

## Synthesis, Spectroscopic and Biological Characterization of Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) Complexes with New Macrocyclic Tetradentate [N<sup>4</sup>] Schiff Base Ligands

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**T**HE SYNTHESSES of three novel tetradentate Schiff base ligands, *i.e.* L<sup>1</sup> = BBICI = benzo [1'',2''-2,1] benzo [1''',2'''-8,7] indolo [3',2'-4,5] cyclododeca [10,11-b] indole, L<sup>2</sup> = DBBICI = 4, 13 - dimethylbenzo [1'',2''-2,1]benzo [1''',2'''-8,7]indolo[3',2'-4,5] cyclo-dodeca[10,11-b]indole and L<sup>3</sup>=HHPPA= 10, 11, 12, 23, 24, 25-hexahydrophenanthro [9,10-a] phenanthro [9,10-h] [14] annulene and their novel complexes with Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) have been reported. The complexes are characterized by the elemental and thermal analyses, molar conductance and magnetic susceptibility, <sup>1</sup>HNMR, IR and UV-Vis spectral also were studied. Cr(III), Mn(II), Co(II), Ni(II), Cd(II) and Cu(II) chloride and nitrate complexes have octahedral geometries while Cu(II) acetato complex has distorted octahedral leading to tetragonal geometry. The biological activities of the ligands and complexes have been screened *in vitro* against some bacteria and fungi to investigate their capacity to inhibit their growth.

**Keywords:** Macrocyclic complexes, Schiff bases, Transition metals complexes, and Microbiological activity.

Macrocyclic Schiff base ligands have been of remarkable versatility in macrocyclic and supramolecular chemistry<sup>(1,2)</sup>. They played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. Macrocyclic Schiff base nitrogen donor ligands have received special attention because of their mixed hard-soft donor character<sup>(3,4)</sup> and versatile coordination behaviour<sup>(5,7)</sup>. Macrocyclic Schiff base complexes of transition metals have been shown to be potentially very useful for their applications to organic syntheses and clarification of the reaction in living processes. A large number of reports have appeared concerning the chemistry of specifically functionalized macrocycles, where the complex contains reactive groups on the periphery of a macrocyclic ring, which has been termed the ligand super - structure<sup>(8,11)</sup>. In the area of bioinorganic chemistry the

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interest in the Schiff base complexes lies in that they provide synthetic models for the metal containing sites in metalloproteins\ enzymes<sup>(1, 2, 12, 13)</sup>. and also contribute enormously to the development of medicinal chemistry, radio immunotherapy, cancer diagnosis and treatment of tumor<sup>(12, 13)</sup>. In addition, some of complexes containing N and O donor atoms are effective as stereospecific catalyst for oxidation<sup>(14)</sup>, reduction<sup>(15)</sup>, hydrolysis<sup>(16)</sup>, biological activity<sup>(17)</sup>, fungi *in vitro*<sup>(18, 19)</sup> and other transformations of organic and inorganic chemistry. Due to resemblance of macrocyclic complexes with biologically active compounds, they are used in identification of diseased and normal tissues<sup>(20)</sup> also macrocyclic Schiff base compounds and their transition metal complexes have antimicrobial activities against some bacterial species and fungi *in vitro*<sup>(21, 22)</sup>. In view of the above applications it is highly desirable to synthesize and characterize transition metal complexes with new macrocyclic Schiff base ligands.

In the present work, we report the synthesis and characterization of three novel tetradentate Schiff base ligands and their new Schiff base complexes in order to throw some light on their molecular structures and biological activities.

### Experimental

The chemicals used were BDH and Aldrich products. The solvents were purified before use according to recommended methods<sup>(23, 25)</sup>.

#### *The apparatus and physical measurements*

The elemental microanalyses of the prepared compounds for C, H and N were performed in the Microanalytical Center, Cairo University. Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer using KBr discs. The UV-Vis spectra were recorded on a SHIMADZU UV - Vis spectrophotometer model V - 550 ranged from 200 to 800 nm. The molar conductance measurements were made on solutions of the complexes in DMF and measured using Sybron-Barnstead conductometer. The magnetic moments of the prepared metal complexes were determined at room temperature by the Gouy method on (TM) Johnson Methy Alpha Products Susceptibility Balance. The thermogravimetric analysis (TGA) were carried out in a dynamic nitrogen atmosphere (20 ml min<sup>-1</sup>) with a heating rate of 5 °C min<sup>-1</sup> using a Shimadzu TGA-50H. The mass spectra were recorded on a Hewlett Packard mass spectrometer model MS-5988. Metal contents of complexes were determined complexometrically using standard EDTA titration.

#### *Synthesis of macrocyclic Schiff base derivatives (Ligands L<sup>1</sup> - L<sup>3</sup>)*

Hot ethanolic solution (20 ml) of 1,2-phenylenediamine(4.32g , 0.04 mol) or 1,3-diaminopropane(2.96g, 0.04 mol) was mixed slowly with constant stirring with hot ethanolic solution (20 ml) of isatin (5.88g , 0.04 mol), 5-methylisatin (6.45g, 0.04 mol) or anthraquinone (8.33g , 0.04 mol). This mixture was refluxed at 80°C for 6 hr in the presence of 2-3 drops of concentrated hydrochloric acid.

On cooling the contents, light yellow(L<sup>1</sup>), dark yellow(L<sup>2</sup>) or yellowish brown(L<sup>3</sup>) colored compound is precipitated out, respectively, which was filtered, washed with cold EtOH, and dried under vacuum over P<sub>4</sub>O<sub>10</sub>. Yield 84%, 87%, and 79%, respectively, m.p. 296°C, 283°C and > 300°C, respectively.

#### *Synthesis of Schiff-base complexes*

The hot ethanolic solution 20 ml each of ligand (0.002 mol) and 20 ml hot ethanolic solution of corresponding metal salts CrCl<sub>3</sub>.6H<sub>2</sub>O, MnCl<sub>2</sub>.4H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, Cu(CH<sub>3</sub>COO)<sub>2</sub>.H<sub>2</sub>O and CdCl<sub>2</sub>.H<sub>2</sub>O (0.001mol) were mixed together with constant stirring. The mixture was refluxed for 6-9 hr at 80°C. On cooling, colored complexes precipitated out. They were filtered, washed with cold EtOH and dried under vacuum over P<sub>4</sub>O<sub>10</sub>.

#### *Biological study*

##### *Bacteria media*

The antibacterial activity of the ligand and its complexes was tested using paper disc diffusion method<sup>(26,29)</sup> against gram positive bacteria (*Staphylococcus aureus*) and gram negative bacteria (*Escherichia coli*). The tested compounds in measured quantities were dissolved in DMF to get concentration of 1000 ppm of compounds. Nutrient Agar media was poured in each Petri dish. After solidification, 0.1 ml of the tested bacteria spread over medium using a spreader. The discs of whatman No.1 filter paper having diameter of 5.00 mm., containing compounds were placed in the inoculated Petri plates. The plates are incubated at 28 °C for 24 - 48 hr and the zone of inhibition was calculated in millimetres carefully.

##### *Fungus media*

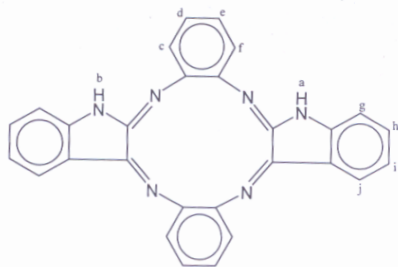
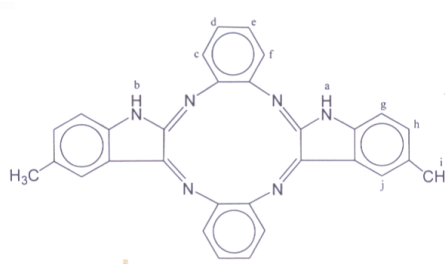
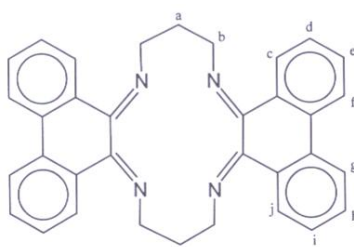
The tested compound in measured quantities was dissolved in DMF to get concentration of 1000 ppm of compounds. Czapek dox agar medium was prepared using paper disc diffusion method<sup>(26, 29)</sup>. *Candida albicans* or *Aspergillus flavus* was spread over each dish by using a sterile bent loop rod. Disks were cut by sterilized cork borer and then taken by sterilized needle. The resulting pits and the plates compounds are sites for the test. The plate is incubated at 30 °C for 24 – 48 hr and any clear zones present were detected, the zone of inhibition was calculated in millimetres carefully.

## **Results and Discussion**

#### *Ligands*

Elemental analysis found(calculated) for L<sup>1</sup> (C<sub>28</sub>H<sub>18</sub>N<sub>6</sub>, M.Wt = 438.52 amu) %C 77.00(76.69), %H 4.32(4.15), %N 19.69(19.17); L<sup>2</sup> (C<sub>30</sub>H<sub>22</sub>N<sub>6</sub>, M.Wt = 466.58 amu) %C 77.33(77.22), %H 5.11(4.76), %N 18.40(18.02); L<sup>3</sup> (C<sub>34</sub>H<sub>28</sub>N<sub>4</sub> M.Wt = 492.66 amu) %C 83.14(82.88), %H 5.55(5.74), %N 10.98(11.37). In the IR spectra of ligands L<sup>1</sup>- L<sup>3</sup> (Table 2, Fig. 1-3), characteristic bands due to ν(C=N) appeared at 1616-1640 cm<sup>-1</sup>, bands corresponding to ν(NH) appeared at 3144, 3129 cm<sup>-1</sup> for L<sup>1</sup> and L<sup>2</sup>, respectively, bands corresponding to ν(CH<sub>2</sub>) appeared at 2940 cm<sup>-1</sup> for L<sup>3</sup>, bands due to ν(CH<sub>3</sub>) appeared at 2847 cm<sup>-1</sup> for L<sup>2</sup>.

$^1\text{H}$  NMR spectra of ligands ( $L^1$ ,  $L^3$ ) in  $\text{DMSO-d}_6$  without and with  $\text{D}_2\text{O}$  are shown in, Fig. 4 & 5. The aromatic proton signals appeared at 7.24-8.86 ppm, the proton signals of NH groups at 12.04, 11.88 ppm for  $L^1$  and  $L^2$ , respectively, which disappeared in the presence of  $\text{D}_2\text{O}$ . The proton signals of  $\text{CH}_3$  groups for  $L^2$  appeared at 2.5 ppm, the proton signals of middle  $\text{CH}_2$  groups for  $L^3$  appeared at ppm and the signals of  $\text{H}_2\text{C}=\text{N}=\text{C}$  groups appeared at 3.46 ppm. Electronic spectral data of ligands ( $L^1$ -  $L^3$ ) were recorded in DMF solution. Three absorption bands at 220.2-233, 267.5-271 and 305-338 nm were characterized and can be assigned to  $\Pi-\Pi^*$  transitions within the aromatic ring,  $\Pi-\Pi^*$  transitions within  $\text{C}=\text{N}$  and an intramolecular charge transfer within the whole molecule. The mass spectra of ligands ( $L^1$ -  $L^3$ ) confirm the proposed formulae of these ligands by showing the molecular ion peaks ( $m/z$ ) at 438, 466 and 492 amu, corresponding to the macrocyclic moieties  $(\text{C}_{28}\text{H}_{18}\text{N}_6)^+$ ,  $(\text{C}_{30}\text{H}_{22}\text{N}_6)^+$  and  $(\text{C}_{34}\text{H}_{28}\text{N}_4)^+$ , respectively, Fig. 6 shows mass spectrum of the ligand  $L^1$ , also the suggested mechanism of the fragmentation of this ligand is shown in Scheme 1.

**L<sup>1</sup> (BBICI)****L<sup>2</sup> (DBBICI)****L<sup>3</sup> (HHPPA)****Structure 1. Schiff base macrocyclic ligands .**

*Metal complexes*

On the basis of elemental analysis (Table 1), the complexes were assigned to possess the composition 1:1(M:L) molar ratio. The molar conductance measurements of complexes (Table 1) in DMF indicate nonelectrolytic nature of all complexes except  $[\text{CrL}^1\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$  complex, the molar conductance value of this complex =  $49.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  which indicate the monoelectrolytic nature of it. Thus, the complexes may be formulated as  $[\text{ML}_x]_n\dot{\text{X}}\text{Y}$  where M = Cr(III), Mn(II), Co(II), Ni(II), Cu(II) or Cd(II); L = L<sup>1</sup>, L<sup>2</sup> or L<sup>3</sup>; x = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> or CH<sub>3</sub>COO<sup>-</sup>; Y = H<sub>2</sub>O or EtOH;  $\dot{\text{X}}$  = Cl<sup>-</sup> or -; n = 1, 2 or -.

*Infrared spectra*

There are four conceptual features in the infrared spectra of the metal complexes (Table 2, Fig. 1-3). The first feature is the shift of the  $\nu(\text{C}=\text{N})$  groups of metal complexes to lower frequencies in the range of  $1600 - 1620 \text{ cm}^{-1}$  than the free ligands ( $1616-1640 \text{ cm}^{-1}$ ), which indicates that the coordination takes place through the nitrogen of the azomethine (C=N) groups, thus implying that the ligands (L<sup>1</sup>- L<sup>3</sup>) are tetradentate toward the metal ion in the metal complexes<sup>(30-34)</sup>. The second feature is the broad bands in the range of  $3380 - 3448 \text{ cm}^{-1}$  in most of complexes which can be assigned to the  $\nu\text{OH}$  of EtOH or H<sub>2</sub>O molecules associated to the complexes. The third feature is the weak and medium bands at  $431 - 473 \text{ cm}^{-1}$  ranges which could be assigned to  $\nu\text{M-N}$  bands<sup>(30)</sup>. The fourth feature is the coordination behavior of NO<sub>3</sub><sup>-</sup> with metal ion as monodentate<sup>(15,16, 31,32)</sup> at  $1334-1338, 992-1007$  and  $1452-1490 \text{ cm}^{-1}$  ranges in Co(II) and Ni(II) complexes, Cl<sup>-</sup> coordinate to the metal ion as monodentate<sup>(15, 30)</sup> at  $335-338 \text{ cm}^{-1}$  range in Cr(III), Mn(II), Cu(II) and Cd(II) complexes. Also, in  $[\text{CuL}^1(\text{CH}_3\text{COO})_2]\cdot 2\text{H}_2\text{O}$  complex, CH<sub>3</sub>COO<sup>-</sup> coordinate to Cu(II) ion as monodentate at  $1372 \text{ cm}^{-1}$  ( $\nu_s\text{OCO}$ ), and  $1558 \text{ cm}^{-1}$  ( $\nu_a\text{OCO}$ )<sup>(30)</sup>.

*Magnetic moment measurements*

Magnetic moment measurements (Table 1) at room temperature indicated that Cr(III) complexes show magnetic moment values corresponding to three unpaired electrons (3.90-4.00 B.M.), Mn(II) complexes show magnetic moment values corresponding to five unpaired electrons (5.90-5.98 B.M.), Co(II) complexes show magnetic moment values corresponding to three unpaired electrons (3.92-3.98 B.M.),  $[\text{NiL}^2(\text{NO}_3)_2]\cdot\text{EtOH}$  shows magnetic moment value corresponding to two unpaired electrons (2.70 B.M.) while Cu(II) complexes show magnetic moment values corresponding to one unpaired electron (1.91-2.01 B.M.).

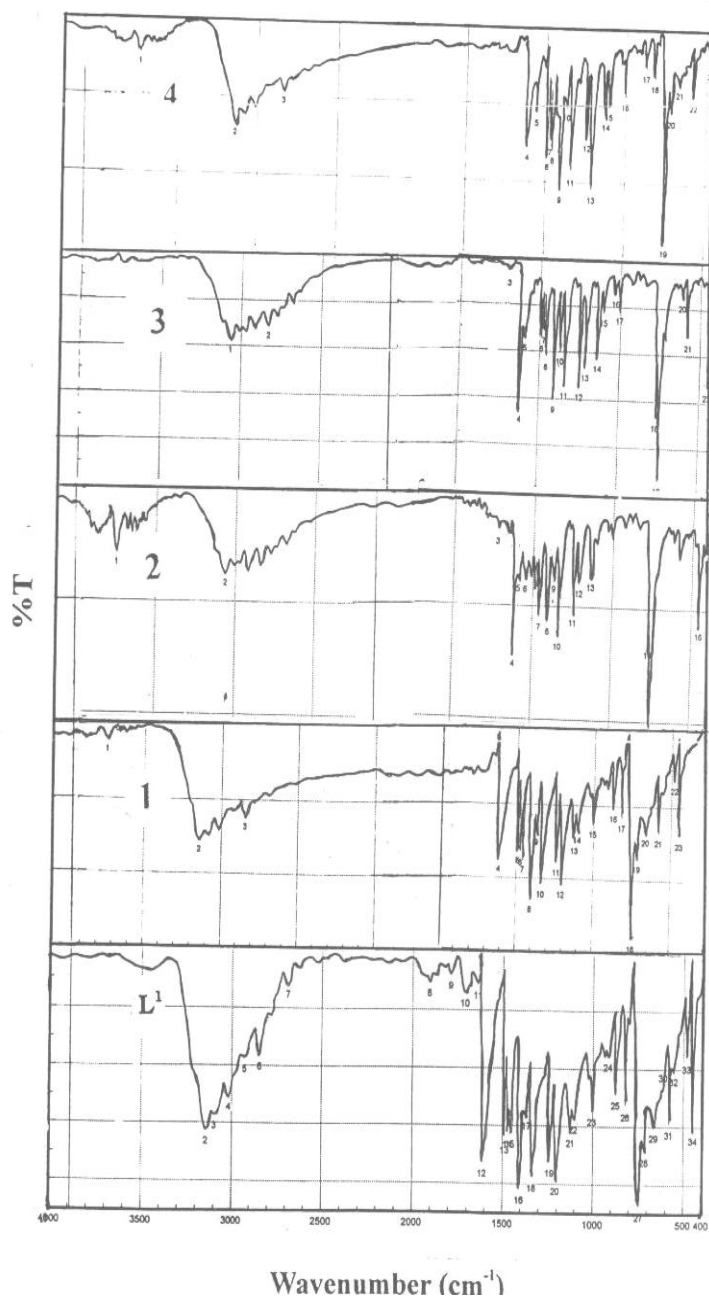
TABLE 1. Elemental analysis and some physical properties of the solid complexes .

No.	Complex	Colour	M.P. °C	M. Wt gm	Analysis found % (Calculated %)				$(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	Magnetic moment values (B. M.)
					% C	% H	% N	% M		
1	$[\text{CrL}^1\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$	Green	297	615.01	(54.67) 54.22	(3.28) 3.61	(13.67) 13.44	(8.45) 8.13	49.50	3.90
2	$[\text{MnL}^1\text{Cl}_2]\cdot\text{EtOH}$	Light brown	298	610.46	(59.02) 58.97	(3.97) 3.99	(13.77) 13.27	(8.99) 9.11	7.00	5.90
3	$[\text{CoL}^1(\text{NO}_3)_2]$	Light orange	294	621.36	(54.12) 54.44	(2.93) 2.59	(18.04) 18.65	(9.48) 9.51	9.80	3.90
4	$[\text{CuL}^1(\text{CH}_3\text{COO})_2]\cdot 2\text{H}_2\text{O}$	Deep orange	280	655.07	(58.58) 58.92	(4.27) 4.71	(12.81) 13.01	(9.69) 9.14	0.00	1.98
5	$[\text{CrL}^2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$	Light green	263	643.08	(56.03) 56.44	(3.77) 4.29	(13.07) 13.33	(8.08) 8.58	43.41	3.95
6	$[\text{CoL}^2(\text{NO}_3)_2]\cdot\text{EtOH}$	Light brown	282	695.54	(55.25) 55.71	(4.07) 3.98	(16.11) 16.38	(8.47) 8.59	23.70	3.98
7	$[\text{NiL}^2(\text{NO}_3)_2]\cdot\text{EtOH}$	Green	> 300	695.31	(55.27) 55.26	(4.00) 4.51	(16.12) 16.61	(8.44) 8.40	6.50	2.70
8	$[\text{CuL}^2\text{Cl}_2]\cdot\text{EtOH}$	Light brown	264	647.2	(59.38) 59.71	(4.37) 4.89	(12.99) 12.87	(9.82) 9.45	15.11	2.01
9	$[\text{CrL}^3\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$	Brown	> 300	669.16	(61.02) 61.51	(4.53) 5.00	(8.38) 8.11	(7.77) 8.21	43.40	4.00
10	$[\text{MnL}^2\text{Cl}_2]\cdot\text{H}_2\text{O}$	Brown	> 300	636.61	(64.14) 64.31	(4.76) 4.76	(8.80) 9.12	(8.63) 9.02	14.31	5.98
11	$[\text{CoL}^3\text{NO}_3)_2]$	Light brown	> 300	675.55	(60.45) 60.11	(4.19) 4.55	(12.44) 13.01	(8.72) 9.12	28.31	3.92
12	$[\text{CuL}^3\text{Cl}_2]$	Deep brown	> 300	627.21	(65.10) 65.03	(4.51) 4.89	(8.93) 9.45	(10.13) 9.78	21.21	1.91
13	$[\text{CdL}^3\text{Cl}_2]$	Light brown	> 300	675.07	(60.49) 60.91	(4.19) 4.22	(8.30) 8.80	(16.65) 16.12	17.20	-

TABLE 2. Important IR spectral bands (cm<sup>-1</sup>) and their assignment for the ligands and their metal complexes .

No.	Compound	$\nu_{OH}$ (H <sub>2</sub> O or EtOH)	$\nu_{NH}$	$\nu_{CH_2}$	$\nu_{CH_3}$	$\nu_{C-N}$	$\nu_{M-N}$	$\nu_{M-OOCCH_3}$	$\nu_{M-NO_3}$	$\nu_{M-Cl}$
	L <sup>1</sup>	-	3144 s, br			1640 vs	-	-	-	-
1	[CrL <sup>2</sup> Cl <sub>2</sub> ][Cl.H <sub>2</sub> O]	3600-3700 w, br	3142 m, br			1604 s	449 m	-	-	335 m, br
2	[MnL <sup>2</sup> Cl <sub>2</sub> ].EtOH	3742 m, br	3065 m, br			1617 s	453 m	-	-	336 m, br
3	[CoL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	-	3066 m, br			1612 s	450 m	-	1489 s, 1338 s, 1005 w	-
4	[CuL <sup>1</sup> (CH <sub>3</sub> COO) <sub>2</sub> ].2 H <sub>2</sub> O	3600-3700 w, br	3144 m, br			1615 s	445 m	1558 (ν <sub>2</sub> OCO), 1372 (ν <sub>2</sub> OCO)	-	-
	L <sup>2</sup>	-	3129 m, br		2847 m	1625 m	-	-	-	-
5	[CrL <sup>2</sup> Cl <sub>2</sub> ][Cl.H <sub>2</sub> O]	3386 w, br	3206 m, br		2921 m	1616 s	449 w	-	-	335 m, br
6	[CoL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ].EtOH	3400 m, br	3200 m, br		2916 m	1616 s	451 m	-	1489 s, 1335 s, 1007 w	-
7	[NiL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ].EtOH	3414 s, br	3222 m, br		2918 m	1617 s	450 w	-	1490 s, 1336 s, 1008 w	-
8	[CuL <sup>2</sup> Cl <sub>2</sub> ].EtOH	3380 m, br	3268 m, br		2856 m	1620 m	468 m	-	-	337 m, br
	L <sup>3</sup>	-	-	2940 w		1616 m, br	-	-	-	-
9	[CrL <sup>3</sup> Cl <sub>2</sub> ][Cl.H <sub>2</sub> O]	3448 w, br	-	2920 w		1600 m, br	431 w	-	-	338 w, br
10	[MnL <sup>3</sup> Cl <sub>2</sub> ].H <sub>2</sub> O	3424 m, br	-	2922 w		1610 m, br	435 w	-	-	335 w, br
11	[CoL <sup>3</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	-	-	2920 w		1603 m, br	434 w	-	1452 s, 1334 m, 992 w	-
12	[CuL <sup>3</sup> Cl <sub>2</sub> ]	-	-	2919 w		1602 m, br	435 w	-	-	337 m, br
13	[CdL <sup>3</sup> Cl <sub>2</sub> ]	-	-	2921 w		1604 m, br	473 w	-	-	336 m, br

s = strong, m = medium, br = broad, w = weak



**Fig.1.** IR spectra of the Ligand L<sup>1</sup> and their metal complexes (1), (2), (3) and (4).

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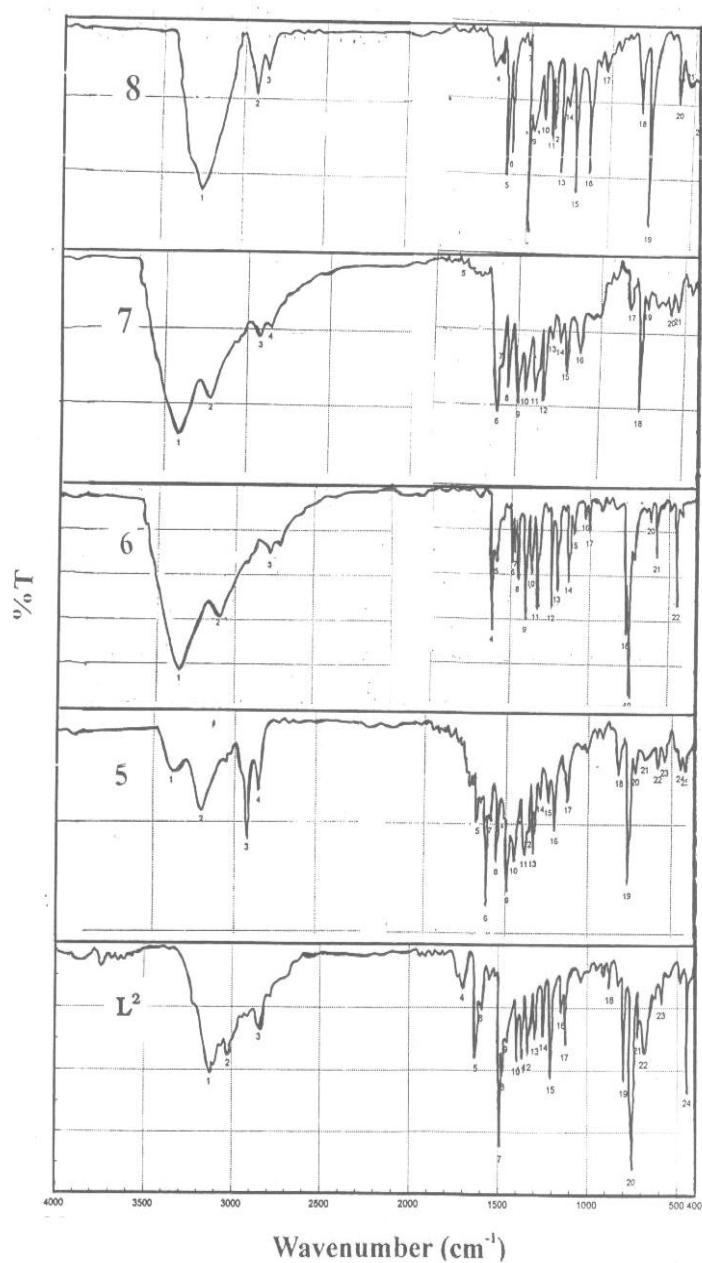
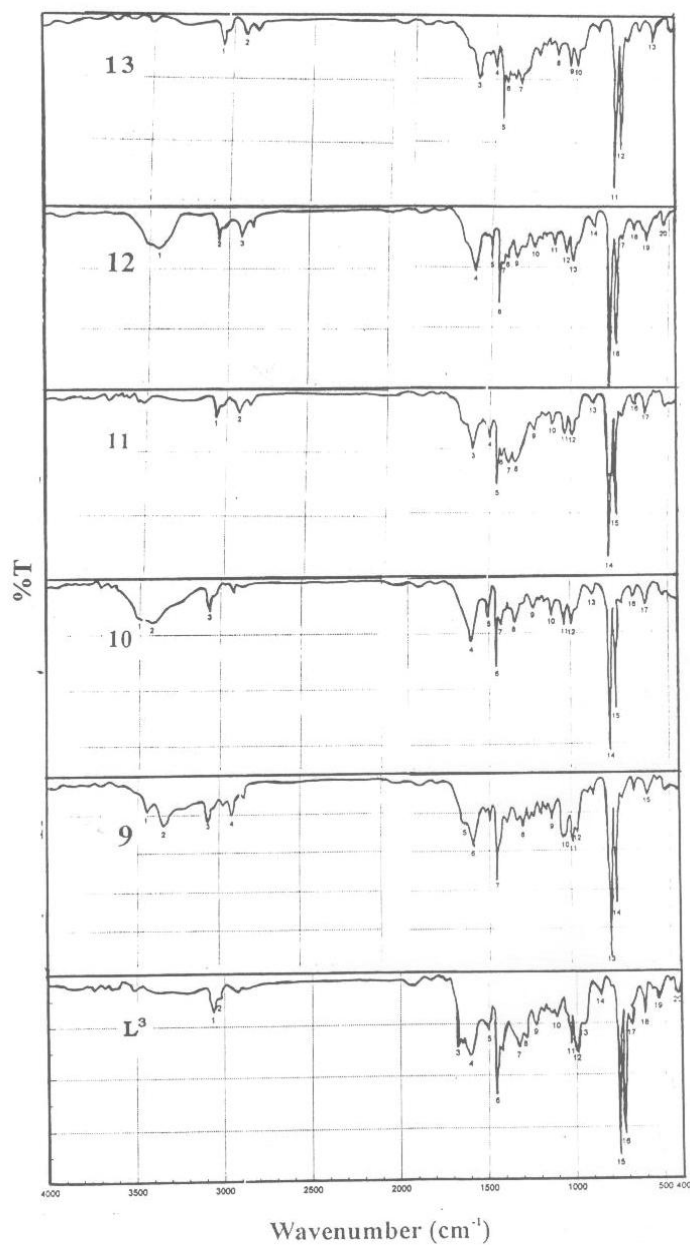


Fig.2. IR spectra of the Ligand  $L^2$  and their metal complexes (5), (6), (7) and (8).



**Fig.3.** IR spectra of the Ligand L<sup>3</sup> and their metal complexes (9), (10), (11), (12) and (13).

*Electronic spectra*

Electronic spectra of the metal complexes (Table 3) were recorded in DMF solution. Electronic spectra of Cr(III), Mn(II), Co(II) and Cu(II) complexes display four absorption bands (except Cu(II) acetato complex which display five absorption bands) with  $\lambda_{\max}$  at (205-250), (267-272), (306-337) and (518-700) nm, the first three bands can be assigned to  $\Pi-\Pi^*$  transitions within the aromatic rings,  $\Pi-\Pi^*$  transitions within C=N groups (these bands show small shifts from those of the free ligands as a result of complex formation<sup>(20-22, 35-37)</sup> and intramolecular charge transefer (L→M)[except Mn(II) complex]. The last band can be assigned to d-d transition bands which indicate octahedral geometries around all metal ions<sup>(14, 17, 21, 23, 33, 34, 36)</sup>, while  $[\text{CuL}^1(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$  complex displays five absorption bands with  $\lambda_{\max}$  at 213, 270, 337, 550 and 810 nm. The first three bands can be assigned to  $\Pi-\Pi^*$  transitions within the aromatic rings,  $\Pi-\Pi^*$  transitions within C=N groups and intramolecular charge transefer (L→Cu), The last two bands can be assigned to d-d transition bands which indicate distorted octahedral lead to tetragonal geometry<sup>(38)</sup>.

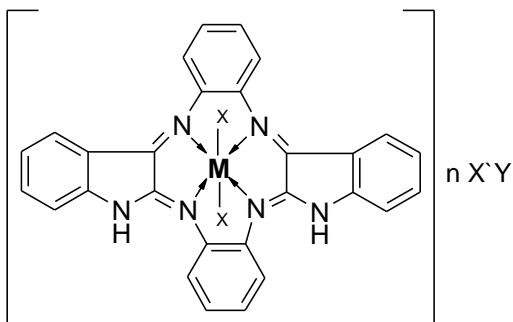
*<sup>1</sup>H NMR spectra for  $[\text{CdL}^3\text{Cl}_2]$  complex*

<sup>1</sup>H NMR spectrum of ligand  $\text{L}^3$ , (Fig. 5), gave bands of proton signals of middle  $\text{CH}_2$  groups and signals of  $-\text{H}_2\text{C}-\text{N}=\text{C}$  groups at  $\delta$  2.53 ppm and  $\delta$  3.46 ppm, respectively, which shifted upfield in its diamagnetic complex of Cd(II), (Fig. 5), to  $\delta$  2.50 ppm and  $\delta$  3.33 ppm, respectively, confirming coordination of  $-\text{N}=\text{C}$  with Cd(II)<sup>(22)</sup>. The aromatic proton signals did not shifted upfield<sup>(39-40)</sup>.

*Thermogravimetric analysis (TGA)*

TGA of some solid complexes indicate a common behavior (Tables 4, 5 and Fig. 7,8). The thermograms can be subdivided into four main regions: the first region extends up to 120°C for elimination of EtOH or H<sub>2</sub>O lattice. The second region extends up to 275°C includes elimination of coordinated or noncoordinated Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup> or CH<sub>3</sub>COO<sup>-</sup> ions. The third region indicates thermal stability and extends up to 360 °C. The fourth region extends up to 400°C and represents decomposition of the complex to the metal oxide. The metal content in the residue was calculated and found to be consistent with elemental analyses of the complexes.

Based on the above results gained from elemental analyses, conductance measurements, thermal analyses, IR, UV/Vis as well as magnetic moments studies, the geometric structures of the complexes under investigation can be formulated as follows:

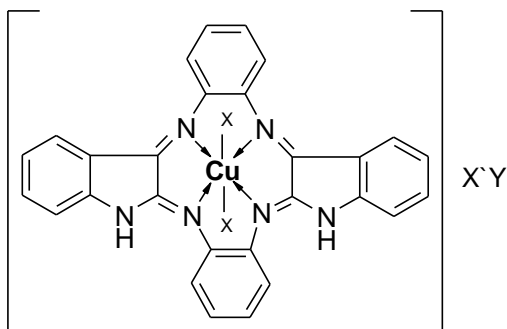


**Structure 2. Octahedral metal complexes of ligand L<sup>1</sup>**

**M = Cr(III), Mn(II) and Co(II);**

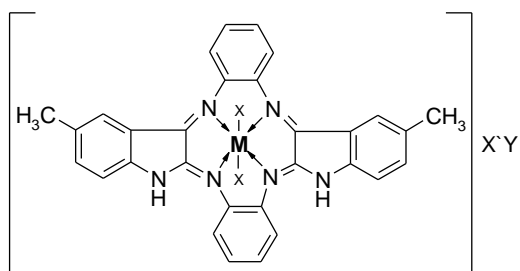
**x = Cl<sup>-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>; Y = H<sub>2</sub>O, EtOH, -;**

**X̂ = Cl<sup>-</sup>, -, -; n = 1, 1, - respectively**



**Structure 3. Distorted octahedral of Cu(II) complex of ligand L<sup>1</sup>**

**x = CH<sub>3</sub>COO<sup>-</sup>; Y = H<sub>2</sub>O, X̂**



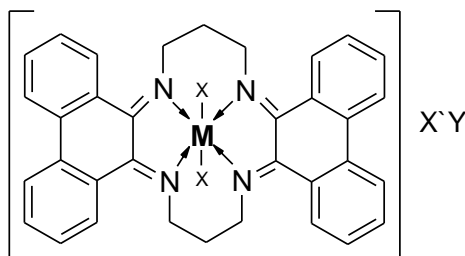
**Structure 4. Octahedral metal complexes of ligand L<sup>2</sup>**

**M = Cr(III), Co(II), Ni(II) and Cu(II);**

**x = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>;**

**Y = H<sub>2</sub>O, EtOH, EtOH, EtOH;**

**X̂ = Cl<sup>-</sup>, -, -, - respectively**



**Structure 5. Octahedral metal complexes of ligand L<sup>3</sup>**

**M = Cr(III), Mn(II), Co(II), Cu(II) and Cd(II);**  
**x = Cl<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Cl<sup>-</sup>; Y = H<sub>2</sub>O, H<sub>2</sub>O, -, -, -;**  
**X<sup>-</sup> = Cl<sup>-</sup>, -, -, -, - respectively**

#### *Biological studies*

Antibacterial and antifungal activity of the ligands and their complexes were tested, the results are collected in Table 6. The antimicrobial screening data show that, the metal chelates exhibit more inhibitory effects than the parent ligand. From the data obtained it is observed that, the inhibition zone against the gram positive bacteria (*Staphylococcus aureus*); gram negative bacteria (*Escherichia coli*) of the ligands and their metal complexes are higher than the solvent (DMF) and those of the control (ampicillin). The inhibition zone against the fungi (*Aspergillus flavus* and *Candida albicans*) of the ligands are higher than the solvent (DMF) but lower than those of the control (amphotricine B), while the inhibition zone of the metal complexes are higher than the solvent and those of the control. The increased activity of the metal chelates than the ligands can be explained by the chelation of the Schiff bases with the metal ions<sup>(23, 32, 41, 42)</sup>, the chelation reduces the polarity of the central metal atom, mainly because of partial sharing of its positive charge with the ligand. Also, the normal cell process may be affected by the formation of hydrogen bond, through the azomethine nitrogen atom with the active centers of cell constituents. There is a marked increase in the activities of the ligands and complexes for gram positive bacteria (*Staphylococcus aureus*) gram negative bacteria (*Escherichia coli*) and fungi (*Aspergillus flavus* and *Candida albicans*). The biological activities of the produced ligands and their complexes can be arranged in the following:

The order of activities of *Escherichia*:

$L_1 < L_2 < L_3 < \text{complex 2} < \text{complex 1} < \text{complex 6} = \text{complex 7} < \text{complex 11} < \text{complex 12}$

The order of activities of *Staphylococcus aureus*:

$L_2 < L_1 < L_3 < \text{complex 1} = \text{complex 6} < \text{complex 2} = \text{complex 7} < \text{complex 11} = \text{complex 12}$

The order of activities of *Candida albicans*:

$L_2 < L_1 < L_3 < \text{complex 7} < \text{complex 1} = \text{complex 2} = \text{complex 6} < \text{complex 11} < \text{complex 12}$

The order of activities of *Aspergillus flavus*:

$L_1 = L_2 = L_3 < \text{complex 1} = \text{complex 2} = \text{complex 6} = \text{complex 7} = \text{complex 11} < \text{complex 12}$

TABLE 3. UV-Visible spectral values for some metal complexes of the macrocyclic Schiff bases in DMF .

No.	Complex	Colour	$\lambda_{\text{max}}$ (nm)		C. T L → M	Band assignment due to d-d transition, $\lambda_{\text{max}}$ nm					
			$\pi - \pi^*$ aromatic ring	$\pi - \pi^*$ C=N		$\lambda_{\text{max}}$ (nm)	d-d Transition band	$\lambda_{\text{max}}$ (nm)	d-d Transition band		
5	[CuL <sup>2</sup> Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	Light green	225	272	331	-	<sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)	550	<sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F)	-	<sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (P)
9	[CuL <sup>3</sup> Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	brown	224	267	310	-	<sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)	618	<sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F)	-	<sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (P)
2	[MnL <sup>1</sup> Cl <sub>2</sub> ].EtOH	Light brown	250	271	-	70	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> (G)	518	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (G)	-	-
6	[CoL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ].EtO H	Light brown	218	272	331	-	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)	540	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> A <sub>2g</sub>	-	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F)
11	[CoL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	Light brown	205	267	307	-	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)	560	<sup>4</sup> T <sub>1g</sub> → <sup>4</sup> A <sub>2g</sub>	-	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F)
7	[NiL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ].EtOH	green	237	271	331	-	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)	520	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> ((F))	-	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>2g</sub> (F)
4	[CuL <sup>1</sup> (CH <sub>3</sub> COO) <sub>2</sub> ]. 2H <sub>2</sub> O	Deep orange	213	270	337	-	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>	550	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub>	810	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>1g</sub>
8	[CuL <sup>2</sup> Cl <sub>2</sub> ].EtOH	Light brown	220	271	330	680	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>	-	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub>	-	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>1g</sub>
12	[CuL <sup>3</sup> Cl <sub>2</sub> ]	Deep brown	213	267	306	700	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>	-	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub>	-	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>1g</sub>

TABLE 4. Thermogravimetric analysis of the metal complexes of ligand L<sup>1</sup>

No.	Complex	Temp. range (°C)	% loss calcd (found)	Lost fragments	Residue
1	[CrL <sup>1</sup> Cl <sub>2</sub> ].Cl.H <sub>2</sub> O	40 – 110	2.95 (2.93)	One H <sub>2</sub> O lattice Loss of a Cl <sup>-</sup> ion 2 Cl <sup>-</sup> ion coordinated	[CrL <sup>1</sup> Cl <sub>2</sub> ].Cl [CrL <sup>1</sup> Cl <sub>2</sub> ] [CrL <sup>1</sup> ]
		190 – 225	5.43 (5.77)		
		225 – 270	11.84 (11.54)		
2	[MnL <sup>1</sup> Cl <sub>2</sub> ].EtOH	270 – 300	Thermal stability	One EtOH lattice 2 Cl <sup>-</sup> ion coordinated	Cr <sub>2</sub> O <sub>3</sub>
		320 – 400	71.04 – (71.30)		
		30 – 120 120 – 260	7.42 (7.54) 11.87 (11.63)		
3	CoL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub>	280 – 300	Thermal stability	2 NO <sub>3</sub> coordinated	MnO [CoL <sup>1</sup> ]
		300 - 340	71.24 (71.95)		
		200 – 235	19.75 (19.95)		
4	[CuL <sup>1</sup> (CH <sub>3</sub> COO) <sub>2</sub> ].2H <sub>2</sub> O	235 – 300	Thermal stability	2H <sub>2</sub> O lattice 2 CH <sub>3</sub> COO <sup>-</sup> coordinated	CoO [CuL <sup>1</sup> (CH <sub>3</sub> COO) <sub>2</sub> ] [CuL <sup>1</sup> ]
		300 - 360	70.11 (70.57)		
		28 – 120 182 – 260 260 – 300	5.96 (5.50) 18.19 (18.01) Thermal stability		
		300 - 400	66.68 (66.94)		CuO

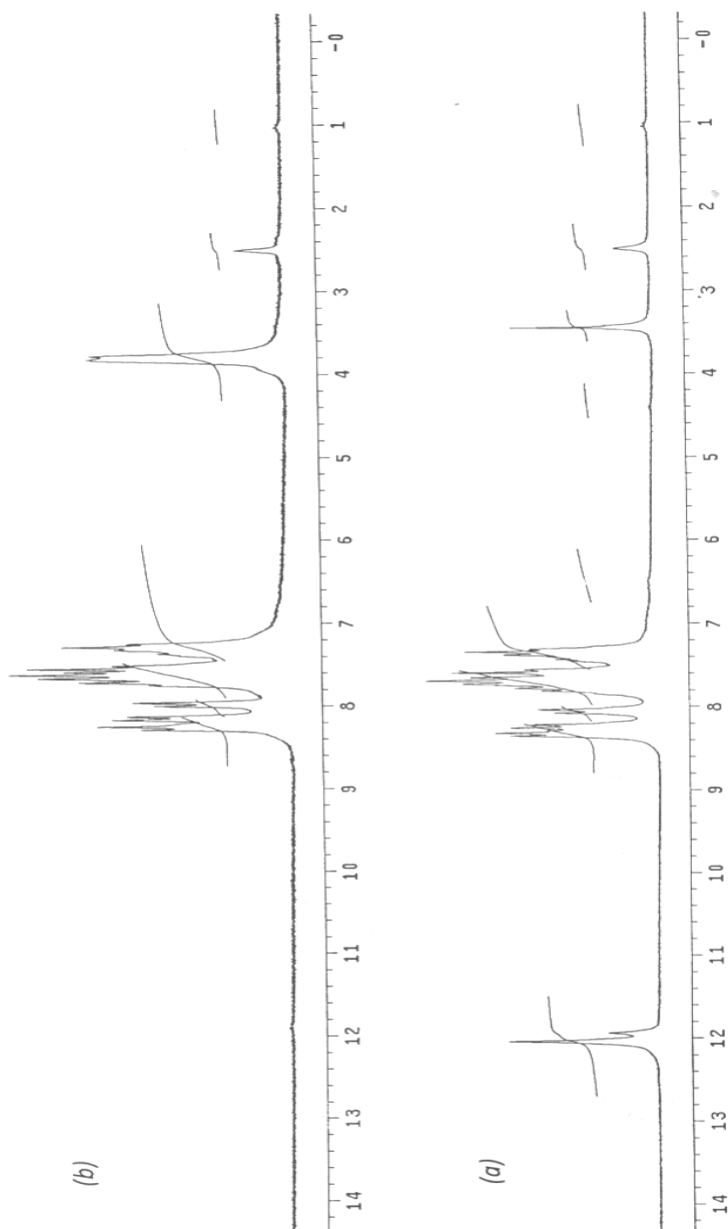
**TABLE 5. Thermogravimetric analysis of the metal complexes of ligand L<sup>2</sup> and L<sup>3</sup>.**



**TABLE 6. Biological activity of the macrocyclic Schiff base ligands and some of their metal complexes .**

Sample	Inhibition Zone diameter (mm / mg sample)			
	<i>Escherichia coli</i> G (-ve)	<i>Staphylococcus aureus</i> G (+ve)	<i>Candida albicans</i> (fungus)	<i>Aspergillus flavus</i> (fungus)
Solvent (DMF)	0.0	0.0	0.0	0.0
Control: Antibacterial agent (Ampicillin)	10	12	-	-
Antifungal agent (Amphotericine B)	-	-	21	17
L <sup>1</sup>	12	14	13	15
[CrL <sup>1</sup> Cl <sub>2</sub> ]Cl.H <sub>2</sub> O	25	24	24	26
[MnL <sup>1</sup> Cl <sub>2</sub> ].EtOH	23	25	24	26
L <sup>2</sup>	14	13	12	15
[CoL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ].EtOH	26	24	24	26
[NiL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ].EtOH	26	25	23	26
L <sup>3</sup>	16	15	14	15
[CoL <sup>3</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	27	26	25	26
[CuL <sup>3</sup> Cl <sub>2</sub> ]	28	26	26	27

Concentration of tested compounds = 1000 ppm



**Fig.4.**  $^1\text{H}$  – NMR spectrum of (a) Ligand L<sup>1</sup> DMSO -  $d_6$  solvent at room temperature (b) Ligand Li in DMSO -  $d_6$  solvent and one drop of  $\text{D}_2\text{O}$ .

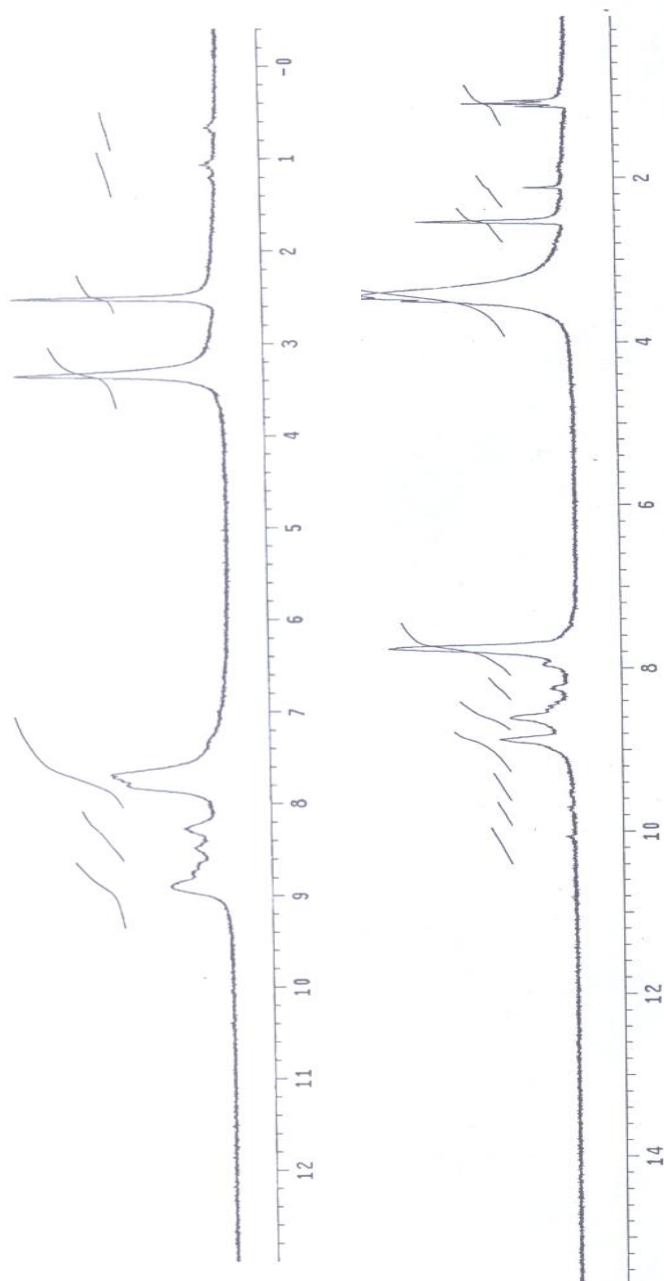
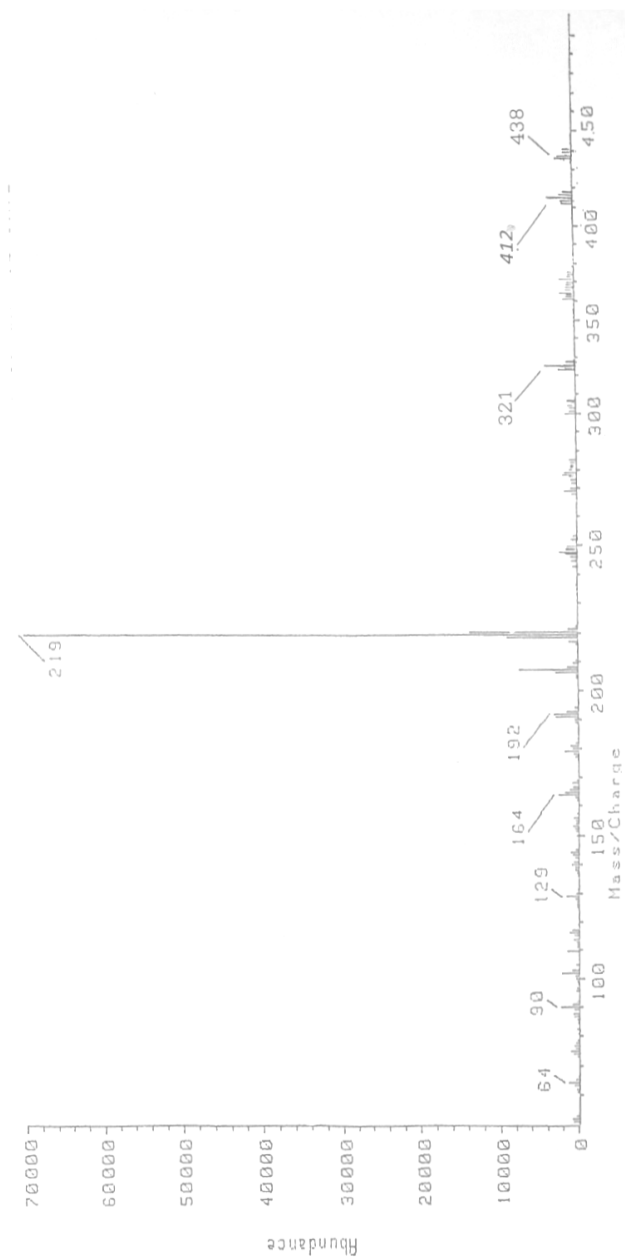


Fig. 5. <sup>1</sup>H-NMR spectra of Ligand L<sup>3</sup> and [CdL<sup>3</sup>Cl<sub>2</sub>] complex in DMSO-d<sub>6</sub> solvent at room temperature.



**Fig. 6.** Mass spectrum of ligand L<sup>1</sup>.

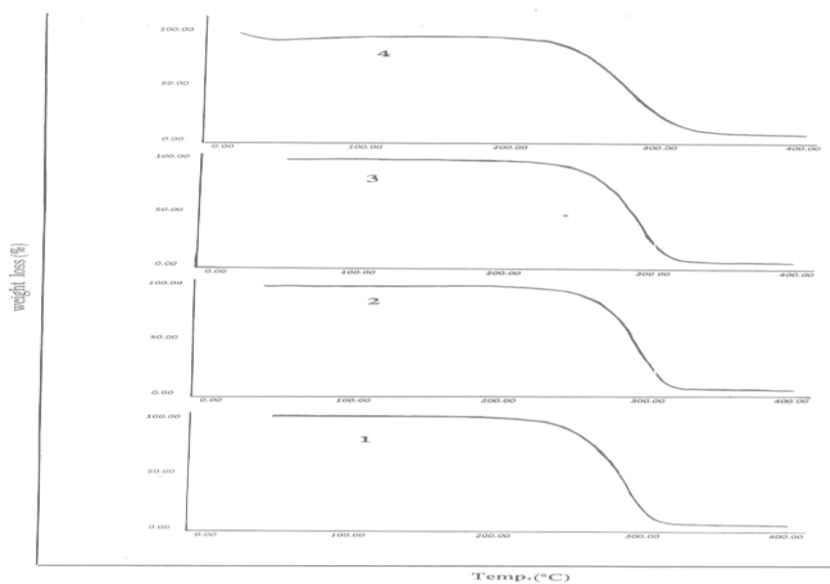


Fig. 7. Thermogravimetric analysis of the metal complexes of ligand  $L^1$ .

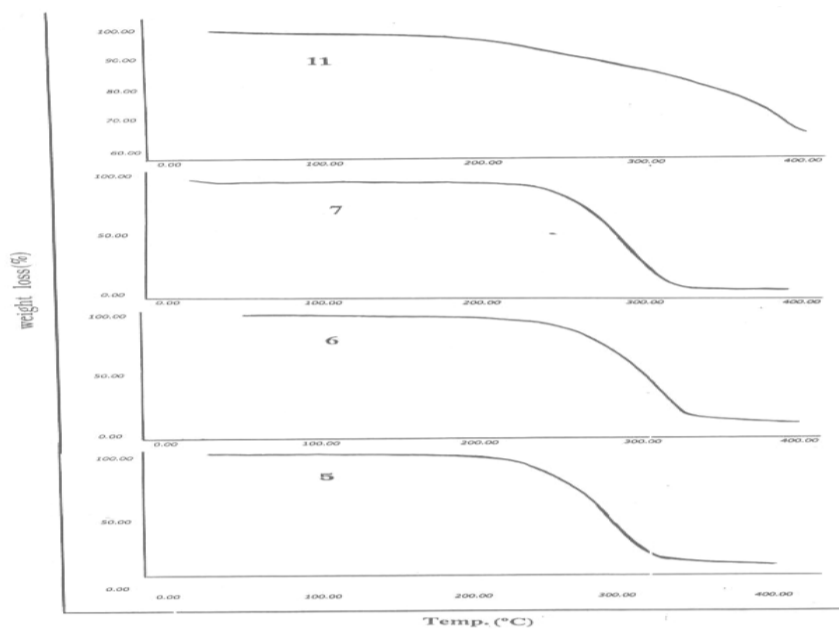
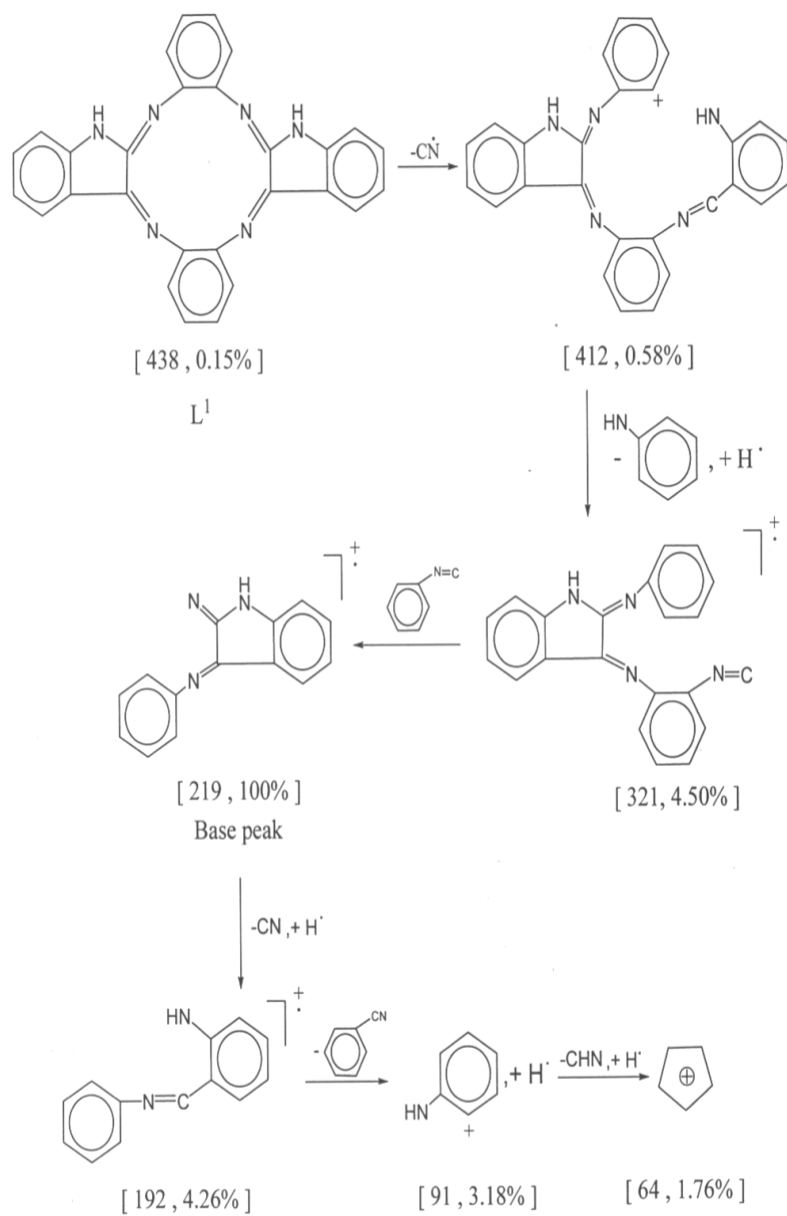


Fig. 8. Thermogravimetric analysis of some metal complexes of ligands  $L^2$  and  $L^3$ .



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

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### تحضير ودراسات طيفية وبيولوجية لمتراكبات الكروم ثلاثية الشحنة والمنجنيز والكوبلت والنيكل والنحاس والكادميوم ثنائية الشحنة مع ليجاندات قواعد شيف الجديدة رباعية العطاء ذات الحلقات الكبيرة

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تم تحضير ثلاث ليجاندات جديدة لقواعد شيف رباعية العطاء ذات الحلقات الكبيرة من مشتقات الأراتين والأنثراكينون مع مشتقات الفينيلين داي أمين وأمينوبروبان وتم تحضير متراكبات هذه الليجاندات مع أيونات المنجنيز والكوبلت والنيكل والنحاس والكادميوم ثنائية الشحنة وأيونات الكروم الثلاثي وتم التعرف على الصيغ البنائية باستخدام التحليل العنصري والتحليل الحرارى الوزنى وكذلك تم التعرف على الأشكال الفراغية للمتراكبات المختلفة عن طريق قياس العزوم المغناطيسية وأطياف الأشعة تحت الحمراء والمرئية وطيف الرنين النووي المغناطيسى وقياس التوصيلة الكهربائية حيث دلت النتائج ان كل المتراكبات تأخذ شكل الهرم ثمانى الأوجه ماعدا متراكبات الخلاتو حيث حدث تشويه للشكل الثمانى ليصبح رباعى الأوجه . كما تم دراسة التأثير البيولوجى لليجاندات ومتراكباتها تجاه بعض البكتريا والفطريات وقد وجد أن للمتراكبات نشاط أعلى من الليجاندات فى القضاء على هذه النوعية من البكتريا والفطريات.