

# A new Tetradentat Macrocyclic Ligands and their Complexes with Fe(II),Co(II),Ni(II),Cu(II) and Zn(II)

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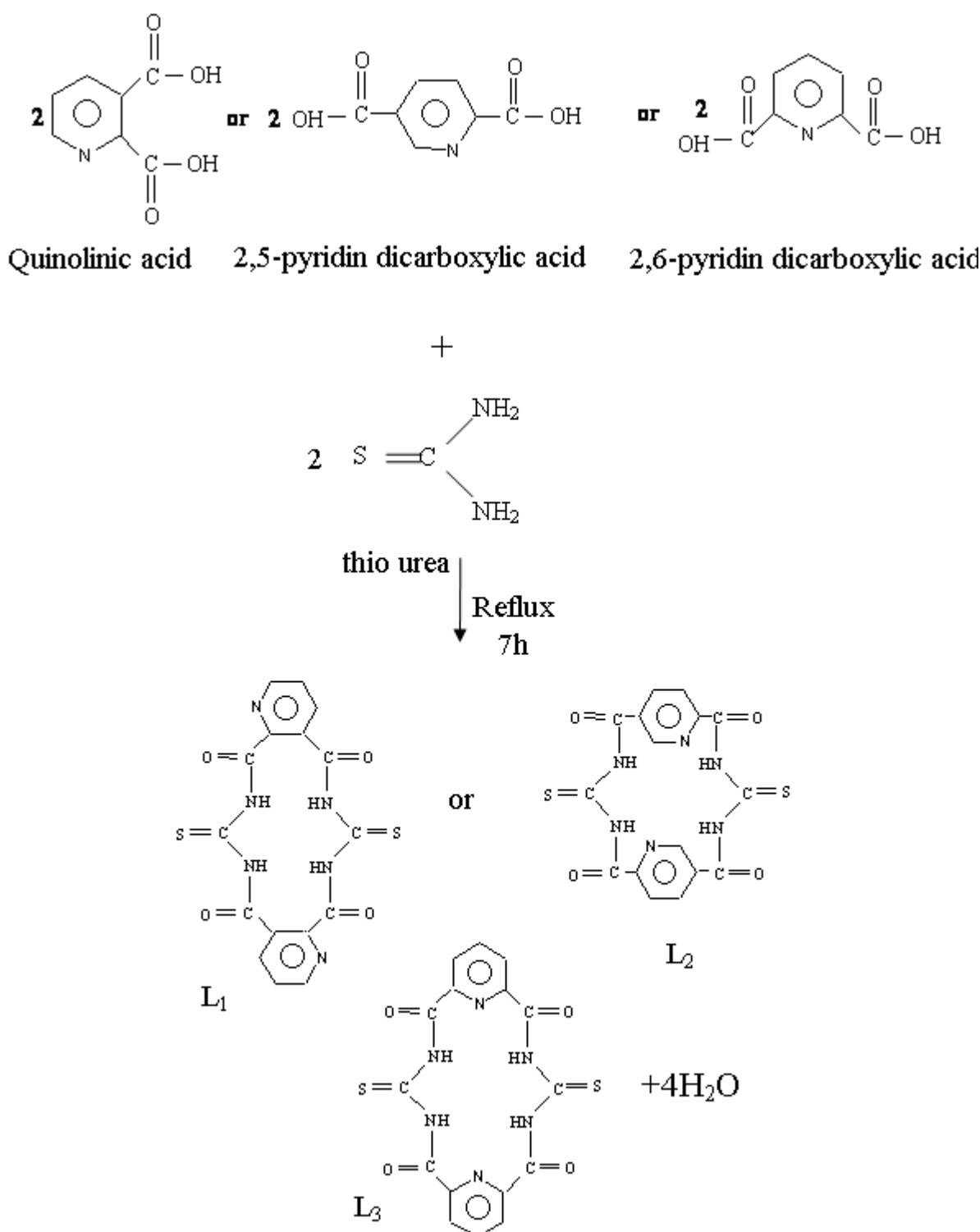
## Abstract:

Complexes of the type  $[M(L_1)Cl_2]$ ,  $[M(L_2)Cl_2]$  and  $[M(L_3)Cl_2]$  ( $M = Fe(II), Co(II), Ni(II), Cu(II)$  and  $Zn(II)$ ;  $L_1 = \text{Bis}(2\text{-pyridyl-3-(1,5-dioxo-2',4'-diaz-3'-thiopentyl)})$ ,  $L_2 = \text{Bis}(2\text{-pyridyl-5-(1',5'-dioxo-2',4'-diaz-3'-thiopentyl)})$ ,  $L_3 = \text{Bis}(2\text{-pyridyl-6-(1,5'-dioxo-2',4'-diaz-3'-thiopentyl)})$ ) have been prepared and characterized by means of micro analysis (N&M), molar conductance measurements, magnetic measurements IR, and electronic spectral studies, according to these studies the prepared complexes may have octahedral configuration.

## Introduction:

The last several years show, growing interest in the N-alkyl and N-aryl substituted thioacetamide<sup>(1-3)</sup>. Also the macrocyclic ligands (with  $-NH$  group( $N_4$ )) derived from thioacetamide and their complexes have an intensive area of study and numerous transition metal complexes. This partially was due to their wide range of different molecular topologies and sets of donor atoms<sup>(4)</sup>. In addition to their interesting ligational properties. They had competence biological and industrial applications and the field of anti-inflammatory action and bacterial growth inhibitors<sup>(5)</sup>. Chandra and Gupta<sup>(6)</sup> reported the synthesis and spectroscopic characterization of macrocyclic  $Mn(II)$ ,  $Co(II)$ ,  $Ni(II)$  and  $Cu(II)$  complexes with macrocyclic tetradentate nitrogen donor ( $N_4$ ) ligand. The ligand and its complexes were also evaluated against the growth of bacteria and pathogenic fungi in vitro.

As continuation of our interest in investigation the interaction between some of the first transition metal ions and several donating ligand<sup>(7-8)</sup>. We have prepared in the present work a new class of tetradentate ( $N_4$ ) ligand Fig 1.



**Fig 1: Preparation and structure of the ligands**

#### Experimental:

The ligands has been synthesized according to the following procedure<sup>(6)</sup>.

Quinolinic acid (8.35 g, 0.05 mol) was dissolved in hot ethanol (20 ml) and mixed slowly with a hot ethanolic solution (20 ml) of thiourea (3.80 g, 0.05 mol) with stirring. The mixture then refluxed at ~ 78°C for 7h in the presence of few drops of concentrated hydrochloric acid. On cooling a white precipitate formed which was filtered off washed with cold ethanol and dried under vacuum (Fig 1). The same procedure was carried out with 2,5-pyridin dicarboxylic acid (8.35 g, 0.05 mol) and 2,6-pyridin dicarboxylic acid (8.39 g, 0.05 mol) to prepare L<sub>5</sub> and L<sub>6</sub> ligands. Some of their physical properties are listed in Table 1.

**Table 1:** Molar conductance and elemental analysis data of the complexes

No.	Complex	Colour	M.P (°C)	Yield (%)	Molar conductivity $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Elemental analysis data found (calculated) %	
						N	Metal
	L <sub>1</sub>	White	180-182	60	---	19.98 (20.28)	---
1	[Fe(L <sub>1</sub> )Cl <sub>2</sub> ]	Ridish-brown	172-175	72	15.5	15.42 (15.56)	10.12 (10.33)
2	[Co(L <sub>1</sub> )Cl <sub>2</sub> ]	Yellow	285-287	58	16.4	15.31 (15.47)	10.65 (10.84)
3	[Ni(L <sub>1</sub> )Cl <sub>2</sub> ]	Green	262-264	64	17.3	15.40 (15.47)	10.72 (10.81)
4	[Cu(L <sub>1</sub> )Cl <sub>2</sub> ]	blue	250-355	75	17.6	15.25 (15.35)	11.42 (11.59)
5	[Zn(L <sub>1</sub> )Cl <sub>2</sub> ]	white	288-291	58	14.3	15.10 (15.29)	11.78 (11.88)
	L <sub>2</sub>	white	125-128	80	---	20.14 (20.28)	---
6	[Fe(L <sub>2</sub> )Cl <sub>2</sub> ]	Brown	254-255	82	12.2	15.32 (15.56)	10.01 (10.33)
7	[Co(L <sub>2</sub> )Cl <sub>2</sub> ]	Yellow	310-313	55	12.0	15.38 (15.47)	10.77 (10.84)
8	[Ni(L <sub>2</sub> )Cl <sub>2</sub> ]	blue	290-295	66	10.4	15.29 (15.47)	10.80 (10.81)
9	[Cu(L <sub>2</sub> )Cl <sub>2</sub> ]	Dark blue	276-278	68	15.5	15.23 (15.35)	11.50 (11.59)
	L <sub>3</sub>	Yellowish white	186-188	85	---	20.08 (20.28)	---
10	[Co(L <sub>3</sub> )Cl <sub>2</sub> ]	Brown	318-320	76	10.8	15.33 (15.47)	10.79 (10.84)
11	[Ni(L <sub>3</sub> )Cl <sub>2</sub> ]	Green	276-289	58	17.0	15.42 (15.47)	10.68 (10.81)
12	[Cu(L <sub>3</sub> )Cl <sub>2</sub> ]	Brown	253-254	53	17.5	15.26 (15.35)	11.34 (11.59)
13	[Zn(L <sub>3</sub> )Cl <sub>2</sub> ]	white	198-201	78	9.4	15.02 (15.29)	11.54 (11.88)

**A: Preparation of complexes:**

The hot ethanolic solution of ligands (0.001 mol)(20 ml) and ethanolic solution of corresponding metal salt (0.001 mol)(20 ml) were mixed together with stirring. The mixture was refluxed for 5h at 60-90°C. Cooling gives a colored precipitate of the complexes. It was filtered, washed with cold EtOH and dried under vacuum.

**B: Physical measurements:**

Analysis of ligands and complexes were carried out using Kildal method to determine N and atomic absorption to determine all the metal ions. Infrared spectra in the range 4000-400 cm<sup>-1</sup> were recorded on a Perkin-Elmer 580 B spectrophotometer, as KBr, or CsI discs. Electronic spectra were obtained with Shimadzu UV/vis, recording UV160 spectrophotometer at room temperature. The measurement were recorded using a concentration of 10<sup>-3</sup> M of the complexes in DMSO. The magnetic measurements were carried out at 25°C on the solid by a Faraday's method using Bruker BM6. Instrument. Conductivities were measured using a conductivity meter mode PCM3-JenWay. These measurements were obtained using DMSO over concentration of 10<sup>-3</sup> M at 25°C.

**Results And Discussion:****Ligands:**

IR spectrum of the ligand does not exhibit any band corresponding for the free primary diamine and hydroxyl group<sup>(8)</sup>. Four new bands appear in the spectrum of the free ligands (L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>) assignable to amide I [ $\nu(\text{C}=\text{O})$ ], amide II [ $\nu(\text{C}-\text{N}) + \delta(\text{N}-\text{H})$ ], amide III [ $\delta(\text{N}-\text{H})$ ] and amide IV [ $\delta(\text{C}=\text{O})$ ] bands, respectively<sup>(9,10)</sup>. Bands at (811-735) cm<sup>-1</sup> may be due to the thioamides I and II respectively. The ligands also have additional bands due to pyridine (C=N), (C=O) and (C=S) which appeared at ~1650, 1690 and 1250 respectively. These bands does not exhibite any change in position in all the complexes which indicate that these groups does not involve in coordination with the metal ions<sup>(6,11,12)</sup>.

A sharp band observed at 3328-3367 cm<sup>-1</sup> may be assigned to [ $\nu(\text{N}-\text{H})$ ] of the secondary amino group Table 2<sup>(13)</sup>.

**Table 2:** Selected I.R band, and their assignment in cm<sup>-1</sup>

No.	compound	$\nu(\text{C}=\text{O})$ amid I	$(\nu\text{C}-\text{N} + \delta\text{N}-\text{H})$ amid II	$\delta(\text{N}-\text{H})$ III	$\delta(\text{C}=\text{O})$ IV	Thioamid I and II	$\nu(\text{N}-\text{H})$	$\nu(\text{M}-\text{N})$
	L <sub>1</sub>	1600 <sub>s</sub>	1583 <sub>s</sub>	1393 <sub>s</sub>	763 <sub>s</sub>	779 <sub>s</sub>	3419 <sub>B</sub>	---
1	[Fe(L <sub>1</sub> )Cl <sub>2</sub> ]	1697 <sub>s</sub>	1557 <sub>s</sub>	1370 <sub>s</sub>	749 <sub>s</sub>	783 <sub>s</sub>	3280 <sub>B</sub>	500 <sub>s</sub>
2	[Co(L <sub>1</sub> )Cl <sub>2</sub> ]	1653 <sub>s</sub>	1559 <sub>s</sub>	1372 <sub>s</sub>	689 <sub>s</sub>	758 <sub>s</sub>	3300 <sub>B</sub>	442 <sub>s</sub>
3	[Ni(L <sub>1</sub> )Cl <sub>2</sub> ]	1682 <sub>s</sub>	1560 <sub>s</sub>	1266 <sub>s</sub>	716 <sub>s</sub>	761 <sub>s</sub>	3300 <sub>B</sub>	446 <sub>s</sub>
4	[Cu(L <sub>1</sub> )Cl <sub>2</sub> ]	1683 <sub>s</sub>	1558 <sub>s</sub>	1372 <sub>s</sub>	688 <sub>s</sub>	758 <sub>s</sub>	3280 <sub>B</sub>	440 <sub>s</sub>
5	[Zn(L <sub>1</sub> )Cl <sub>2</sub> ]	1683 <sub>s</sub>	1558 <sub>s</sub>	1264 <sub>s</sub>	688 <sub>s</sub>	758 <sub>s</sub>	3290 <sub>B</sub>	440 <sub>s</sub>
	L <sub>2</sub>	1626 <sub>s</sub>	1596 <sub>s</sub>	1385 <sub>B</sub>	698 <sub>s</sub>	748 <sub>s</sub>	3350 <sub>B</sub>	---
6	[Fe(L <sub>2</sub> )Cl <sub>2</sub> ]	1577 <sub>s</sub>	1488 <sub>s</sub>	1366 <sub>s</sub>	691 <sub>s</sub>	749 <sub>s</sub>	3300 <sub>B</sub>	448 <sub>s</sub>
7	[Co(L <sub>2</sub> )Cl <sub>2</sub> ]	1606 <sub>s</sub>	1578 <sub>s</sub>	1361 <sub>s</sub>	686 <sub>s</sub>	750 <sub>s</sub>	3243 <sub>B</sub>	511 <sub>s</sub>

8	[Ni(L <sub>2</sub> )Cl <sub>2</sub> ]	1622 <sub>S</sub>	1575 <sub>S</sub>	1366 <sub>S</sub>	688 <sub>S</sub>	743 <sub>S</sub>	3300 <sub>B</sub>	421 <sub>S</sub>
9	[Cu(L <sub>2</sub> )Cl <sub>2</sub> ]	1610 <sub>B</sub>	1485 <sub>S</sub>	1365 <sub>S</sub>	702 <sub>S</sub>	754 <sub>S</sub>	3300 <sub>B</sub>	455 <sub>S</sub>
	L <sub>3</sub>	1619 <sub>S</sub>	1578 <sub>S</sub>	1391 <sub>S</sub>	722 <sub>S</sub>	752 <sub>S</sub>	3326 <sub>B</sub>	---
10	[Co(L <sub>3</sub> )Cl <sub>2</sub> ]	1635 <sub>B</sub>	---	1387 <sub>w</sub>	---	742 <sub>w</sub>	3308 <sub>B</sub>	434 <sub>S</sub>
11	[Ni(L <sub>3</sub> )Cl <sub>2</sub> ]	1615 <sub>S</sub>	1433 <sub>S</sub>	1284 <sub>S</sub>	728 <sub>S</sub>	770 <sub>S</sub>	3233 <sub>B</sub>	444 <sub>S</sub>
12	[Cu(L <sub>3</sub> )Cl <sub>2</sub> ]	1622 <sub>S</sub>	1509 <sub>m</sub>	1252 <sub>w</sub>	697 <sub>S</sub>	811 <sub>w</sub>	3278 <sub>B</sub>	472 <sub>S</sub>
13	[Zn(L <sub>3</sub> )Cl <sub>2</sub> ]	1622 <sub>S</sub>	1557 <sub>S</sub>	1373 <sub>S</sub>	690 <sub>S</sub>	735 <sub>S</sub>	3370 <sub>B</sub>	430 <sub>S</sub>

### Complexes:

On the basis of (N & M) analysis, the complexes were assigned to possess the composition show in Table 1. The molar conductance measurements of the complexes in DMSO shown to be nonelectrolyte in nature for Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) .

On complex formation the shifting toward lower side of  $[\nu(\text{N-H})]$  amides II and III bands suggest the coordination through nitrogen of -NH group (N<sub>4</sub>) which is further supported by the appearance of a medium intensity band in the rang 421-511 cm<sup>-1</sup> attributed to  $[\nu(\text{M-N})]$ . The M-Cl bands did not appeared due to instrument limitation.

### Iron(II) complexes:

The magnetic moment values at room temperature 4.65, 4.72 BM for the Fe(II) complexes, which were below the spin only value may be due to distortion were well in accord with those having distorted octahedral structure<sup>(14)</sup>. The electronic spectra showed a band at 10256, 10917 cm<sup>-1</sup> which attributed to the (<sup>5</sup>T<sub>2g</sub> → <sup>5</sup>E<sub>g</sub>) transition and could be assigned to a distorted octahedral structure. The nonelectrolytic nature of those complexes were in accord with their tentative structure<sup>(14,15)</sup>.

### Co(II) complexes:

The magnetic moment measurements of cobalt (II) complexes lie in the range 4.88-4.95 B.M corresponding to three unpaired electrons, which were higher than the spin only value may be due to orbital contribution Table 3.

**Table 3:** Magnetic moments and electronic spectral data of the complexes

No.	compound	$\mu_{\text{eff}}$ B.M (25°C)	d-d transition and C.T
1	[Fe(L <sub>1</sub> )Cl <sub>2</sub> ]	4.65	10917, 33783 C.T
2	[Co(L <sub>1</sub> )Cl <sub>2</sub> ]	4.93	10152, 13888, 19841, 36231 C.T
3	[Ni(L <sub>1</sub> )Cl <sub>2</sub> ]	2.82	10460, 16778, 18315, 33557 C.T
4	[Cu(L <sub>1</sub> )Cl <sub>2</sub> ]	1.92	10917, 30674 C.T
5	[Zn(L <sub>1</sub> )Cl <sub>2</sub> ]	---	35714 C.T
6	[Fe(L <sub>2</sub> )Cl <sub>2</sub> ]	4.72	10256, 32786 C.T
7	[Co(L <sub>2</sub> )Cl <sub>2</sub> ]	4.95	10152, ---, 19230, 35714 C.T
8	[Ni(L <sub>2</sub> )Cl <sub>2</sub> ]	3.12	10152, 15243, 24552, 35971 C.T
9	[Cu(L <sub>2</sub> )Cl <sub>2</sub> ]	1.88	11947, 35714 C.T
10	[Co(L <sub>3</sub> )Cl <sub>2</sub> ]	4.88	14836, 16474, 19723, 32679 C.T
11	[Ni(L <sub>3</sub> )Cl <sub>2</sub> ]	3.23	9803, 15503, 25000, 35842 C.T
12	[Cu(L <sub>3</sub> )Cl <sub>2</sub> ]	1.86	12674, 38314 C.T
13	[Zn(L <sub>3</sub> )Cl <sub>2</sub> ]	---	---, 35842 C.T

The electronic spectra of all the cobalt (II) complexes showed an absorption in the region 10152, 13888-16474, 19841-19230 and 32679-36231 cm<sup>-1</sup>. These bands may be assigned to the transitions: <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F)(v<sub>1</sub>), <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>A<sub>2g</sub>(v<sub>2</sub>) and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(p)(v<sub>3</sub>) respectively<sup>(15)</sup>. It is difficult to give the assignments for the fourth band and it may be due to charge transfer. The position of electronic spectral bands indicates that these complexes have distorted octahedral geometry<sup>(9,10,13)</sup> Fig (2).

### Nickel (II) complexes:

The Ni(II) complexes shows a magnetic moments 2.82-3.23 BM at room temperature, these values are in turn with a high-spin configuration and shows the presence of an octahedral environment around Ni(II) ions in the complexes<sup>(16)</sup>. The electronic spectrum of the complexes shows three bands at 9803-10460, 15243-16778 and 18315-25000 cm<sup>-1</sup> correspond to the three spin-allowed transition <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F)(v<sub>1</sub>), <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F)(v<sub>2</sub>) and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(p)(v<sub>3</sub>) respectively.

An examination of these bands indicate that the complexes has octahedral geometry Fig (2).

### Copper (II) complexes:

The magnetic moment of the Cu(II) complexes at room temperature lie in the rang 1.86-1.96 BM corresponding to one unpaired electron.

Electronic spectra of copper (II) complexes consist of 1 broad band due to combined transitions <sup>2</sup>B<sub>1g</sub> → A<sub>1g</sub>, <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>B<sub>2g</sub>, <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>E<sub>g</sub> and located below 15000 cm<sup>-1</sup> or three combined transitions the electronic spectra of the complexes display bands in the range (10917-12674 and 17822-18522) cm<sup>-1</sup> which may due to distorted octahedral structure around the Cu (II) ions<sup>(17)</sup>. Fig (2).

As the spectrum of Zn(II) complexes is not well resolved it is not interpreted but its  $\mu_{\text{eff}}$  value show that they are diamagnetics as expected<sup>(8)</sup>.

On the basis of the above discussions we propose the following structure for metal (II) complexes as shown in Fig (2).

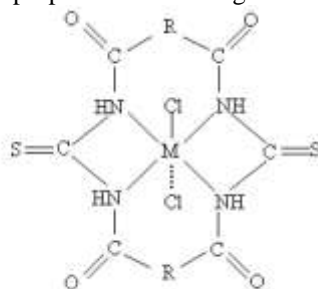
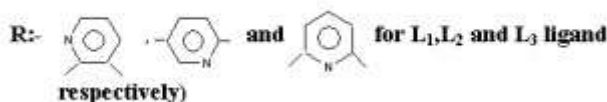


Fig 2: Suggested structure of the complexes  
(where M: Fe(II), Co(II), Ni(II), Cu(II) and Zn(II))



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## تحضير ودراسة معقدات مع ليكاندات الجزيئات الكبيرة رباعية

### السن مع العناصر الانتقالية Fe(II) و Co(II) و Ni(II) و Cu(II) و Zn(II)

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#### الملخص:

تم تحضير معقدات جديدة من نوع  $[M(L_1)Cl_2]$  و  $[M(L_2)Cl_2]$  و  $[M(L_3)Cl_2]$  حيث كانت M = Fe(II) ، Co(II) ، Ni(II) ، Cu(II) و Zn(II) و  $L_1$  = بس(٢-بريدائل-٣-٥،١-ثنائي اوكسو-٤،٢-ثنائي آزا-٣-ثايوبنتايل)) و  $L_2$  = بس(٢-بريدائل-٥-١-ثنائي اوكسو-٤،٢-ثنائي آزا-٣-ثايوبنتايل)) و  $L_3$  = بس(٢-بريدائل-٦-١،٥-ثنائي اوكسو-٤،٢-ثنائي آزا-٣-ثايوبنتايل)) وقد درست هذه المعقدات وشخصت من خلال التحليل الدقيق للعناصر (M و N) وقياسات التوصيلية المولارية والقياسات المغناطيسية والأشعة تحت الحمراء والطيف الالكتروني، واعتمادا على هذه القياسات يعتقد ان المعقدات لها شكل ثماني السطوح.