensation of a primary amine with an active carbonyl compound<sup>(1,2)</sup>. Schiff bases have been used extensively as ligands in the field of coordination chemistry, some of the reasons are that the intramolecular hydrogen bonds between the (O) and the (N) atoms which play an important role in the formation of metal complexes and that Schiff base compounds show

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photochromism and thermochromism in the solid state by proton transfer from the hydroxyl (O) to the imine (N) atoms<sup>(3)</sup>.

A large number of Schiff bases and their complexes have been investigated for their interesting and important properties, such as their ability to reversibly bind oxygen, catalytic activity in the hydrogenation of olefins, photochromic properties and complexing ability towards some toxic metals, furthermore complexes of Schiff bases showed promising applications in biological activity and biological modeling applications<sup>(4-7)</sup>.

As an extension of our work on the structural characterization of Schiff base ligands and their metal complexes<sup>(8-12)</sup>, the main target of the present article is to study the coordination behavior of the two ligands  $H_2L^1$  and  $HL^2$  (Fig.1) and its binary as well as its ternary complexes, also to evaluate the relative thermal stability of the synthesized complexes and evaluation of the biological activity against different species of bacteria.

## Experimental

### *Reagents and instruments*

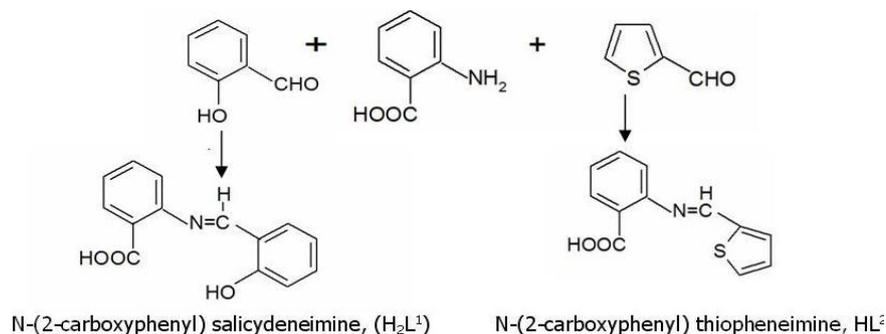
All chemicals available were of highest purity: salicylaldehyde and 2-thiophene carboxaldehyde (Aldrich); Anthranilic acid (Fluka); pyridine; dimethylformide (DMF), dimethylsulphoxide (DMSO) and diethylether were BDH or Merck; ethyl alcohol was analytical grade and was purified by standard method prior its use<sup>(13)</sup>.  $CoCl_2 \cdot 6H_2O$ ,  $NiCl_2 \cdot 6H_2O$ ,  $CdCl_2 \cdot H_2O$ ,  $FeCl_3 \cdot 6H_2O$  and  $UO_2(NO_3)_2 \cdot 6H_2O$  (Merck). Nitric acid, perchloric acid, sulphuric acid, ammonia solution, ethelendiaminetetraacetic acid disodium salt (EDTA), murexide, eriochrome black T, and silver nitrate were analytical grade and were used as supplied.

The elemental analysis of carbon, hydrogen, nitrogen, and sulphur were made using Perkin–Elmer 2408 CHN analyzer at the Microanalytical Center, Cairo University, Giza, Egypt. Metal contents were determined by titration against standard EDTA solution after complete decomposition of the complexes with nitric acid and perchloric acid in Kjeldahl flask several times and the chloride contents were determined gravimetrically. Melting or decomposition points of the prepared compounds were measured by electronic melting point apparatus: Griffin & George made in Britain. The IR spectra of the prepared compounds were recorded as KBr discs using a Perkin – Elmer 437 IR spectrometer ( $400 - 4000\text{ cm}^{-1}$ ) at the Microanalytical Center, Cairo University, Giza, Egypt. Mass spectra were recorded at 70 eV and 300 °C on a Hewlett – Packard mass spectrometer model MS 5988 at the Microanalytical Center, Cairo University, Giza, Egypt. The proton NMR spectra (DMSO–d<sub>6</sub>) were recorded on a Bruker FT- 400 MHz spectrometer without using internal standard. The ultraviolet and visible spectra were measured at room temperature in the UV/visible range (200–800nm) using UV-VIS-NIR Shimadzu 3101pc, at the Microanalytical Center,

Cairo University , Giza , Egypt. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a Johnson Matthey , Alfa product , model MKI magnetic susceptibility balance. The effective magnetic moments were calculated using the relation  $\mu_{\text{eff}} = 2.828(Xm.T)^{1/2}$  B.M. where, Xm is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds. The molar conductance measurements were measured in solution of the complexes in DMF ( $10^{-3}$  M ) using JEN WAY 4510 conductivity meter. A thermogravimetric analyzer TGA-50 SHIMA VZU and DTA, TA50 shimadzu, at the Micro Analytical Center, Mubarak City for Scientific Research , Borg El Arab , Alexandria, Egypt and at the Micro Analytical Center, Cairo University , Giza , Egypt were used to record simultaneously the TG curves, the experiments were carried out in dynamic nitrogen atmosphere ( $20 \text{ ml min}^{-1}$ ) with a heating rate  $10^\circ\text{C min}^{-1}$  in the temperature range  $20\text{--}1000^\circ\text{C}$  using platinum crucibles. Highly sintered  $\alpha\text{-Al}_2\text{O}_3$  was used as a reference. Antibacterial activity of all prepared compounds, free ligands and their binary and ternary complexes were tested using the diffusion agar method<sup>(14)</sup>. The chosen strains were bacillus cereus and bacillus subtilis as a Gram – positive bacteria and *Escherichia coli* as a Gram – negative bacteria. The antibiotic Chloramphenicol was used as standard antibacterial control and agar nutrient as the medium.

#### Schiff base ligands synthesis

The two Schiff base ligands,  $\text{H}_2\text{L}^1$  and  $\text{HL}^2$  (Fig.1) were prepared according to the previously published methods<sup>(15,16)</sup> by refluxing 0.1 mol of salicylaldehyde (10.66 ml) and 0.1 mol of phenyl hydrazine (9.84ml) in 60 ml of ethyl alcohol for 4hr in a water bath and cooling the reaction mixture . Then , the product was collected by filtration, washed several times with ethanol and diethyl ether then dried in a desiccator over anhydrous calcium chloride to give orange powder of Schiff base ligand,  $\text{H}_2\text{L}^1$  in 78.22% yield or yellow powder of Schiff base ligand,  $\text{HL}^2$  in 64.11% yield. Some physico-chemical characteristics of both ligands and their elemental analysis are collected in Table 1.



**Fig.1. Structure of Schiff base ligands used ( $\text{H}_2\text{L}^1$ ) and ( $\text{HL}^2$ ), N-(2-carboxyphenyl) salicylideneimine ( $\text{H}_2\text{L}^1$ ) and N-(2 carboxyphenyl) thiopheneimine ( $\text{HL}^2$ ).**

TABLE I. Analytical data and some physical properties of Schiff base ligands, (HL<sup>1</sup>) and HL<sup>2</sup> and their binary and ternary complexes.

Compd No	Molecular formula (MWT)	colour	M.P (°C)	Am*	Elem. anal. found / (Calcd.)				
					C	H	N	Cl	M
HL <sup>1</sup>					69.63	4.55	5.8	-	-
C <sub>10</sub> H <sub>11</sub> NO <sub>4</sub>		Orange	200	-	-69.69	-4.61	-5.81	-	-
(1) [Co(HL <sup>1</sup> ) <sub>3</sub> H <sub>2</sub> O]Cl <sub>2</sub> ·H <sub>2</sub> O		Dark Green	Over 300	126	37.45	3.98	2.84	15.76	12.96
[Co C <sub>10</sub> H <sub>11</sub> NO <sub>4</sub> Cl <sub>2</sub> 4H <sub>2</sub> O] (443.17)					-37.94	-4.33	-3.16	-16.02	-13.3
(2) [Ni(HL <sup>1</sup> )Cl <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub> ·2H <sub>2</sub> O		Green	Over 300	87	37.84	4.21	2.98	19.25	15.04
[Ni C <sub>10</sub> H <sub>11</sub> NO <sub>4</sub> Cl <sub>2</sub> 4H <sub>2</sub> O] (442.93)					-37.96	-4.33	-3.16	-18.32	-15.17
(3) [Cd(HL <sup>1</sup> ) <sub>3</sub> H <sub>2</sub> O]Cl <sub>2</sub>		Dark Orange	Over 300	119	34.86	3.21	2.52	14.62	23.53
[Cd C <sub>10</sub> H <sub>11</sub> NO <sub>4</sub> Cl <sub>2</sub> 3H <sub>2</sub> O] (478.63)					-35.13	-3.59	-2.93	-14.83	-23.49
(4) [Fe(HL <sup>1</sup> ) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub> ·2H <sub>2</sub> O		Black	Over 300	121	35.15	3.89	2.78	21.95	11.55
[Fe C <sub>10</sub> H <sub>11</sub> NO <sub>4</sub> Cl <sub>2</sub> 4H <sub>2</sub> O] (475.54)					-35.36	-4.04	-2.95	-22.4	-11.74
(5) [UO <sub>2</sub> (HL <sup>1</sup> ) <sub>2</sub> H <sub>2</sub> O]2NO <sub>3</sub>		Orange	Over 300	123	24.28	2.35	7.98	-	-
[U C <sub>10</sub> H <sub>11</sub> N <sub>2</sub> O <sub>11</sub> 3H <sub>2</sub> O] (689.38)					-24.39	-2.49	-8.13	-	-
(6) [Co(HL <sup>1</sup> ) <sub>2</sub> (py) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub>		Faint Pink	Over 300	127	46.85	3.98	5.67	14.45	12.11
[Co C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub> 2H <sub>2</sub> O] (486.24)					-46.93	-4.15	-5.76	-14.6	-12.12
(7) [Ni(HL <sup>1</sup> ) <sub>2</sub> (py) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub> ·2H <sub>2</sub> O		Bluish White	Over 300	126	43.61	4.42	5.16	14.65	11.1
[Ni C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub> 4H <sub>2</sub> O] (522.04)					-43.71	-4.64	-5.37	-14.79	-11.24
(8) [Cd(HL <sup>1</sup> ) <sub>2</sub> (py) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub>		Pink	Over 300	126	42.15	3.65	4.95	12.99	20.62
[Cd C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub> 2H <sub>2</sub> O] (539.72)					-42.28	-3.74	-5.19	-13.16	-20.83
(9) [Fe(HL <sup>1</sup> ) <sub>2</sub> (py) <sub>2</sub> H <sub>2</sub> O]Cl <sub>2</sub> ·H <sub>2</sub> O		Black	Over 300	112	43.85	3.82	5.15	22.09	10.53
[Fe C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub> 2H <sub>2</sub> O] (518.61)					-44	-3.9	-5.4	-22.55	-10.76
(10) [UO <sub>2</sub> (HL <sup>1</sup> ) <sub>2</sub> (py) <sub>2</sub> H <sub>2</sub> O]2NO <sub>3</sub>		Orange	Over 300	124	30.35	2.59	7.36	-	-
[UO <sub>2</sub> C <sub>10</sub> H <sub>16</sub> N <sub>2</sub> O <sub>7</sub> 2H <sub>2</sub> O] (750.47)					-30.41	-2.69	-7.47	-	-

TABLE I. Cont.

Chemical No.	Molecular formula (M.WT)	color	M.P. (°C)	$\Delta \epsilon^a$	Elec. anal. Band ( $\nu_{\text{obs}}$ )					
					C	B	M	S	Cl	M
171	$\text{Co}_2\text{H}_2\text{NO}_5 \cdot 2\text{H}_2\text{O}$	Yellow	172-174	-	62.25	3.29	6.05	13.23	-	-
(11)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}$	White	Oxide 300	82	-49.31	-3.93	-6.06	-13.84	10.24	17.15
(12)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	23	-49.06	-2.95	-4.09	-9.34	-10.36	-17.2
(13)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	White	Oxide 300	19	-39.92	-2.12	-3.29	-8.85	-8.85	-16.28
(14)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	17	-38.59	2.99	3.48	7.98	17.88	14.19
(15)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	96	-22.09	2.74	4.25	4.87	-	-
(16)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	13	-42.32	3.42	6.59	7.51	8.32	1.225
(17)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	13	-42.41	-3.59	-6.64	-9.59	-8.42	-13.97
(18)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	99	-41.33	-2.81	-6.25	-7.15	8.02	13.35
(19)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	90	-41.39	3.36	5.54	6.36	7.16	23.65
(20)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	95	-44.28	3.21	5.97	6.94	-7.2	-21.79
(21)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	95	-44.28	-3.33	-6.16	-9.03	15.47	13.16
(22)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	95	-39.86	2.21	6.24	4.78	-15.61	-12.28
(23)	$\text{K}_2\text{Co}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$	White	Oxide 300	95	-39.96	-2.3	-6.37	-4.85	-	-

<sup>a</sup> Molar conductance in  $10^{-4}$  M DMF solution  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$

Preparation of metal complexes

*preparation of binary complexes*

A general method has been adopted to prepare the binary complexes: A hot ethanolic solution ( 20 ml) of the appropriate metal chloride salt namely , (CoCl<sub>2</sub> . 6H<sub>2</sub>O , NiCl<sub>2</sub>.6H<sub>2</sub>O , CdCl<sub>2</sub>.H<sub>2</sub>O, or FeCl<sub>3</sub>.6H<sub>2</sub>O) or nitrate UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O (0.01mol) was added dropwise to a solution of the Schiff-base ligands, H<sub>2</sub>L<sup>1</sup>,HL<sup>2</sup> (0.01mol). The resulting mixture was stirred under reflux for 2hr on a water bath . The isolated product was washed with ethanol and diethyl ether then dried in a desiccator over anhydrous calcium chloride. These complexes are soluble in DMF and DMSO while insoluble in most organic solvents.

*Preparation of mixed ligand complexes*

A general method has been adopted to prepare the mixed ligand complexes in which the prepared Schiff base ligands act as primary ligands and the secondary ligand was pyridine. A hot ethanolic solution ( 20 ml ) of the appropriate metal chloride salt namely, (CoCl<sub>2</sub> .6H<sub>2</sub>O , NiCl<sub>2</sub>.6H<sub>2</sub>O , CdCl<sub>2</sub>.H<sub>2</sub>O, or FeCl<sub>3</sub>.6H<sub>2</sub>O) or nitrate UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (0.01mol) was added dropwise to a mixture of the Schiff base ligands, H<sub>2</sub>L<sup>1</sup>,HL<sup>2</sup> (0.01mol) and pyridine (0.01mol). The resulting mixture was stirred under reflux for 3hr on a water bath. The isolated product was washed with ethanol and diethyl ether then dried in a desiccator over anhydrous calcium chloride. These complexes are soluble in DMF and DMSO while insoluble in most organic solvents.

**Results and Discussion**

Condensation of the aldehyde with amine readily gives rise to the corresponding imines "Schiff base ligands, H<sub>2</sub>L<sup>1</sup> and HL<sup>2</sup> " (Fig.1). Their reaction with the metal ions Co (II), Ni (II), Cd (II), Fe (III) and UO<sub>2</sub> (II), afford the binary complexes (1-5, 11-15).). Also , the same reactions in presence of pyridine as secondary ligand afforded the ternary complexes (6-10, 16-20). Table 1 shows the analytical data and some physical properties of the prepared compounds.

The suggested structure of the prepared compounds were elucidated by elemental analysis , (Table 1), IR,<sup>1</sup>H-NMR and mass spectra as well as electronic absorption spectra , conductance , magnetic moments and TGA measurements . Moreover, the antibacterial activity of the free ligands and its binary and ternary complexes were tested against different strains of bacteria at different concentrations.

*<sup>1</sup>H-NMR spectra*

The proton magnetic resonance of the free Schiff base ligands, (H<sub>2</sub>L<sup>1</sup>) and (HL<sup>2</sup>) and their diamagnetic binary complexes, (3, 5, 13, 15) in addition to ternary complexes , (8, 10, 18, 20) have been recorded in DMSO-d<sub>6</sub> as solvent. The <sup>1</sup>H-NMR spectrum of free ligands showed a singlet peaks at 8.84-9.95, 10.26 and 10.70-15.99 ppm that was assigned to azomethine , phenolic and carboxylic protons, respectively , in addition to multiplet signals at 6.50-8.72 ppm attributed to protons of aromatic / thiophene ring<sup>(16,17)</sup>. The comparison of

the  $^1\text{H-NMR}$  data of the free ligands and their Cd(II) and  $\text{UO}_2(\text{II})$  complexes clarifies the mode of coordination between the ligand and its metal ions. Upon complexation, it was found that the spectra of metal complexes display a significant shift of the signals due to azomethine, phenolic and carboxylic protons indicating in turn the involvement of azomethine group in coordination as well as the involvement of both phenolic and carboxylic groups in coordination to the metal ions without their deprotonation suggesting that the ligand,  $\text{H}_2\text{L}^1$  acts as neutral tridentate ligand, ONO coordination sphere.

Also, it was found that the spectra display a significant shift of the signals due to azomethine and thiophene protons indicating their involvement in chelation. Also, the absence of the signal due to carboxylic proton in all complexes favors the loss of OH-proton due to complexation suggesting that the ligand,  $(\text{HL}^2)$  acts as monobasic tridentate ligand, ONS coordination sphere. Moreover, the spectra of ternary complexes, (8, 10, 18, 20) showed multiplet signals at 7.72-8.60 ppm due to pyridine ring protons<sup>(18)</sup>. The spectral data are listed in Table 2.

**TABLE 2.**  $^1\text{H-NMR}$  data (ppm) for Schiff base ligands,  $(\text{H}_2\text{L}^1)$  and  $(\text{HL}^2)$  and their diamagnetic complexes.

Compd. No .	$\delta_{\text{phenyl/thiophen}}$	$\delta_{\text{py}}$	$\delta_{\text{CH=N}}$	$\delta_{\text{OH}}$	$\delta_{\text{COOH}}$
$\text{H}_2\text{L}^1$	6.50-7.89	-	8.84	10.26	10.7
3	6.48-7.70	-	8.7	10.24	10.7
5	6.47-8.18	-	9.34	10.25	10.66
8	6.45-7.68	7.72-7.86	8.65	10.26	10.7
10	6.70-7.75	8.13-8.17	9.33	10.21	10.7
$\text{HL}^2$	6.99-8.72	-	9.95	15.99	-
13	6.48-8.43	-	9.96	-	-
15	6.45-8.92	-	9.95	-	-
18	7.38-7.82	8.58-8.60	8.88	-	-
20	6.48-8.02	8.13-8.58	9.95	-	-

#### *IR Spectra*

The mode of binding of both Schiff base ligands to the metal ions was elucidated by recording the IR spectra of the complexes as compared with the spectra of the free ligands. The small difference between the infrared spectra of both Schiff base ligands indicates that, the ligands have a similar structure but the spectra of the free ligands differ obviously from that of their complexes as shown in Tables 3 & 4. The spectra of both free ligands show two strong bands at 1617 and 1609  $\text{cm}^{-1}$  characteristics of the  $\nu\text{C=N}$  (azomethine) stretching mode for

( $H_2L^1$ ) and ( $HL^2$ ), respectively<sup>(19)</sup>, indicating the formation of the Schiff base products. These bands are shifted towards lower frequencies in the spectra of all metal complexes  $1603-1497\text{ cm}^{-1}$  compared with the free Schiff base indicating the involvement of the azothemine nitrogen in chelation with the metal ions, the coordination of nitrogen to the metal ion would be expected to reduce the electron density of the azomethine link and thus cause a shift in the  $\nu C=N$  group. The intense bands at  $1685$  and  $1705\text{ cm}^{-1}$  present in the IR spectra of the free ligands may be assigned to the  $\nu C=O$  (carboxylic group), similar bands were observed at the same frequency region in the IR spectra of some organic acid ligands<sup>(20)</sup>. However, the spectra of all complexes show the absence of this bands accompanied by the appearance of two characteristic bands at  $1703-1599$  and  $1458-1327\text{ cm}^{-1}$  correlated to  $\nu_{asy.}(COO^-)$  and  $\nu_{sy}(COO^-)$ , respectively indicating the participation of the carboxylate oxygen atom in coordination, moreover, the difference between the asymmetric and symmetric stretching frequencies of the coordinated carboxyl group lie in the range  $289-205\text{ cm}^{-1}$  suggesting the monodentate coordination mode of the carboxyl group<sup>(21)</sup>.

The observed broad band at  $3445\text{ cm}^{-1}$  in the IR spectrum of the ligand,  $H_2L^1$  was attributed to OH of the phenolic and carboxylic OH groups<sup>(22)</sup>. The IR spectrum displays also medium bands at  $850\text{ cm}^{-1}$  may be assigned to  $\nu C-OH$  of carboxylic group<sup>(23)</sup>, in addition to another band at  $1292\text{ cm}^{-1}$  due to  $\nu C-O$  (phenolic group)<sup>(22)</sup>.

A careful comparison of the IR spectra of the metal complexes with those of the free ligand,  $H_2L^1$  reveals that: the band at  $3445\text{ cm}^{-1}$  is found to be shifted to lower frequency region at  $3422-3306\text{ cm}^{-1}$  in all metal complexes suggesting the involvement of OH groups of the phenolic and carboxylic groups in complex formation without their deprotonation confirmed by  $^1H-NMR$  spectra data and the ligand acts as neutral ligand. The strong band at  $1292\text{ cm}^{-1}$  due to  $\nu C-O$  (phenolic), which undergoes a shift toward lower frequencies in the region  $1288-1242\text{ cm}^{-1}$  in the metal complexes (2-10), indicating the coordination of phenolic oxygen to the metal ions.

The observed band, at  $799\text{ cm}^{-1}$  in the IR spectrum of the free ligand,  $HL^2$  was assigned to  $\nu C-S-C$  stretching vibration of thiophene moiety<sup>(16,24)</sup> which shifts to lower frequencies in the spectra of metal complexes (11-20) in the region  $756-730\text{ cm}^{-1}$ , suggesting the coordination of metal ions through the sulphur atom of thiophene moiety supported from  $^1HNMR$  data.

The IR spectra of uranyl complexes, (5,10,15,20) display strong bands at  $1389-1373\text{ cm}^{-1}$  and  $922-918\text{ cm}^{-1}$  characteristic to  $\nu_{NO_3^-}$  (ionic) and  $\nu_{O=U=O}$  modes, respectively<sup>(25-28)</sup>. The IR spectra of ternary complexes, (6-10,16-20) exhibited additional bands at  $1543-1450\text{ cm}^{-1}$  and  $1080-1022\text{ cm}^{-1}$  due to skeletal vibration of pyridine ring and pyridine ring breathing mode, respectively suggesting the participation of ring nitrogen in complex formation<sup>(29)</sup>.

TABLE 3. Significant IR- spectral bands (cm<sup>-1</sup>) of Schiff base ligand, (H<sub>2</sub>L<sup>+</sup>) and its binary and ternary complexes.

Additional bands	ν <sub>N-H</sub>	ν <sub>N-H</sub>	ν <sub>C=O</sub>	ν <sub>C=O</sub>	ν <sub>C=N</sub>	Δν	ν <sub>C=O</sub>	ν <sub>C=O</sub>	ν <sub>C=O</sub>	Compd.
		(carboxy)	(phenol.)	(azome.)	ν <sub>ar</sub> -ν <sub>tr</sub>	(carboxy)	(carboxy /phenol.)	(carboxy /phenol.)		
-	-	850	1292	1617	-	-	1685	3445	No	
-	453	522	804	1246	1609	265	1636;1571	3400	<b>1</b>	
-	483	527	836	1288	1581	220	1628;1408	3376	<b>2</b>	
-	490	522	832	1246	1587	237	1633;1398	3421	<b>3</b>	
-	449	505	801	1281	1597	237	1633;1396	3421	<b>4</b>	
922 (C=U=O) and 1384 (ionic nitrate)	496	522	827	1280	1595	236	1633;1399	3421	<b>5</b>	
1543(skeletal vibration of pyridine ring) and 1038 (pyridine ring breathing mode)	467	517	810	1242	1593	289	1616;1327	3306	<b>6</b>	
1535(skeletal vibration of pyridine ring) and 1069 (pyridine ring breathing mode)	471	521	810	1277	1593	212	1620;1408	3422	<b>7</b>	
1555(skeletal vibration of pyridine ring) and 1038 (pyridine ring breathing mode)	455	517	802	1242	1589	212	1616;1404	3379	<b>8</b>	
1486(skeletal vibration of pyridine ring) and 1049 (pyridine ring breathing mode)	522	560	796	1251	1536	206	1599;1393	3367	<b>9</b>	
1474 (skeletal vibration of pyridine ring) ; 1022 (pyridine ring breathing mode); 922 (O=U=O) and 1373 (ionic nitrate)	455	521	829	1261	1543	205	1603;1400	3422	<b>10</b>	

TABLE 4. Significant IR spectral bands ( $\text{cm}^{-1}$ ) of Schiff base ligand, (HL<sup>-</sup>) and its binary and ternary complexes.

Compound	$\nu_{\text{O-H}}$ (carboxyl/ $\text{H}_2\text{O}$ )	$\nu_{\text{C=O}}$ (carboxyl)	$\nu_{\text{C=O}}$ (arome.)	$\nu_{\text{C=C}}$ (arome.)	$\nu_{\text{C-OH}}$ (arome.)	$\nu_{\text{C-OH}}$ (carboxyl)	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$	Additional bands
BL <sup>2</sup>	3422	1705	1609	1599	845	-	-	-	-	-
11	3307	1615, 1409	1592	1554	870	517	466	419	-	-
12	3303	1636, 1407	1593	1555	871	520	472	423	-	-
13	3389	1630, 1400	1603	1445	830	525	471	419	-	-
14	3389	1619, 1396	1542	1554	804	558	481	429	-	-
15	3410	1620, 1410	1520	1530	810	621	465	421	1389 (ionic NO <sub>3</sub> ) and 922 (O-U-O)	-
16	3306	1631, 1408	1593	1556	810	517	467	421	1535 (stretch vibration of pyridine ring) and 1042 (pyridine ring stretching mode)	-
17	3306	1628, 1412	1589	1556	810	521	471	424	1535 (stretch vibration of pyridine ring) and 1069 (pyridine ring stretching mode)	-
18	3044	1705, 1458	1593	1556	837	529	465	436	1532 (stretch vibration of pyridine ring) and 1020 (pyridine ring stretching mode)	-
19	3200	1616, 1389	1566	1488	833	544	494	416	1533 (stretch vibration of pyridine ring) and 1057 (pyridine ring stretching mode)	-
20	3364	1616, 1340	1487	1488	837	563	529	410	1450 (stretch vibration of pyridine ring) and 1026 (pyridine ring stretching mode)	-

Conclusive evidence of the bonding is also shown by observing new bands in the IR spectra of metal complexes in low frequency region at 621-

505  $\text{cm}^{-1}$  and 529-449  $\text{cm}^{-1}$  may be due to  $\nu_{\text{M-O}}$ ,  $\nu_{\text{M-N}}$  and,  $\nu_{\text{M-S}}$ , respectively that are not observed in the spectrum of both free ligands<sup>(16,26)</sup>. Additionally, not all metal complexes (1-10) exhibited coordinated / hydrated water molecules and it is difficult to draw conclusions based on  $\nu_{\text{OH}}$  to detect the nature of water molecules due to the different probabilities in the  $\nu_{\text{OH}}$  water region resulted from the presence of  $\nu_{\text{OH}}$  of the phenolic and carboxylic OH groups in addition to water molecules associated with the complex formation. Furthermore, observed broad bands appear at 3652-3425  $\text{cm}^{-1}$  in complexes (11-20) indicates the existence of coordinated/lattice water molecules<sup>(30)</sup>. The nature of water molecules was detected using the thermal gravimetric analysis technique as clear letter.

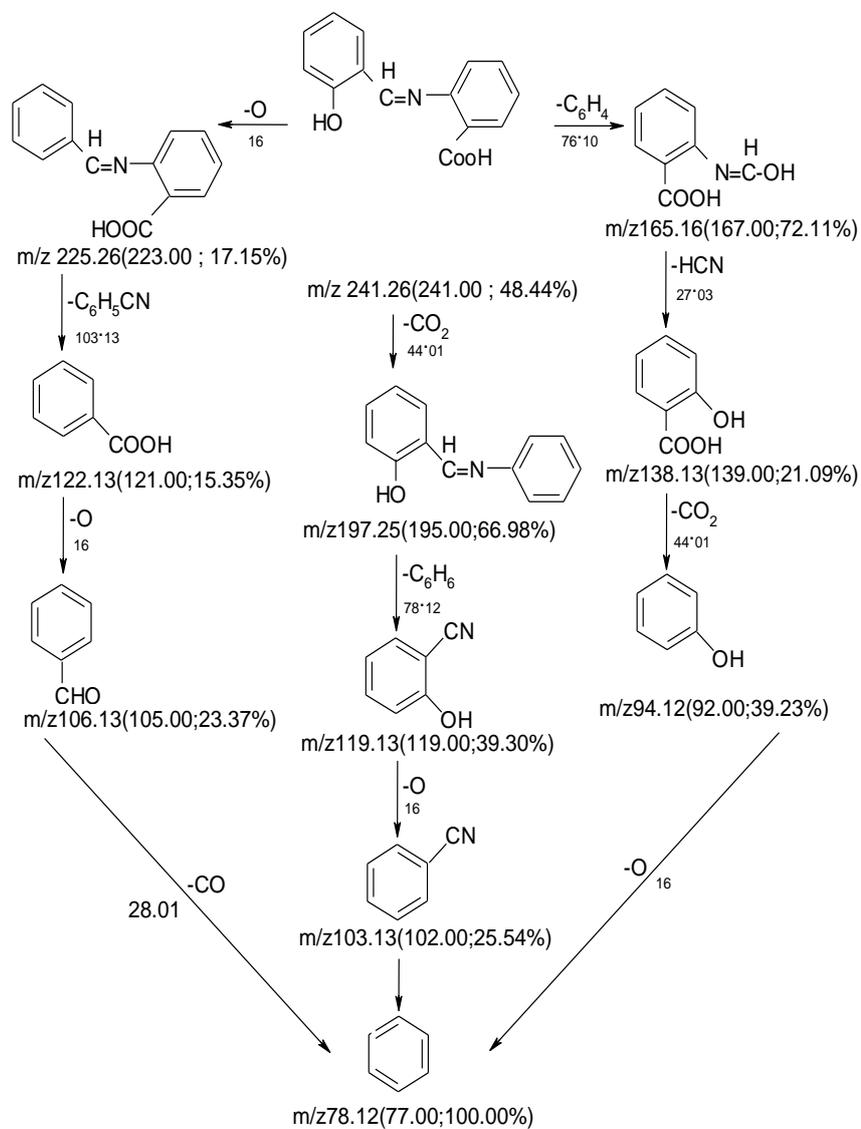
Furthermore the observed broad bands appear at 3652-3425  $\text{cm}^{-1}$  in complexes (11-20) indicates the existence of coordinated / lattice water molecules<sup>(30)</sup>.

#### *Mass spectra*

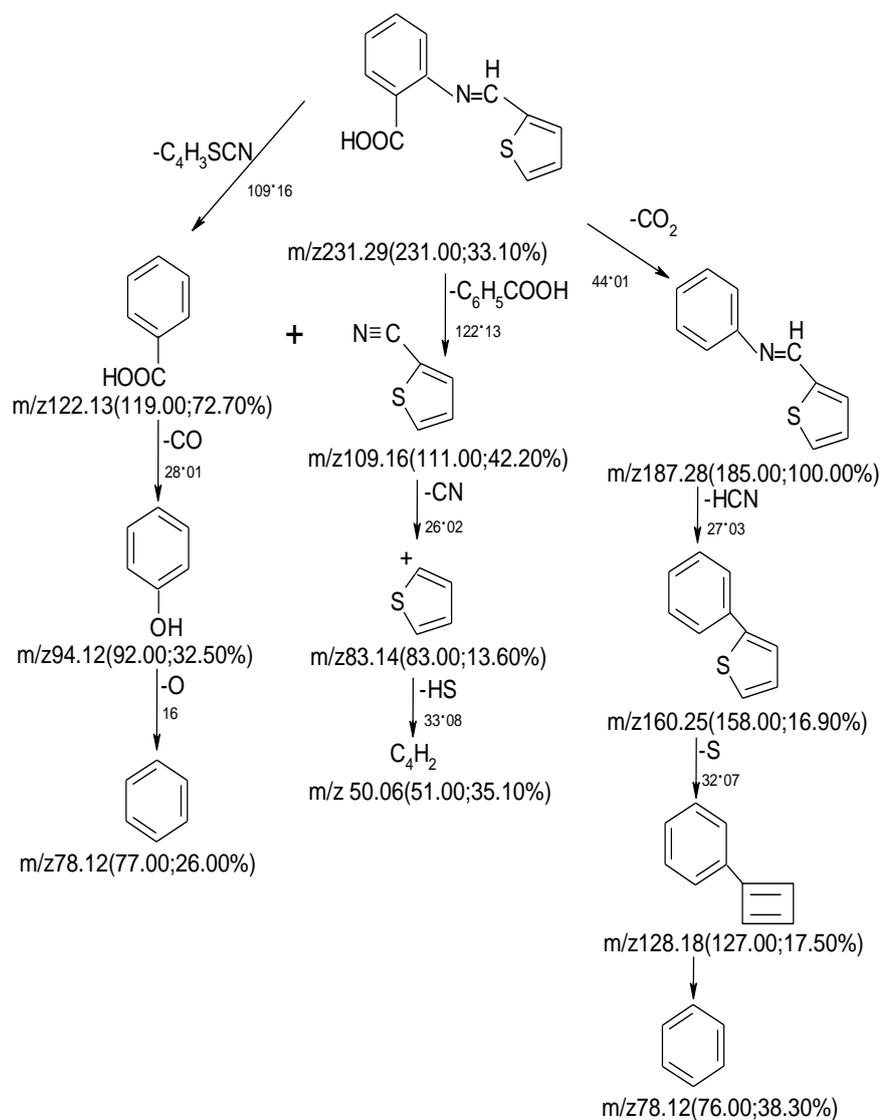
The mass spectra of the ligands used,  $\text{H}_2\text{L}^1$  and  $\text{HL}^2$  exhibit the parent peaks at  $m/e$  (241.00 and 231.00) (calculated 241.26 and 231.29) with abundance 48.44% and 33.10%, respectively. Also, the spectrum shows numerous peaks corresponding to various fragments, their intensity gives an idea on the stability of the fragments. Schemes 1&2 shows the proposed paths of the decomposition steps for the ligands.

#### *Molar conductivity measurements*

The metal complexes were dissolved in DMF and the molar conductivities of  $10^{-3}$  M of their solutions at room temperature were measured. Table 1 shows the molar conductance values of the metal complexes and it is concluded from the results that only the metal (1,3-10) complexes are found to have molar conductance values of 127-119  $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$  indicating that these complexes are 1:2 electrolytic nature confirming the presence of ionic chloride/nitrate anions in complexes. On the other hand, the molar conductivity values of metal complexes (2,11,15,18-20) are found to be 99-82  $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$  suggesting 1:1 electrolytic nature, while the other metal complexes (12-14,16,17) having conductance values of 23-13  $\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$  indicating that these complexes are neutral<sup>(31,32)</sup>



**Scheme 1.** Mass fragmentation pattern of Schiff base ligand,  $H_2L^1$ .

Scheme 2. Mass fragmentation pattern of Schiff base ligand,  $\text{HL}^2$

*Electronic spectra and magnetic moment data*

The electronic spectra of both free understudy ligands, and its complexes were recorded in DMF at room temperature and all data are given in Table 4. Two absorption bands were observed in the spectra of the free ligands in the region 261-358, nm due to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions, respectively due to benzene, thiophene and the azomethine (CH=N) function<sup>(33)</sup>.

In the spectra of metal complexes, the absorption bands due to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transition were found to be shifted to lower or higher frequency due to the coordination of the ligands with the metal ions .

The electronic spectra of the two Co(II) complexes, (1,6) showed two absorption bands at 606-580 and 690-675 nm may be assigned to the transition,  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  and  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ , respectively suggesting the octahedral structure. The magnetic moment values are in the range 4.97-4.75 B.M. confirmed the suggested structure<sup>(24)</sup>.

The electronic spectra of the two Co(II) complexes , (11) showed one absorption bands at 698 nm may be assigned to the transition ,  ${}^4A_2(F) \rightarrow {}^4T_1(P)$  suggesting tetrahedral structure. The magnetic moment values 3.11 B.M. confirmed the suggested structure<sup>(2)</sup> . While, the Co(II) complex , (16) , showed absorption bands at 503, 554 and 781 nm which could be attributed to the transition  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ , respectively, this transitions together with the magnetic moment value 4.82 B.M. characterized Co(II) ion in octahedral geometry<sup>(24)</sup>.

The electronic spectra of the Ni(II) complexes, (2,7,12,17) showed three absorption bands at 561-552 nm, 619-596 and 731-660 nm corresponding to the transition,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ , respectively, suggesting octahedral geometry, additionally, the magnetic moment values of 3.10-2.77 B.M. confirmed the octahedral suggestion<sup>(16)</sup>.

Fe (III) complexes , (4,9,14,19) have one absorption band at 671-519 nm due to the transition  ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$  in octahedral geometry and the magnetic moment values are 5.70-5.40 B.M.<sup>(16)</sup>.

Both Cd(II) and  $UO_2(II)$  complexes are diamagnetic in nature and so no d-d transition were observed and according to correlation of all obtained data, the octahedral structure may be suggested. The magnetic moment values are listed in Table 5.

**TABLE 5.** Magnetic moment and electronic spectral data of the Schiff base ligands ( $H_2L^1$ ) and ( $HL^2$ ) and their metal complexes.

Compd. No.	$\mu_{\text{eff}}$ (B.M.)	Absorption bands (nm)		
		$\pi-\pi^*$	$n-\pi^*$	d-d transition
$H_2L^1$	-	261	332	-
<b>1</b>	4.75	267	318	606,675
<b>2</b>	3.1	279	320	555,597,670
<b>3</b>	Diamagnetic	272	337	-
<b>4</b>	5.41	268	326	573
<b>5</b>	Diamagnetic	276	323	-
<b>6</b>	4.97	316	277	580 , 690
<b>7</b>	2.84	263	289	565,620,740
<b>8</b>	Diamagnetic	294	360	-
<b>9</b>	5.65	268	319	519
<b>10</b>	Diamagnetic	296	385	-
$HL^2$	-	291	358	-
<b>11</b>	3.11	227	335	698
<b>12</b>	2.77	239	317	552 , 596 , 660
<b>13</b>	Diamagnetic	261	340	-
<b>14</b>	5.4	346	406	554
<b>15</b>	Diamagnetic	284	361	-
<b>16</b>	4.82	265	335	503 , 554 , 781
<b>17</b>	2.84	282	341	561 , 619 , 731
<b>18</b>	Diamagnetic	266	330	-
<b>19</b>	5.7	349	382	671
<b>20</b>	Diamagnetic	326	382	-

*Thermal gravimetric analysis*

Thermal gravimetric analysis (TGA) of metal complexes was used as a probe the associated water molecules to be in the coordination sphere or in the crystalline form of the complexes. The thermograms obtained were analyzed to give the percentage weight loss as a function of temperature. The decomposition stages, temperature ranges, decomposition product as well as the found and calculated weight lost percentages are depicted in Tables 6 & 7. Figure 2 is a representative example for thermal analysis of nickel (II) complexes; (2, 7, 12 and 17) for both binary and ternary complexes for two Schiff base ligands  $H_2L^1$  and  $HL^2$  under study.

**TABLE 6. Thermoanalytical results of binary and ternary complexes of Schiff base ligands, H<sub>2</sub>L<sup>1</sup>**

Complex compd.	TG range / °C	Mass loss % obs.(calc.)	Assignment
(1) [Co(H <sub>2</sub> L <sup>1</sup> ).3H <sub>2</sub> O]Cl <sub>2</sub> .H <sub>2</sub> O	24-85	10.28 (10.17)	Loss of H <sub>2</sub> O (lattice)and 1.5 H <sub>2</sub> O (coord.)
	85-270	20.02 (19.64)	Loss of 1.5 H <sub>2</sub> O (coord.) , O <sub>2</sub> and CO
	270-704	41.08 (40.90)	Loss of HCN and C <sub>6</sub> H <sub>5</sub> - C <sub>6</sub> H <sub>5</sub> , leaving Co Cl <sub>2</sub> residue
		71.38 (70.71)*	
(2) [Ni(H <sub>2</sub> L <sup>1</sup> )Cl.2H <sub>2</sub> O]Cl .2H <sub>2</sub> O	28-114	23.23 (22.60)	Loss of 2H <sub>2</sub> O (lattice),2H <sub>2</sub> O (coord.) and CO
	114-231	22.55 (22.11)	Loss of HCN and Cl <sub>2</sub>
	231-500	38.28 (38.43)	Loss of 0.5O <sub>2</sub> and C <sub>6</sub> H <sub>5</sub> - C <sub>6</sub> H <sub>5</sub> leaving NiO residue
		84.06 (83.14)*	
(3) [Cd(H <sub>2</sub> L <sup>1</sup> ).3H <sub>2</sub> O]Cl <sub>2</sub>	156-320	32.01 (31.96)	Loss of 3H <sub>2</sub> O (coord.) , Cl <sub>2</sub> and CO
	320-473	18.01 (19.66)	Loss of C <sub>6</sub> H <sub>5</sub> OH
	473-730	26.10 (25.94)	Loss of C <sub>6</sub> H <sub>5</sub> OH and HCN , leaving Cd residue
		76.12 (77.56)*	
(4) [Fe(H <sub>2</sub> L <sup>1</sup> )Cl.2H <sub>2</sub> O]Cl <sub>2</sub> .2H <sub>2</sub> O	31-110	3.59 (3.79)	Loss of H <sub>2</sub> O (lattice)
	110-308	18.96 (18.82)	Loss of H <sub>2</sub> O (lattice), 2H <sub>2</sub> O (coord.) and 0.5 Cl <sub>2</sub>
	308-555	49.85 (50.73)	Loss of H <sub>2</sub> L <sup>1</sup> , leaving FeCl <sub>2</sub> residue
		72.40 (73.34)*	
(5) [UO <sub>2</sub> (H <sub>2</sub> L <sup>1</sup> ).3H <sub>2</sub> O]2NO <sub>3</sub>	318-381	10.87 (11.76)	Loss of 3H <sub>2</sub> O (coord.) and HCN
	381-430	30.98 (31.08)	Loss of O <sub>2</sub> , CO and C <sub>6</sub> H <sub>5</sub> - C <sub>6</sub> H <sub>5</sub> , leaving UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> residue
		41.85 (42.84)*	

\*Total mass loss

TABLE 6. Cont .

Complex compd.	TG range / °C	Mass loss % obs.(calc.)	Assignment
(6) [Co(H <sub>2</sub> L <sup>1</sup> )(py).2H <sub>2</sub> O]Cl <sub>2</sub>	260-360	19.38 (18.73)	Loss of 2H <sub>2</sub> O (coord.) , CO and HCN
	360-386	55.06 (54.57)	Loss of O <sub>2</sub> , C <sub>5</sub> H <sub>5</sub> N and C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>5</sub> , leaving Co Cl <sub>2</sub> residue
		74.44 (73.30)*	
(7) [Ni(H <sub>2</sub> L <sup>1</sup> )(py)2H <sub>2</sub> O]Cl <sub>2</sub> .2H <sub>2</sub> O	28-91	1.67 (1.73)	Loss of 0.5H <sub>2</sub> O (lattice)
	91-401	50.10 (50.05)	Loss of 1.5H <sub>2</sub> O(lattice),2H <sub>2</sub> O (coord.),CO <sub>2</sub> and C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>5</sub>
	401-587	24.41 (23.40)	Loss of 0.5O <sub>2</sub> , HCN and C <sub>5</sub> H <sub>5</sub> N , leaving NiCl <sub>2</sub> residue
		76.18 (75.18)*	
(8) [Cd(H <sub>2</sub> L <sup>1</sup> )(py).2H <sub>2</sub> O]Cl <sub>2</sub>	128-243	34.73 (35.25)	Loss of 2H <sub>2</sub> O (coord.) and C <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>5</sub>
	243-301	10.21 (10.20)	Loss of CO and HCN
	301-643	34.06 (33.72)	Loss of O <sub>2</sub> , Cl <sub>2</sub> and C <sub>5</sub> H <sub>5</sub> N , leaving Cd residue
(9) [ Fe (H <sub>2</sub> L <sup>1</sup> )(py) Cl.H <sub>2</sub> O ]Cl <sub>2</sub> .H <sub>2</sub> O		79.00 (79.17)*	
	40-234	35.59 (35.87)	Loss of H <sub>2</sub> O (lattice), H <sub>2</sub> O (coord.) , Cl <sub>2</sub> and C <sub>5</sub> H <sub>5</sub> N
	234-741	50.32 (50.47)	Loss of HCl,HCN,CO <sub>2</sub> andC <sub>6</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>5</sub> , leavingFeO residue
(10) [UO <sub>2</sub> (H <sub>2</sub> L <sup>1</sup> )(py).2H <sub>2</sub> O]2NO <sub>3</sub>		85.91 (86.34)*	
	300-362	12.31 (12.14)	Loss of 2H <sub>2</sub> O (coord.) , CO and HCN
	362-415	21.84 (20.95)	Loss of C <sub>5</sub> H <sub>5</sub> N and C <sub>6</sub> H <sub>6</sub>
	415-435	13.85 (14.67)	Loss of O <sub>2</sub> and C <sub>6</sub> H <sub>6</sub> , leaving UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> residue
		48.00 (59.76)*	

\*Total mass loss

**TABLE 7. Thermoanalytical results of binary and ternary complexes of Schiff base ligand, HL<sup>2</sup>.**

Complex compd.	TG range / °C	Mass loss % obs.(calc.)	Assignment
(11) [Co(L <sup>2</sup> ).H <sub>2</sub> O]Cl	350-458	72.70(73.44)	Loss of H <sub>2</sub> O (coord.), 0.5 Cl <sub>2</sub> and L <sup>2</sup> , leaving CoS residue
(12) [Ni (L <sup>2</sup> )Cl.2H <sub>2</sub> O]	323-423	74.33 (74.82)	Loss of 2H <sub>2</sub> O(Coord.), 0.5Cl <sub>2</sub> and L <sup>2</sup> , leaving NiS residue.
	65-235	27.67 (28.24)	Loss of 2H <sub>2</sub> O (lattice), 2H <sub>2</sub> O (coord.), CO and HCN
(13) [Cd(L <sup>2</sup> )Cl.2H <sub>2</sub> O].2H <sub>2</sub> O	235-520	22.59 (22.24)	Loss of 0.5 O <sub>2</sub> and C <sub>4</sub> H <sub>4</sub> S
	520-670	25.50 (25.00)	Loss of C <sub>6</sub> H <sub>5</sub> Cl, leaving Cd residue
		75.76 (75.48)*	
	31-85	9.84 (9.17)	Loss of H <sub>2</sub> O (lattice) and H <sub>2</sub> O (coord.)
(14) [Fe(L <sup>2</sup> )(Cl <sub>2</sub> ).H <sub>2</sub> O].H <sub>2</sub> O	261-570	67.73 (68.46)	Loss of Cl <sub>2</sub> and L <sup>2</sup> , leaving FeS residue
		77.57 (77.63)*	
	30-353	13.01 (13.81)	Loss of 3H <sub>2</sub> O (lattice) and 2H <sub>2</sub> O (coord.)
(15) [UO <sub>2</sub> (L <sup>2</sup> ).2H <sub>2</sub> O]NO <sub>3</sub> .3H <sub>2</sub> O	353-511	24.02 (23.79)	Loss of HCN,CO <sub>2</sub> and C <sub>4</sub> H <sub>4</sub> S
	511-524	22.00(21.48)	Loss of NO <sub>3</sub> and C <sub>6</sub> H <sub>6</sub> , leaving UO <sub>2</sub> residue
		59.03(59.08)*	
(16) [Co(L <sup>2</sup> )(py)Cl.H <sub>2</sub> O]	303-544	79.22 (78.43)	Loss of H <sub>2</sub> O (coord.), 0.5 Cl <sub>2</sub> C <sub>5</sub> H <sub>5</sub> N and L <sup>2</sup> , leaving Co S residue
	25-88	3.68 (4.10)	Loss of water lattice
(17) [Ni(L <sup>2</sup> )(py)Cl.H <sub>2</sub> O].H <sub>2</sub> O	148-344	76.32 (75.25)	Loss of water (coord.)
		80.00 (79.35)*	0.5Cl <sub>2</sub> ,C <sub>5</sub> H <sub>5</sub> N and L <sup>2</sup> , leaving NiS residue
	219-392	31.14 (31.55)	Loss of 2H <sub>2</sub> O (coord.), 0.5 Cl <sub>2</sub> and C <sub>4</sub> H <sub>4</sub> S
(18) [Cd(L <sup>2</sup> )(py).2H <sub>2</sub> O]Cl	392-574	45.86 (46.28)	Loss of HCN, CO <sub>2</sub> , C <sub>5</sub> H <sub>5</sub> N and C <sub>6</sub> H <sub>6</sub> , leaving Cd residue
		77.00 (77.83)*	
	100-248	17.12 (16.38)	Loss of H <sub>2</sub> O (coord.), NO <sub>3</sub> and CO
	248-418	17.43 (18.37)	Loss of HCN and C <sub>6</sub> H <sub>5</sub> OH
(20) [UO <sub>2</sub> (L <sup>2</sup> )(py).H <sub>2</sub> O]NO <sub>3</sub>	418-516	24.10 (24.70)	Loss of C <sub>5</sub> H <sub>5</sub> N and C <sub>4</sub> H <sub>4</sub> S, leaving UO <sub>2</sub> residue
		58.65 (59.45)*	

\*Total mass loss

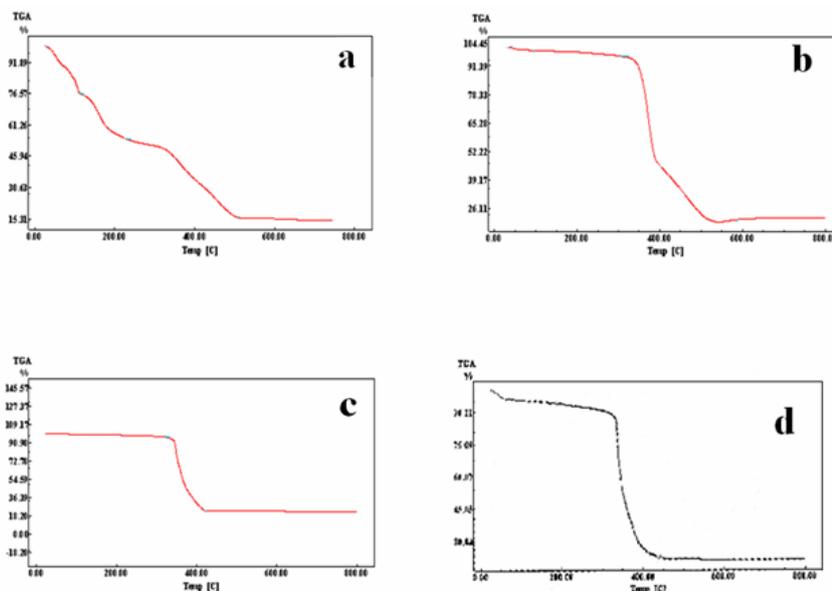


Fig. 2. TG curve of (a)  $[\text{Ni}(\text{H}_2\text{L}^1)\text{Cl}.2\text{H}_2\text{O}]\text{Cl}.2\text{H}_2\text{O}$  (2), (b)  $[\text{Ni}(\text{H}_2\text{L}^1)(\text{Py}).2\text{H}_2\text{O}]\text{Cl}.2\text{H}_2\text{O}$  (7), (c)  $[\text{Ni}(\text{L}^2)\text{Cl}.2\text{H}_2\text{O}]$  (12) and (d)  $[\text{Ni}(\text{L}^2)(\text{Py})\text{Cl}.\text{H}_2\text{O}].\text{H}_2\text{O}$  (17).

The decomposition of complex (2)  $[\text{Ni}(\text{H}_2\text{L}^1)\text{Cl}.2\text{H}_2\text{O}]\text{Cl}.2\text{H}_2\text{O}$  takes place in three stages. The first stage occurs at a temperature range of 28-114°C due to loss of two molecules of lattice water, two coordinated water molecules and the CO with estimated mass loss 23.13% (calc. 22.60%). The second stage in the temperature range 114-231°C is related to loss of HCN and  $\text{Cl}_2$ . The observed mass loss is 22.55% (calc. 22.11%). The final stage corresponding to loss of  $0.5\text{O}_2$  and  $\text{C}_6\text{H}_5-\text{C}_6\text{H}_5$  in temperature range 231-500°C with estimated mass loss 38.28% (calc. 38.43%) leaving NiO residue. The overall mass losses are observed to be 84.06% (calc. 83.14%).

Complex (7)  $[\text{Ni}(\text{H}_2\text{L}^1)(\text{py}).2\text{H}_2\text{O}]\text{Cl}.2\text{H}_2\text{O}$  undergoes three steps of decomposition. The first stage occurs at a temperature range of 28-91°C due to loss of half molecule of lattice water with estimated mass loss 1.67% (calc. 1.73%). The second stage in the temperature range 91-401°C with estimated mass loss 50.10% (calc. 50.05%) is related to loss of one and half molecules of lattice water, two coordinated water molecule,  $\text{CO}_2$  and  $\text{C}_6\text{H}_5-\text{C}_6\text{H}_5$ . The final stage at 401-587°C with estimated mass loss 24.41% (calc. 23.40%) due to loss of  $0.5\text{O}_2$ , HCN and  $\text{C}_5\text{H}_5\text{N}$  leaving  $\text{NiCl}_2$  residue. The overall mass losses are observed to be 76.18% (calc. 75.18%).

The thermal decomposition of complex (12)  $[\text{Ni}(\text{L}^2)\text{Cl}.2\text{H}_2\text{O}]$  undergoes one step of decomposition in a temperature range of 323-423°C confirming the

absence of lattice water molecules. This step attributed to loss of two coordinated water molecule, 0.5 Cl<sub>2</sub> and L<sup>2</sup> with estimated mass loss of 74.33% (calc.74.82%) leaving NiS residue.

The thermal measurement of complex (17) [Ni(L<sup>2</sup>)(py)Cl.H<sub>2</sub>O].H<sub>2</sub>O occurs in two stages. The first one at a temperature range 25-88 °C with estimated mass loss of 3.68 % (calc.4.10 %) due to loss of one lattice water molecule. The second stage at a temperature range 148-344 °C. The observed mass loss is 76.32 % (calc.75.25 %) due to loss of one coordinated water molecule, 0.5 Cl<sub>2</sub>, C<sub>5</sub>H<sub>5</sub>N and L<sup>2</sup> leaving NiS residue.

#### *Antibacterial activity*

The two Schiff base ligands, H<sub>2</sub>L<sup>1</sup>, and HL<sup>2</sup> and their binary and ternary complexes, (1-20), were screened against three bacterial species, *Bacillus cereus*, *Bacillus subtilis* and *Escherichia coli* to assess their potential antibacterial activity. The action of the simple salts, free ligands and the metal complexes against bacterial species are recorded in Table 8 and the results lead to the following conclusions:

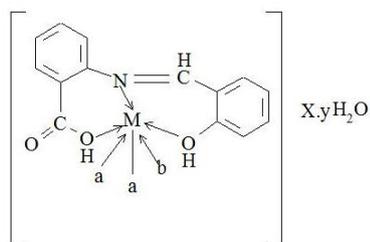
- The prepared compounds inhibit the growth of bacteria to a greater extent as the concentration is increased<sup>(34)</sup>.
- The free ligands were found to show very high activity against all three bacterial species.
- The metal salts were found to show antibacterial activity less than the free ligands or the metal complexes.
- The antibacterial activity of the free ligand H<sub>2</sub>L<sup>1</sup> decreases on complexation against *Bacillus cereus* and increases against *Escherichia coli* except UO<sub>2</sub>(II) and Co(II) complexes, (5,6).
- Among the prepared complexes, both Cd(II), complexes (3,18) and UO<sub>2</sub>(II) complex (10) and Co(II) complex (16) are very highly active against all three types of bacterial species. Moreover, Co(II) complex (1) showed the maximum activity against *Escherichia coli* than the other metal complexes and the free ligand, H<sub>2</sub>L<sup>1</sup>. Also, Cd(II) complex (3) showed the same effect against *Bacillus subtilis*. Moreover, Cd(II) complex (18) showed the maximum activity against *Bacillus subtilis* and *Escherichia coli* than the other metal complexes and both free ligands. Also, Co (II) complex (16), showed the same effect against *Bacillus cereus*.
- The antibacterial activity of the free ligand, HL<sup>2</sup> decreases on complexation in the binary complexes against *Bacillus subtilis* and *Escherichia coli* and increases on complexation in the ternary complexes specially for Co (II) and Cd (II) complexes (16,18) may be due to presence of pyridine molecule increasing the heterocyclic moiety<sup>(35)</sup>.
- Generally, the antibacterial data reveal that increasing the heterocyclic moiety increases the activity of the compounds and some complexes are more active than the free ligands may be ascribed to the increased lipophilic nature of the complexes arising due to chelation, it is due to faster diffusion of the chelates as a whole through the cell membrane or due to the chelation theory<sup>(27)</sup>.

Correlation of all results obtained for the complexes under study gives us information regarding the suggested structure of the complexes to be as in Fig. 3, 4, 5 and 6.

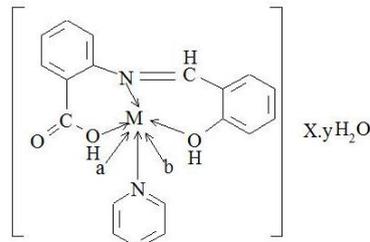
**TABLE 8. Antibacterial activity of Schiff base ligands ( $H_2L^1$ ) and ( $HL^2$ ) and their metal complexes .**

Strain	Gram – positive bacteria						Gram –negative		
	<i>Bacillus Cereus</i>			<i>Escherichia coli</i>			<i>Escherichia coli</i>		
Conc. mg/ml	5	2.5	1	5	2.5	1	5	2.5	1
$H_2L^1$	17	13	10	18	16	13	17	16	16
1	0	0	0	0	0	0	26	23	19
2	-	-	-	-	-	-	-	-	-
3	16	11	11	24	16	11	19	14	11
4	11	0	0	17	11	11	23	19	10
5	11	0	0	16	11	0	16	14	11
6	0	0	0	0	0	0	0	0	0
7	0	0	0	0	0	0	21	15	11
8	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-
10	15	13	11	19	16	12	18	15	11
$HL^2$	16	15	15	15	14	14	26	24	23
11	0	0	0	11	11	11	25	23	20
12	0	0	0	11	11	11	20	12	0
13	0	0	0	11	11	11	21	16	11
14	17	11	11	11	11	11	24	24	24
15	-	-	-	-	-	-	-	-	-
16	32	32	28	29	24	21	26	23	19
17	-	-	-	-	-	-	-	-	-
18	26	21	16	30	24	19	28	25	21
19	-	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-	-	-
$CoCl_2 \cdot 6H_2O$	1.3	3.8	8	3.8	7.2	12.15	3.1	4.6	7.8
$NiCl_2 \cdot 6H_2O$	1.3	3.8	8	3.8	7.2	12.15	3.1	4.6	7.8
$CdCl_2 \cdot H_2O$	1.9	4.6	10.87	2	5.1	9.2	1.12	5.21	9.53
$FeCl_3 \cdot 6H_2O$	1.4	5.2	9.1	1.7	4.9	8.1	3.21	7.34	9.43
$UO_2(NO_3)_2 \cdot 6H_2O$	0.6	3.5	6.2	2	3.8	6.5	1.25	3.54	7.43
St.	14	12	8	14	12	8	14	13	9

The test done using the diffusion agar technique. St.= reference standard; chloramphenicol was used as a standard antibacterial agent Well diameter = 0.6 cm. Inhibition values 1-5 mm beyond control = (less active). Inhibition values 6-10 mm beyond control = (moderate active). Inhibition values 11-15 mm beyond control = (highly active). Inhibition values over 15mm beyond control = (very highly active). Not active = 0.(-) not detected.



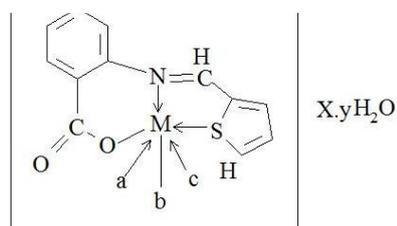
- In Complex (1): M = CO(II); a=b=H<sub>2</sub>O;  
X= Cl<sub>2</sub>; y=1  
In Complex (2): M = Ni(II); a=H<sub>2</sub>O; b=Cl  
X= Cl; y=2  
In Complex (3): M = Cd(II); a=b=H<sub>2</sub>O;  
X= Cl<sub>2</sub>; y=nil  
In Complex (4): M = Fe(III); a=H<sub>2</sub>O; b=Cl;  
X= Cl<sub>2</sub>; y=2  
In Complex (5): M = UO<sub>2</sub>(II); a=b=H<sub>2</sub>O;  
X= 2NO<sub>3</sub>; y= nil



- In Complex (6): M = CO(II); a=b=H<sub>2</sub>O;  
X= Cl<sub>2</sub>; y=nil  
In Complex (7): M = Ni(II); a=b=H<sub>2</sub>O;  
X= Cl<sub>2</sub>; y=2  
In Complex (8): M = Cd(II); a=b=H<sub>2</sub>O;  
X= Cl<sub>2</sub>; y=nil  
In Complex (9): M = Fe(III); a=H<sub>2</sub>O; b=Cl;  
X= Cl<sub>2</sub>; y=1  
In Complex (10): M = UO<sub>2</sub>(II); a=b=H<sub>2</sub>O;  
X= 2NO<sub>3</sub>; y= nil

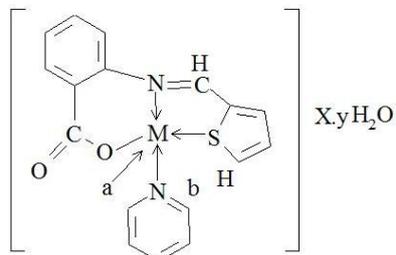
**Fig. 3.** Suggested structure of binary complexes (1-5) of H<sub>2</sub>L<sup>1</sup> ligand.

**Fig. 4.** Suggested structure of ternary complexes (6-10) of H<sub>2</sub>L<sup>1</sup> ligand.



- In Complex (11): M = CO(II); a=H<sub>2</sub>O; b=C=nil;  
X= Cl; y=nil  
In Complex (12): M = Ni(II); a=b=H<sub>2</sub>O; C=Cl;  
X=y=nil  
In Complex (13): M = Cd(II); a=b=H<sub>2</sub>O; C=Cl;  
X= nil; y=2  
In Complex (14): M = Fe(III); a=H<sub>2</sub>O; b=C=Cl;  
X= nil; y=1  
In Complex (15): M = UO<sub>2</sub>(II); a=b=H<sub>2</sub>O; C=nil  
X= NO<sub>3</sub>; y= 3

**Fig. 5.** Suggested structure of binary complexes (11-15) of HL<sup>2</sup> ligand.



- In Complex (16): M = CO(II); a=b=H<sub>2</sub>O; b=Cl;  
X=y=nil  
In Complex (17): M = Ni(II); a=b=H<sub>2</sub>O; b=Cl;  
X=nil; y=1  
In Complex (18): M = Cd(II); a=b=H<sub>2</sub>O;  
X= Cl; y=nil  
In Complex (19): M = Fe(III); a=H<sub>2</sub>O; b=Cl;  
X= Cl; y=nil  
In Complex (20): M = UO<sub>2</sub>(II); a=H<sub>2</sub>O; b=nil  
X=NO<sub>3</sub>

**Fig. 6.** Suggested structure of binary complexes (16-20) of HL<sup>2</sup> ligand.

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**دراسة المتراكبات الثنائية والثثية للكوبلت II والنيكل II والكاديوم II والحديد III واليورانييل II مع مشتقات حامض أروماتي أميني والبيريدين . تشييد وتوصيف طيفي ودراسة تحليل حراري ونشاط بيولوجي.**

زينب عبد العليم الشافعي ، زينب حلمي عبد الوهاب ، عايذة عبد العال سالماني و رانيا حسني طه  
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تم تحضير اثنان من الليجانادات وهما ن-(2- كربوكسي فينيل) ساليساليدين-امين ، ن-(2- كربوكسي فينيل) ثيوفين امين بتفاعل الساليساليد والثيوفين كربوكساليد مع 2- أمينو حمض البنزويك. تم تحضير متراكبات الكوبلت II والنيكل II والكاديوم II والحديد III واليورانييل II لهذه الليجانادات وكذلك تم تحضير المتراكبات الثثية مع البيريدين كليجاناد ثانوي. تم التحقق من التركيب البنائي المقترح للمتراكبات المشيده بالتحليل العنصري والتوصيل المولاري وطيف الأشعة تحت الحمراء والرنين النووي المغناطيسي وطيف الأشعة فوق البنفسجية والمرئية وطيف الكتلة والقابلية المغناطيسية والتحليل الحراري وقد تبين من قياسات التوصيل المولاري ان بعض المتراكبات غيرالكتروليتية وبعضها لها خاصية الكتروليتية. الليجانادات كونت رابطة تناسقية مع ايونات الفلزات عن طريق الرابطة ONO ، ONS وذلك من اكسجين الكربونيل ، نيتروجين الازوميثين ، اكسجين الفينولك أو ذرة الكبريت من الثيوفين. ودراسة الطيف الإلكتروني والقابلية المغناطيسية وجد ان المتراكبات لها تركيب هندسي ثماني الاوجه . ودراسة النشاط البيولوجي لليجانادات ومتراكباتها الفلزية المختلفة تجاه ثلاث أنواع من البكتريا وجد ان نشاط المتراكبات الفلزية أكثر فاعليه من الليجانادات.

*Bacillus subtilis*