

Synthesis, Spectroscopic and Biological Characterization of Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) Complexes with New Macrocyclic Tetradentate [N⁴] Schiff Base Ligands

Akila A. Saleh[#], M. A. El- Ghamry, Khadega S. Namasha^{*} and S. M. Abu El- Wafa

Department of Chemistry, Faculty of Education, Ain Shams University, Cairo, Egypt and ^{*}Department of Chemistry, Faculty of Education, King Khaled University, Abha, Saudi Arabia.

THE SYNTHESSES of three novel tetradentate Schiff base ligands, *i.e.* L¹ = BBICI = benzo [1'',2''-2,1] benzo [1''',2'''-8,7] indolo [3',2'-4,5] cyclododeca [10,11-b] indole, L² = 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 L³=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, ¹HNMR, 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^(1,2). 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^(3,4) and versatile coordination behaviour^(5,7). 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^(8,11). In the area of bioinorganic chemistry the

[#]Corresponding author. E-mail: salehakila55@hotmail.com

interest in the Schiff base complexes lies in that they provide synthetic models for the metal containing sites in metalloproteins\ enzymes^(1, 2, 12, 13). and also contribute enormously to the development of medicinal chemistry, radio immunotherapy, cancer diagnosis and treatment of tumor^(12, 13). In addition, some of complexes containing N and O donor atoms are effective as stereospecific catalyst for oxidation⁽¹⁴⁾, reduction⁽¹⁵⁾, hydrolysis⁽¹⁶⁾, biological activity⁽¹⁷⁾, fungi *in vitro*^(18, 19) 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⁽²⁰⁾ also macrocyclic Schiff base compounds and their transition metal complexes have antimicrobial activities against some bacterial species and fungi *in vitro*^(21, 22). 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^(23, 25).

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⁻¹) with a heating rate of 5 °C min⁻¹ 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 L¹ - L³)

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(L¹), dark yellow(L²) or yellowish brown(L³) colored compound is precipitated out, respectively, which was filtered, washed with cold EtOH, and dried under vacuum over P₄O₁₀. 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 CrCl₃.6H₂O, MnCl₂.4H₂O, Co(NO₃)₂.6H₂O, Ni(NO₃)₂.6H₂O, CuCl₂.2H₂O, Cu(CH₃COO)₂.H₂O and CdCl₂.H₂O (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 P₄O₁₀.

Biological study

Bacteria media

The antibacterial activity of the ligand and its complexes was tested using paper disc diffusion method^(26,29) 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^(26, 29). *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 L¹ (C₂₈H₁₈N₆, M.Wt = 438.52 amu) %C 77.00(76.69), %H 4.32(4.15), %N 19.69(19.17); L² (C₃₀H₂₂N₆, M.Wt = 466.58 amu) %C 77.33(77.22), %H 5.11(4.76), %N 18.40(18.02); L³ (C₃₄H₂₈N₄ 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 L¹- L³ (Table 2, Fig. 1-3), characteristic bands due to ν(C=N) appeared at 1616-1640 cm⁻¹, bands corresponding to ν(NH) appeared at 3144, 3129 cm⁻¹ for L¹ and L², respectively, bands corresponding to ν(CH₂) appeared at 2940 cm⁻¹ for L³, bands due to ν(CH₃) appeared at 2847 cm⁻¹ for L².

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 = L¹, L² or L³; x = Cl⁻, NO₃⁻ or CH₃COO⁻; Y = H₂O or EtOH; $\dot{\text{X}}$ = Cl⁻ 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 (L¹- L³) are tetradentate toward the metal ion in the metal complexes⁽³⁰⁻³⁴⁾. 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 νOH of EtOH or H₂O 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⁽³⁰⁾. The fourth feature is the coordination behavior of NO₃⁻ with metal ion as monodentate^(15,16, 31,32) at $1334-1338, 992-1007$ and $1452-1490 \text{ cm}^{-1}$ ranges in Co(II) and Ni(II) complexes, Cl⁻ coordinate to the metal ion as monodentate^(15, 30) 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, CH₃COO⁻ coordinate to Cu(II) ion as monodentate at 1372 cm^{-1} ($\nu_s\text{OCO}$), and 1558 cm^{-1} ($\nu_a\text{OCO}$)⁽³⁰⁾.

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⁻¹) and their assignment for the ligands and their metal complexes .

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

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

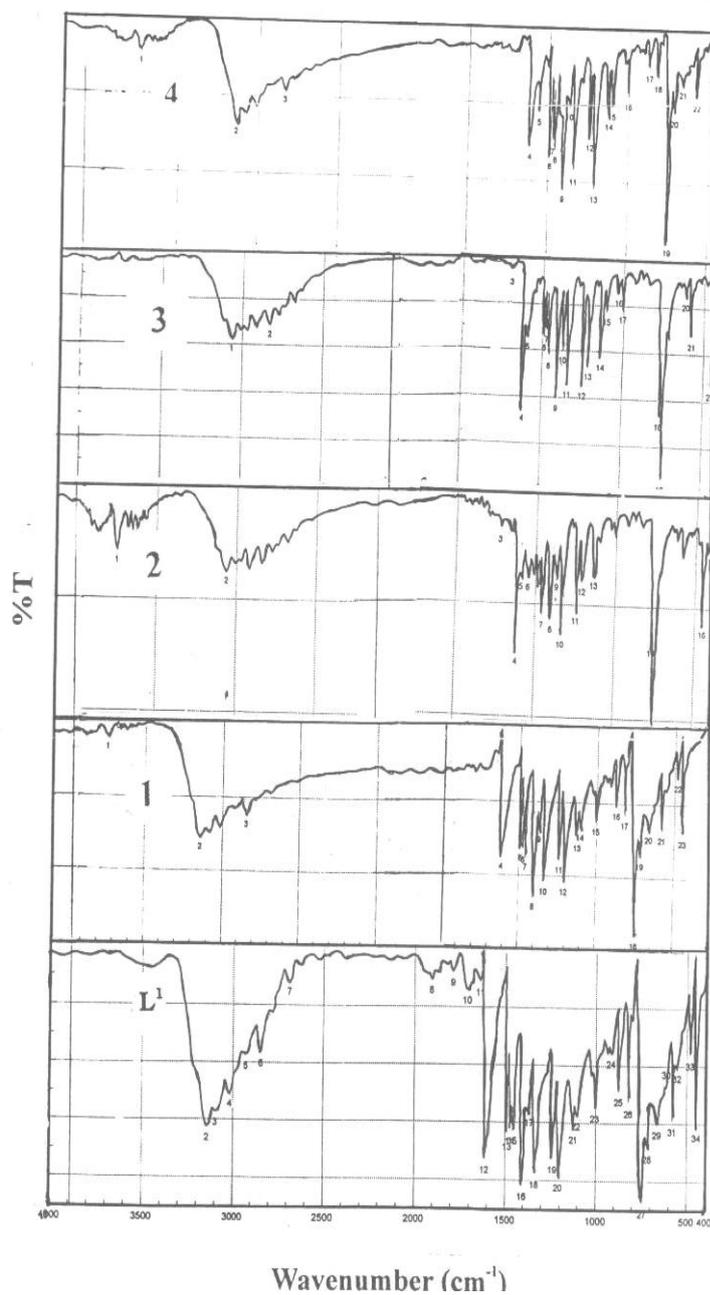


Fig.1. IR spectra of the Ligand L¹ and their metal complexes (1), (2), (3) and (4).

Egypt. J. Chem. **53**, No. 6 (2010)

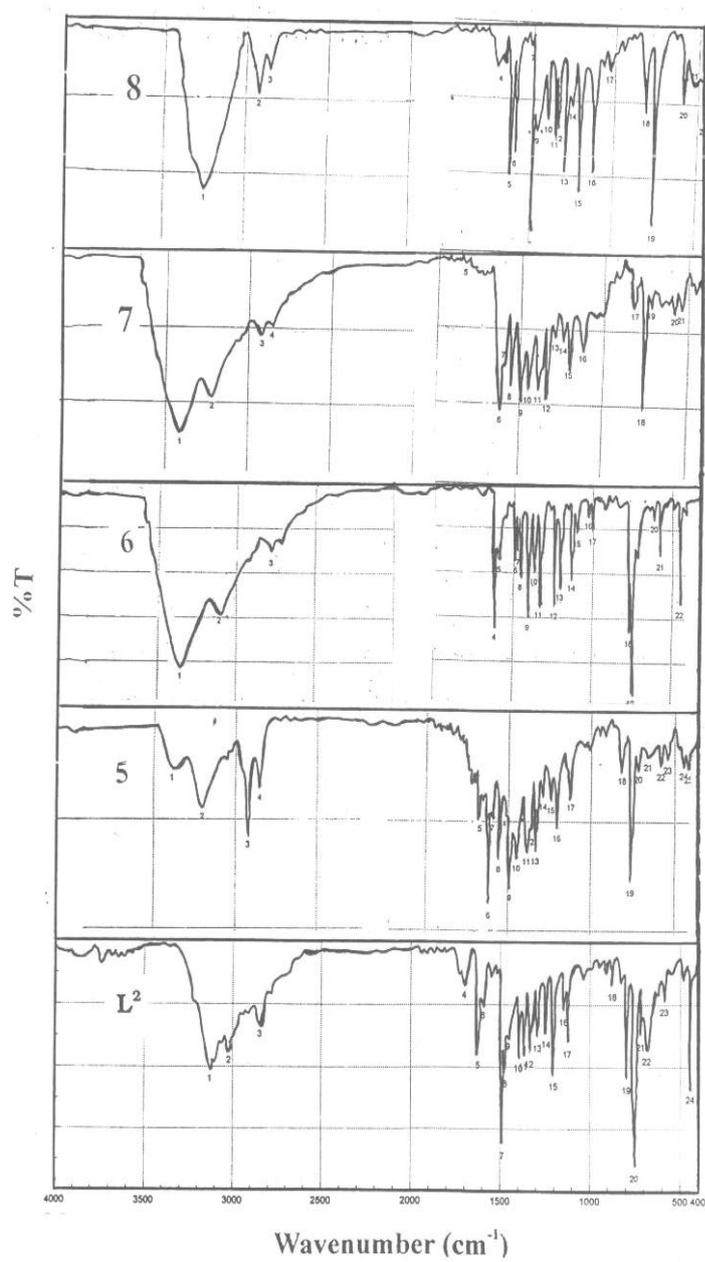


Fig.2. IR spectra of the Ligand L² and their metal complexes (5), (6), (7) and (8).

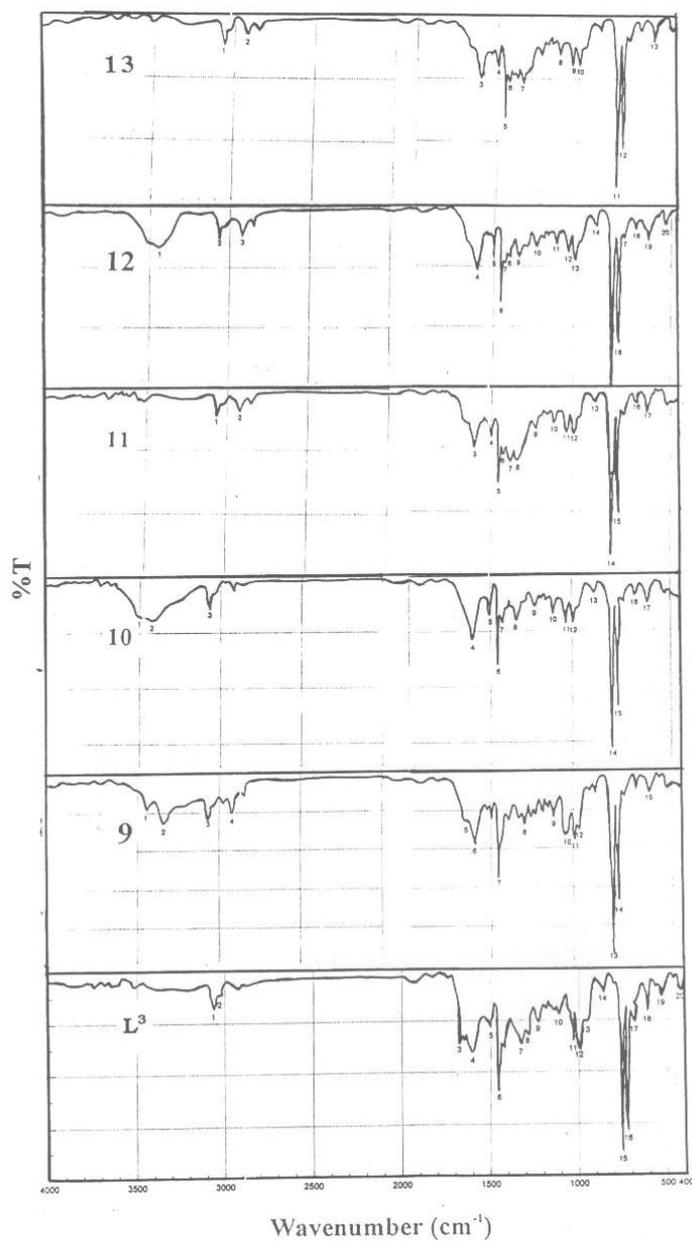


Fig.3. IR spectra of the Ligand L³ and their metal complexes (9), (10), (11), (12) and (13).

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 λ_{\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^(20-22, 35-37) 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^(14, 17, 21, 23, 33, 34, 36), while $[\text{CuL}^1(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$ complex displays five absorption bands with λ_{\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⁽³⁸⁾.

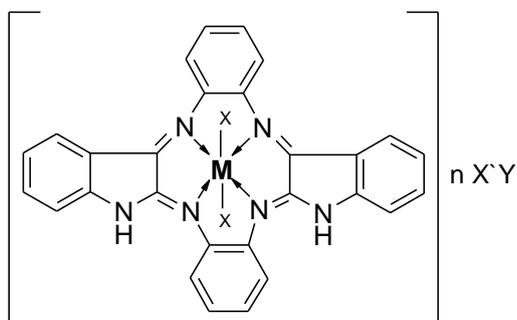
¹H NMR spectra for $[\text{CdL}^3\text{Cl}_2]$ complex

¹H NMR spectrum of ligand L^3 , (Fig. 5), gave bands of proton signals of middle CH_2 groups and signals of $-\text{H}_2\text{C}-\text{N}=\text{C}$ groups at δ 2.53 ppm and δ 3.46 ppm, respectively, which shifted upfield in its diamagnetic complex of Cd(II), (Fig. 5), to δ 2.50 ppm and δ 3.33 ppm, respectively, confirming coordination of $-\text{N}=\text{C}$ with Cd(II)⁽²²⁾. The aromatic proton signals did not shifted upfield⁽³⁹⁻⁴⁰⁾.

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 H₂O lattice. The second region extends up to 275°C includes elimination of coordinated or noncoordinated Cl⁻ or NO₃⁻ or CH₃COO⁻ 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:

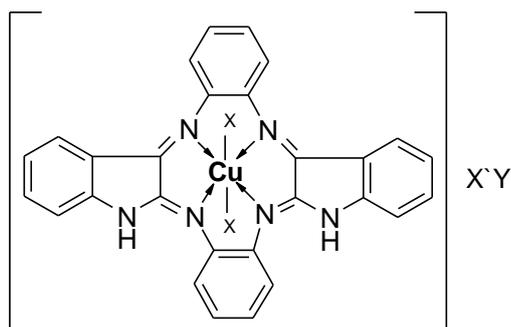


Structure 2. Octahedral metal complexes of ligand L¹

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

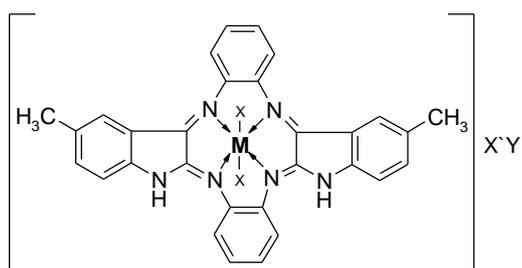
x = Cl⁻, Cl⁻ and NO₃⁻; Y = H₂O, EtOH, -;

X' = Cl⁻, -, -; n = 1, 1, - respectively



Structure 3. Distorted octahedral of Cu(II) complex of ligand L¹

x = CH₃COO⁻; Y = H₂O, X'



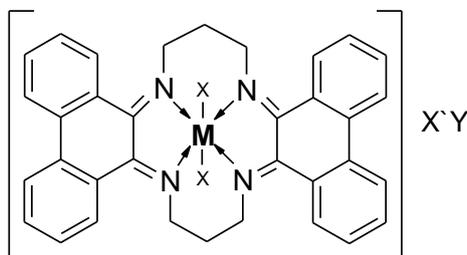
Structure 4. Octahedral metal complexes of ligand L²

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

x = Cl⁻, NO₃⁻, NO₃⁻, Cl⁻;

Y = H₂O, EtOH, EtOH, EtOH;

X' = Cl⁻, -, -, - respectively



Structure 5. Octahedral metal complexes of ligand L³

M = Cr(III), Mn(II), Co(II), Cu(II) and Cd(II);
x = Cl⁻, Cl⁻, NO₃⁻, Cl⁻, Cl⁻; Y = H₂O, H₂O, -, -, -;
X = Cl⁻, -, -, -, - 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^(23, 32, 41, 42), 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	λ_{max} (nm)		C. T L → M	Band assignment due to d-d transition, λ_{max} nm					
			$\pi - \pi^*$ aromatic ring	$\pi - \pi^*$ C=N		λ_{max} (nm)	d-d Transition band	λ_{max} (nm)	d-d Transition band		
5	[CuL ² Cl ₂]Cl.H ₂ O	Light green	225	272	331	-	⁴ A _{2g} (F) → ⁴ T _{1g} (P)	550	⁴ A _{2g} (F) → ⁴ T _{2g} (F)	-	⁴ A _{2g} (F) → ⁴ T _{2g} (P)
9	[CuL ³ Cl ₂]Cl.H ₂ O	brown	224	267	310	-	⁴ A _{2g} (F) → ⁴ T _{1g} (P)	618	⁴ A _{2g} (F) → ⁴ T _{2g} (F)	-	⁴ A _{2g} (F) → ⁴ T _{2g} (P)
2	[MnL ¹ Cl ₂].EtOH	Light brown	250	271	-	70	⁶ A _{1g} → ⁴ T _{2g} (G)	518	⁶ A _{1g} → ⁴ T _{1g} (G)	-	-
6	[CoL ² (NO ₃) ₂].EtO H	Light brown	218	272	331	-	⁴ T _{1g} (F) → ⁴ T _{1g} (P)	540	⁴ T _{1g} → ⁴ A _{2g}	-	⁴ T _{1g} (F) → ⁴ T _{2g} (F)
11	[CoL ² (NO ₃) ₂]	Light brown	205	267	307	-	⁴ T _{1g} (F) → ⁴ T _{1g} (P)	560	⁴ T _{1g} → ⁴ A _{2g}	-	⁴ T _{1g} (F) → ⁴ T _{2g} (F)
7	[NiL ² (NO ₃) ₂].EtOH	green	237	271	331	-	³ A _{2g} (F) → ³ T _{1g} (P)	520	³ A _{2g} (F) → ³ T _{1g} ((F))	-	³ A _{2g} (F) → ³ T _{2g} (F)
4	[CuL ¹ (CH ₃ COO) ₂]. 2H ₂ O	Deep orange	213	270	337	-	² E _g → ² T _{2g}	550	² B _{1g} → ² A _{1g}	810	² B _{1g} → ² E _{1g}
8	[CuL ² Cl ₂].EtOH	Light brown	220	271	330	680	² E _g → ² T _{2g}	-	² B _{1g} → ² A _{1g}	-	² B _{1g} → ² E _{1g}
12	[CuL ³ Cl ₂]	Deep brown	213	267	306	700	² E _g → ² T _{2g}	-	² B _{1g} → ² A _{1g}	-	² B _{1g} → ² E _{1g}

TABLE 4. Thermogravimetric analysis of the metal complexes of ligand L¹

No.	Complex	Temp. range (°C)	% loss calcd (found)	Lost fragments	Residue
1	[CrL ¹ Cl ₂].Cl.H ₂ O	40 – 110	2.95 (2.93)	One H ₂ O lattice Loss of a Cl ⁻ ion 2 Cl ⁻ ion coordinated	[CrL ¹ Cl ₂].Cl [CrL ¹ Cl ₂] [CrL ¹]
		190 – 225	5.43 (5.77)		
		225 – 270	11.84 (11.54)		
2	[MnL ¹ Cl ₂].EtOH	270 – 300	Thermal stability	One EtOH lattice 2 Cl ⁻ ion coordinated	Cr ₂ O ₃
		320 – 400	71.04 – (71.30)		
		30 – 120 120 – 260	7.42 (7.54) 11.87 (11.63)		
3	CoL ¹ (NO ₃) ₂	280 – 300	Thermal stability	2 NO ₃ coordinated	MnO [CoL ¹]
		300 - 340	71.24 (71.95)		
		200 – 235	19.75 (19.95)		
4	[CuL ¹ (CH ₃ COO) ₂].2H ₂ O	235 – 300	Thermal stability	2H ₂ O lattice 2 CH ₃ COO ⁻ coordinated	CoO [CuL ¹ (CH ₃ COO) ₂] [CuL ¹]
		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 L² and L³.

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 ¹	12	14	13	15
[CrL ¹ Cl ₂]Cl.H ₂ O	25	24	24	26
[MnL ¹ Cl ₂].EtOH	23	25	24	26
L ²	14	13	12	15
[CoL ² (NO ₃) ₂].EtOH	26	24	24	26
[NiL ² (NO ₃) ₂].EtOH	26	25	23	26
L ³	16	15	14	15
[CoL ³ (NO ₃) ₂]	27	26	25	26
[CuL ³ Cl ₂]	28	26	26	27

Concentration of tested compounds = 1000 ppm

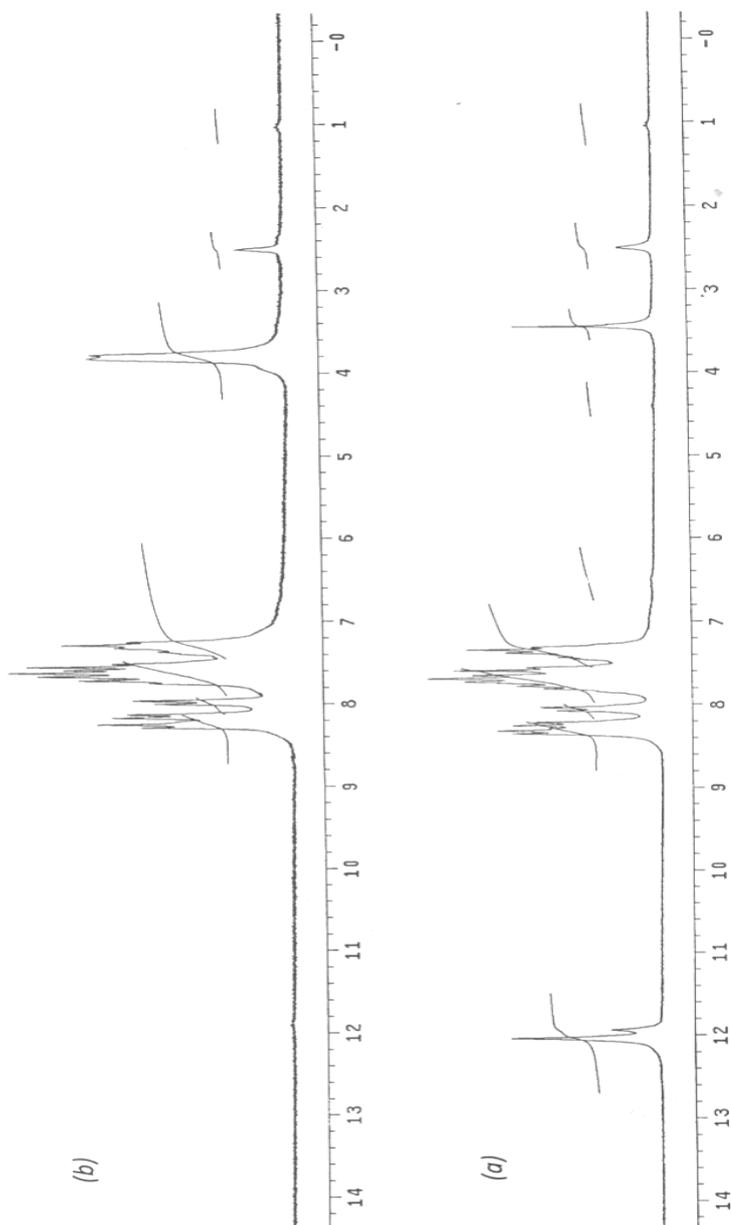


Fig.4. ^1H – NMR spectrum of (a) Ligand L¹ DMSO - d_6 solvent at room temperature (b) Ligand Li in DMSO - d_6 solvent and one drop of D_2O .

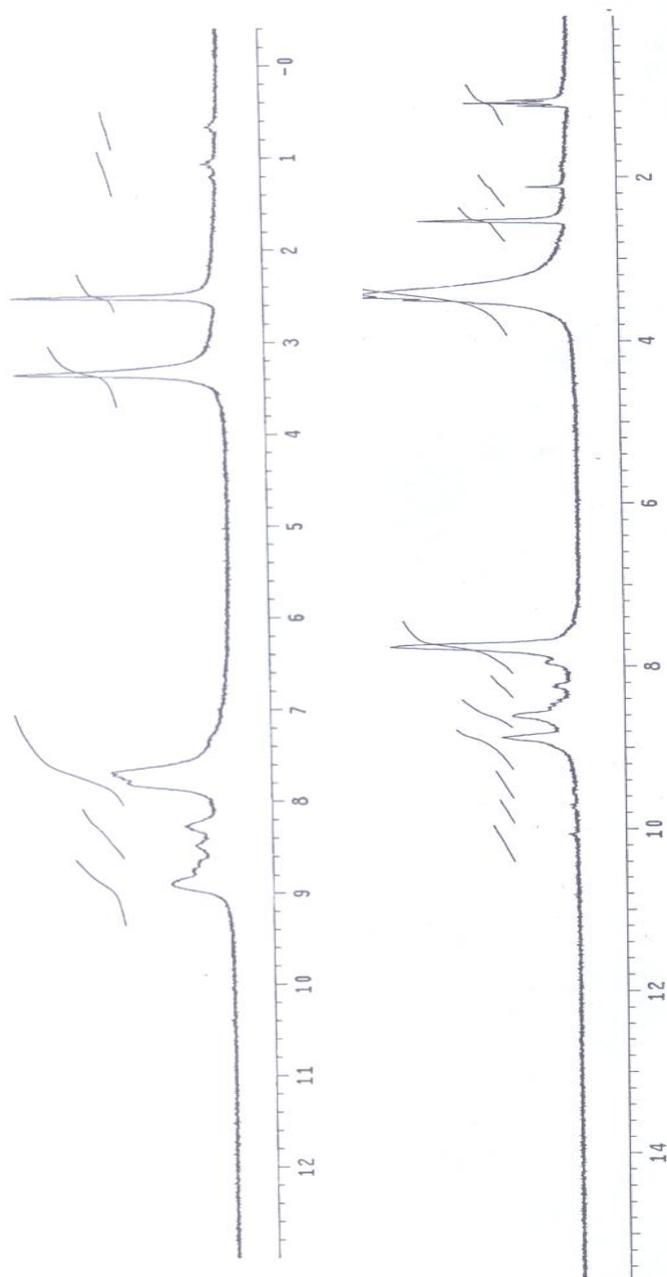


Fig. 5. ¹H-NMR spectra of Ligand L³ and [CdL³Cl₂] complex in DMSO-d₆ solvent at room temperature.

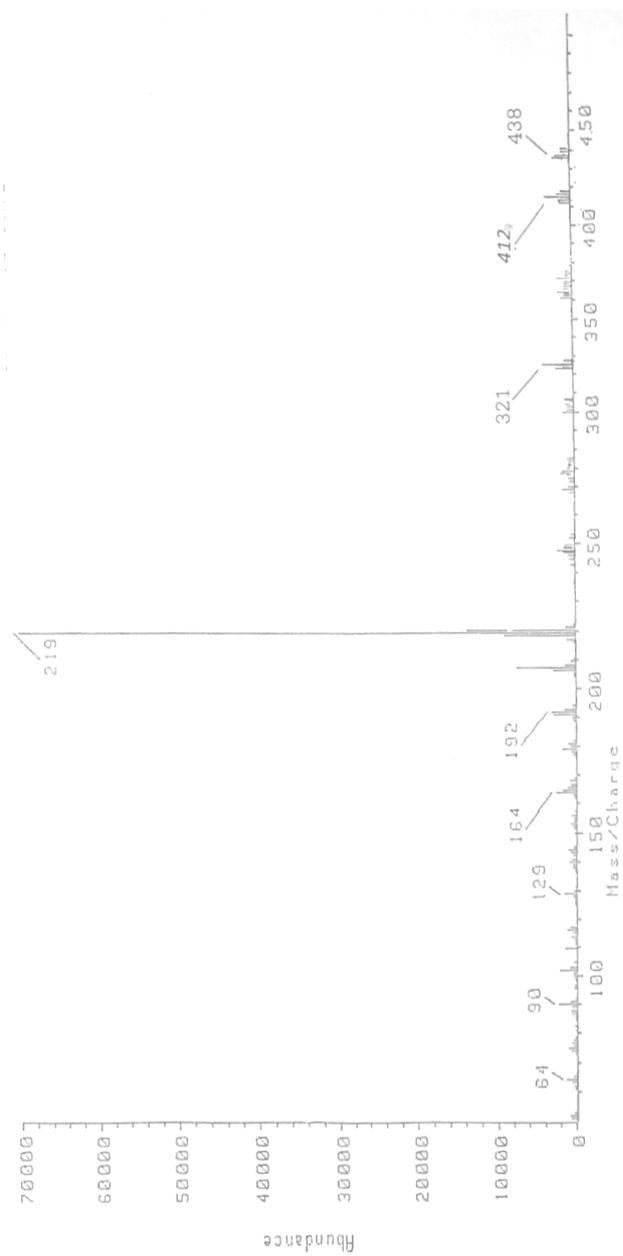


Fig. 6. Mass spectrum of ligand L¹.

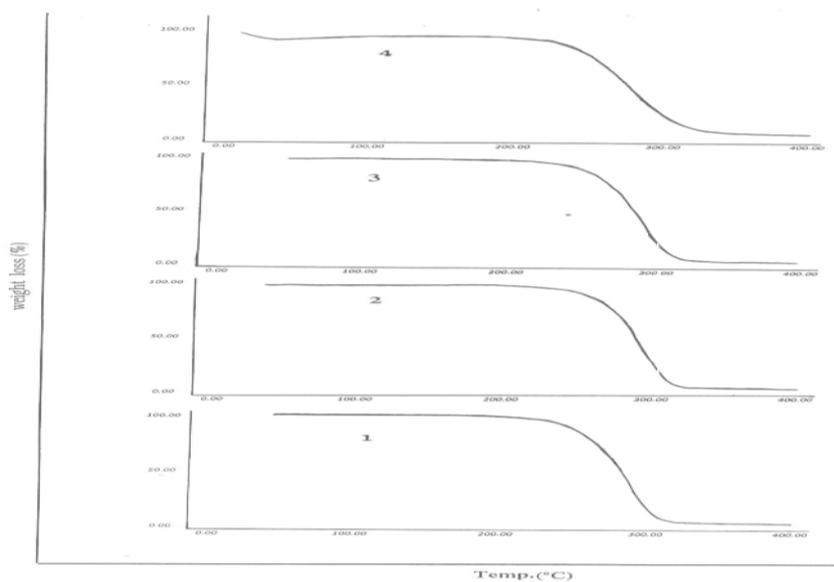


Fig. 7. Thermogravimetric analysis of the metal complexes of ligand L^1 .

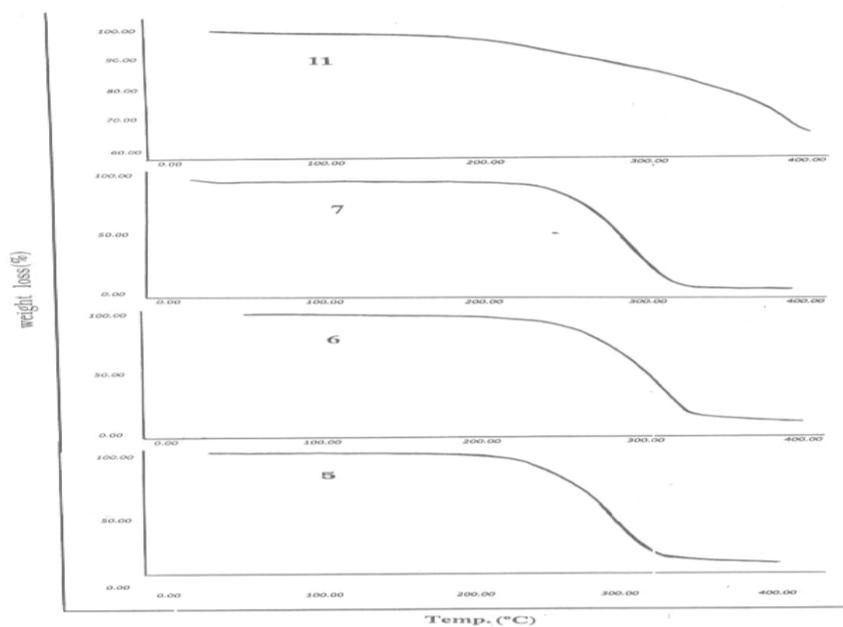
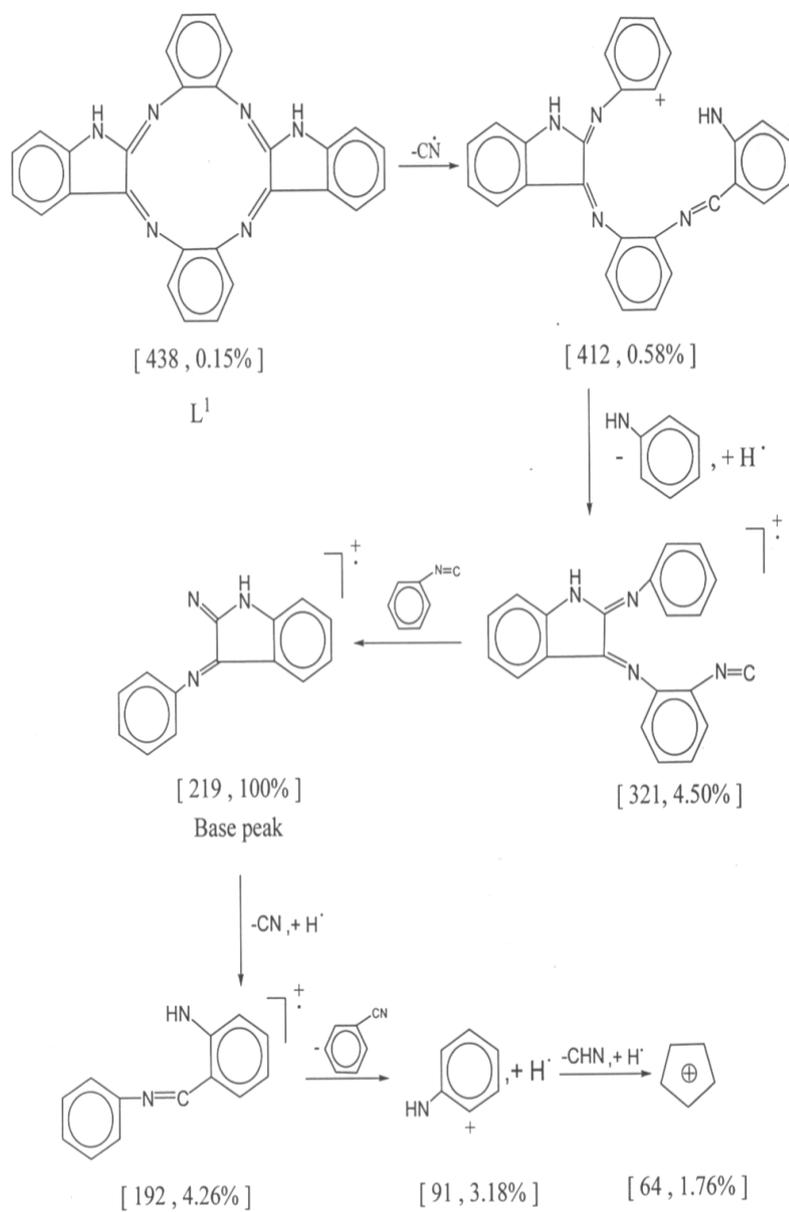


Fig. 8. Thermogravimetric analysis of some metal complexes of ligands L^2 and L^3 .



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

References

1. Borisova, N. E., Reshetova, M. D. and Ustynyuk, Y. A., *Chem. Rev.* **107**, 46 (2007).
2. Paryzek, W.R., Patroniak, V. and Lisowski, J., Metal complexes of polyaza and polyoxaaza Schiff base macrocycles. *Coord. Chem. Rev.* **249**, 2156 (2005).
3. Maji, M., Chatterjee, M., Ghosh, S., Chattopadhyay, S. K., Wu, B. M. and Mak, T. C. W., *J. Chem. Soc. Dalton Trans.* 135 (1999).
4. Sengupta, P., Dinda, R., Ghosh, S. and Sheldrick, W.S., Synthesis and characterization of some biologically active ruthenium(II) complexes. *Polyhedron*, **22**, 447 (2003).
5. Chandra, S., Gupta, R., Gupta, N. and Bawa, S. S., *Trans. Met. Chem.* **31**, 147 (2006).
6. Chandra, S. and Gupta, L. K., Synthesis and spectral studies of transition metal complexes with 2,16- dimethyl 1-3,6,9,12,15,21- hexaaza-bicyclo [15.3.] henicosa-1(21), 2,15,17,19-pentaene. *J. Indian Chem. Soc.* **81**, 833 (2004).
7. Chandra, S. and Sangeetika., *Spectrochimica Acta, Part A*, **60**, 147 (2004).
8. Wölfle, H., Kopacka, H., Wurst, K., Preishuber-Pflügl, P. and Bildstein B., *J. of Organometallic Chemistry*, **694** (16, 15), 2493 (2009).
9. Richardson, D.R., Kalinowski, D.S., Lau, S., Jansson P.J. and Lovejoy D.B., *Biochimica et Biophysica Acta (BBA)*, **1790** (7), 702 (2009).
10. Long, J., Gao, H., Liu, F., Song, K., Hao Hu, Zhang, L. and Zhu F. Q. U., *Inorg. Chim. Acta*, **362** (9), 3035 (2009).
11. McClintock, L.F., Henrik, P.B., Kjaergaard, G. and Blackman, A.G., Co(III) complexes of the type [(L)Co(O₂CO)]⁺(L=tripodal tetraamine ligand): Synthesis structure, DFT calculations and ⁵⁹Co NMR. *Polyhedron*, **28** (8), 1459 (2009).
12. Quiroga, A. G. and Ranninge, C. N., *Coord. Chem. Rev.* **248**, 119 (2004).
13. Yet, L., *Chem. Rev.* **103**, 4283 (2003).
14. Kureshy, R.I., Khan, N. H., Abdi, S. H. R., Patel, S. T. and Iyer, P., *J. Mol. Catal.* **150**, 175 (1999).
15. Aoyama, Y., Kujisawa, J. T., Walanawe, T., Toi, A. and Ogashi, H., *J. Am. Chem. Soc.* **108**, 943 (1986).
16. Sdrawn, R. S., Zamakani, M. and Coho, J. L., *J. Am. Chem. Soc.* **108**, 3510 (1986).
17. Sengupta, P., Ghosh, S. and Mak, T.C.W., A new route for the synthesis of bis (pyridine dicarboxylato) bis (triphenylphosphine)complexes of ruthenium(II). *Polyhedron*, **20**, 975 (2001).
18. Tweedle, M. F. and Runge, Y. M., *Drugs Future*, **17**, 187 (1992).
Egypt. J. Chem. **53**, No. 6 (2010)

19. **Gaballa, A. S., Asker, M.S., Barakat, A.S. and Teleb, S.M.,** *Spectrochimica Acta, Part A*, **67**, 114 (2007)
20. **Shankera, K., Rohinia, R., Ravindera, V., Reddyb, P.M. and Hob Y.P.,** *Spectrochimica Acta Part A*, **73**, 205 (2009).
21. **Shakir, M., Azim, Y., Chishti, H. T. N. and Parveen, S.,** *Spectrochimica Acta, Part A*, **65**, 490 (2006).
22. **Chandra, V., Gupta, L. K.,** *Spectrochimica. Acta, Part A*, (2005).
23. **Saleh, A. A.,** Synthesis and spectroscopic studies of novel mononuclear complexes of cyclic and acyclic Schiff base derivatives of tridentate and tetradentate coordination with some bivalent transition metal ions. *J. Coord. Chem.* **58** (3), 255 (2005).
24. **Vogel, A. I.,** *Quantitative Organic Analysis*. 6th ed. Longman, 100 (2000).
25. **Saleh, A. A. and Crutchley, R.J.,** Solvent dependence of ligand to metal charge – transfer oscillator strength: outer-sphere perturbation of the ruthenium (III)-cyanamide bond. *J. Inorganic Chemistry*, **29**, 2132 (1990).
26. **Bansol, A. and Singh, R. V.,** *Indian J. Chem. Sec. A*, **40**, 989 (2002).
27. **Hanna, W. G. and Moowad, M. M.,** *Transition Met. Chem.* **26**, 644 (2001).
28. **Saleh, A. A., Khalel, S. M. E., Eid, M. F. and El-Ghamry, M. A.,** Synthesis, spectral and magnetic studies of mononuclear and binuclear Mn(II),Co(II),Ni(II) and Cu(II) complexes with semicarbazone ligands derived from sulfonamide, *J. Coord. Chem.* **56**, 467 (2003).
29. **Bodke, Y. and Sangapure, S. S.,** *J. Indian Chem. Soc.* **80**, 187 (2003).
30. **Nakamoto, K.,** *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds*. 4th ed., Wiley Interscience, New York, 258 (1980).
31. **Shakir, M., Nasman, O.S. M., Mohamed, A. K. and Varkey, S.P.,** *Indian J. Chem. Sec. A*, **35**, 710 (1996).
32. **Lever, A.B.P.,** *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier , New York (1997).
33. **Cotton, F. A., Grave, D. M. I. and Sacce, A.,** *J. Am. Chem. Soc.* **83**, 4175 (1961).
34. **Yamada, S.,** *Coord. Chem. Rev.* 237 (1974).
35. **Chandra, S. and Sarma, S.D.,** Template synthesis of copper(II) complexes of two twelve-membered tetradentate nitrogen-donor macrocyclic ligands. *J. Indian Chem. Soc.* **79**, 495 (2002) .
36. **Prasad, R. N. and Mathur, M.,** Cr(III),Fe(III),Co(II),Ni(II) and Zn(II) complexes of 26- and 28-membered tetraazamacrocycles. *J. Indian Chem. Soc.* **83**, 1208 (2006).

37. Singh, V., Bhattacharya, A. and Kumar, P., Synthesis of strapped nickel(II) macrocyclic complex of tetraaza[14] annulene. *J. Indian Chem. Soc.* **74**, 525 (2002).
38. Jain, M., Gaur, S., Singh, V. P. and Singh, R. V., *Appl. Organomet. Chem.* **18** (2), 73 (2004).
39. Tang, H. A., Wang, L. F. and Yang, R. D., *Transition Met. Chem.* **28**, 395 (2003).
40. Sengupta, S. K., Pandey, O. P., Srivastava, B. K. and Sherma V. K., *Transition Met. Chem.* **23** (4), 349 (1998).
41. Neelakantan, M. A., Raj, F.R. and Pillai, M. S., Spectroscopy, electrochemistry and biocidal activity of amino acid Schiff base metal complexes, *J. Indian Chem. Soc.* **85**, 100 (2008).
42. Dayalan, A., Meera, P., Balaraju, K., Agastian, P. and Ignasimuthu S., Halocobaloximes containing axially coordinated imidazole or histidine: Microwave assisted synthesis, characterization and antibacterial activity. *J. Indian Chem.Soc.* **86**, 628 (2009).

(Received 15/6/2010 ;
accepted 22/12/2010)

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

عقيلة أمين صالح ، مسعد عبد الرحمن الغمري ، خديجة سعد نمشة*
وسامى محمد أبو الوفا
قسم الكيمياء - كلية التربية - جامعة عين شمس - القاهرة - مصر* قسم
الكيمياء- كلية التربية- جامعة الملك خالد- أبها - المملكة العربية السعودية .

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.