Synthesis and Characterization of Tetradentate Macrocyclic Ligands and its Complexes with Some Transition Metal Ions.

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(**Received:** 28 / 11 / 2010 ---- **Accepted:** 16 / 3 / 2011)

Abstract
Complexes of the type $[M(L_1)Cl_2]$, $[M(L_2)Cl_2]$ and $[M(L_3)Cl_2]$ (M=Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); L_1=(5,12-dibromo-2,9-dithioxo-1,3,8,10-tetra azacyclo tetra decane-4,7,11,14-tetraone), L_2= (5,6,12,13-tetrabromo-2,9- dithioxo -1,3,8,10- tetraazacyclotetra decane-4,7,11,14-tetraone) and L_3= ((5Z, 12Z) - 2,9 – dithioxo -1,3,8,10-tetraaza cyclotetradeca-5,12-diene-4,7,11,14-tetraone) have been prepared and characterized by means of micro analysis (Metals (M)) molar conductance measurements, magnetic susceptibility measurements, IR and electronic spectral studies the prepared complexes may have octahedral configuration.

Introduction
The Macrocyclic ligands which have $[N_4]$ cavity with NH group have intensive area of study with the a numerous transition metals[1-3]. Macrocyclic molecules containing two polyamine chains linked by different spacers are also capable to form complexes with metal ions in close proximity which is considered to be an important factor in increasing the efficiency in activation of substrates[4-6]. Nature prefers macrocyclic derivatives for biological fields such as photosynthesis and transport of oxygen in mamalian and other respiratory system, beside of antimicrobial, antifertility, antimalarial, anticancer, antiviral and anti-HIV activities[7-12]. Chandra and Gupta[13] reported the synthesis and spectroscopic characterization of macrocyclic complexes with a novel macrocyclic tatradentate nitrogen doner $[N_4]$ ligand, that give rise to environmental, industrial or health-related potential applications [14].

As a continuation of our interest to investigate interaction between some first transition series metal ions and several donating ligands [15-18]. We have prepared in the present work a new class of tetradentate $[N_4]$ ligand (Fig. 1)

Experimental
The ligands L_1 has been synthesized according to the following procedure[16].

Bromosuccinic acid (9.85 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 was refluxed with stirring ~ 80°c for 9 h in the presence of few drops of concentrated hydrochloric acid. On cooling a white precipitate was formed this product was filtered off washed with cold EtOH and dried under vacuum. The same procedure was used for the preparation of L_2 by using 2,3-dibromosuccinic acid (13.79 g, 0.05 mol) and L_3 by using fumaric acid (5.80 g, 0.05 mol). Some of the physical properties for the prepared ligands are listed in table 1.

A: Preparation of the metal complexes:

The hot ethanolic solution (20 ml) of ligands L_1 or L_2 or L_3 (0.001 mol) (0.474, 0.632, 0.312 gm) respectively and hot ethanolic solution (20 ml) of corresponding metal salt (0.001 mol) were mixed together with stirring. The mixture was refluxed for 5h at 60-90°c. Cooling up gave a colored precipitate of the complexes. It was filtered, washed with cold EtOH and dried under vacuum.

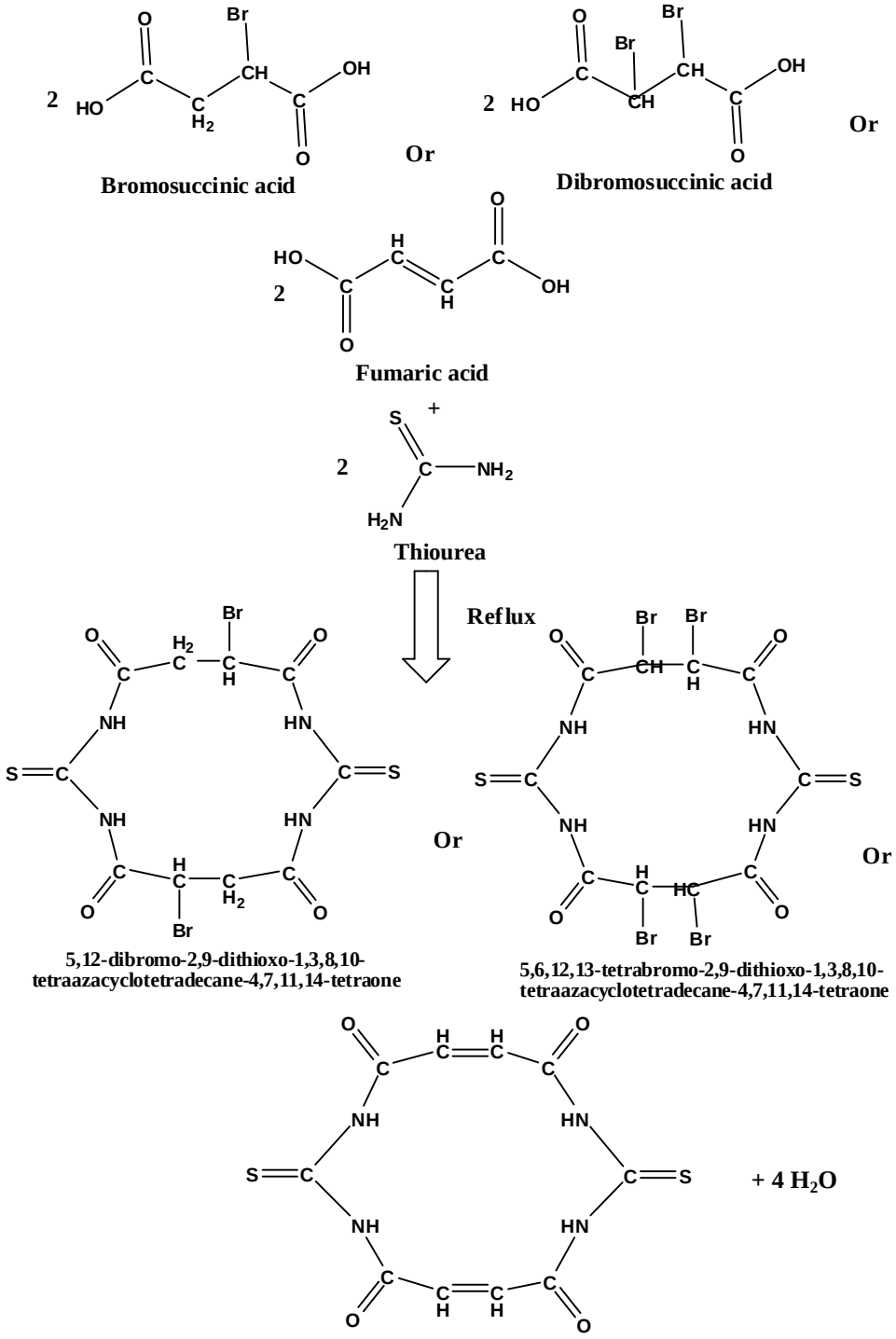


Fig. 1: Preparation and structure of the ligands L_1 , L_2 and L_3.

B: Physical measurements:

Analysis of ligands and complexes were carried out using standard method of analysis. The metals measurement by using atomic absorption spectrophotometer (SP6-350 Visible Spectrophotometer, Pye – Unicam, England). Infrared spectra in the range 200 - 4000 cm^{-1} were recorded on a Fourier-Transform (FT. IR) Spectrophotometer, Tensor 27 Co. Brucker, 2003, by using CsI discs in the range 200 - 4000 cm^{-1} and KBr discs in the range 400 - 4000 cm^{-1}. Electronic spectra of the complexes were obtained with Shimadzu UV/vis, recording UV160 spectrophotometer at room temperature. The measurement were recorded using a concentration of 10^{-3} 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 with concentration of 10^{-3} M at 25 ºc.

Results and discussion

Ligands:

Four new bands appear in the spectrum of infrared for free ligands (L_1, L_2 and L_3) assigned to amide I [υ(C=O) ,amide II [υ(C–N) + υ (N–H)], amide III [δ(N–H)] and amide IV [δ(C=O)] bands, respectively[19,20]. Bands at 750-781 cm^{-1} and 1427-1466 cm^{-1} are due to the thioamides I and II, respectively. A sharp band observed 3182-3284 cm^{-1} may be assigned to [υ(N–H)] of the secondary amino group (Table 2)[21].

IR spectrum of the two ligands does not exhibit any band corresponding to the free primary diamine and hydroxyl group[19].

Complexes:

The molar conductance measurements of the complexes in DMSO shown to be non electrolyte in nature, also the metals analysis assigned to posses the composition shown in Table(1).

On complex formation the shifting toward lower side of [υ(N–H)] band and the band of amides II and III, suggest the coordination through nitrogen of [–NH group [N_4]], which is further supported by the appearance of a medium intensity band in the rang 426-496 cm^{-1} attributed to [υ(M–N)] and [υ(M–Cl)] appearance weak band in the rang 280-320 cm^{-1}[22,23].

Manganese (II) complexes:

The Manganese complexes with L1 , L2 and L3 have magnetic moment values were at room temperature in the range 5.91, 5.82 and 5.90 BM respectively, these values were in accord with those having octahedral structure with five unpaired electrons[19-20]. The electronic spectra exhibit bands at (16760, 21097 and 31777 cm^{-1}),(17447 ,21455 and 32051 cm^{-1}), (16339, 21638,31820 cm^{-1}) respectively Table 2. These bands may be assigned to the transition $^6A_1g \longrightarrow {}^4T_1g(^4G)(\upsilon_1)$, $^6A_1g \longrightarrow {}^4Eg\ (^4G)\ )(\upsilon_2)$ and $^6A_1g \longrightarrow {}^4T_1g(^4P)\ )(\upsilon_3)$ respectively. The bands at 37167, 36847 and 37460 cm^{-1} may be due to charge transfer [21,24].

Iron (II) complexes:

The magnetic moments values 4.78, 4.87 and 4.82 B.M of the Fe (II) complexes were well in accord with those having distorted octahedral structure[25]. Electronic spectra showed bands at 12200, 11985 and 11290 cm^{-1} for the complexes respectively, which are attributed to the $^5T_2g \longrightarrow {}^5Eg$ transition and could be assigned to a distorted octahedral structure, the molar conductance measurements in accord with their tentative structure [25,26].

Co(II) complexes:

The magnetic moment measurements of cobalt (II) complexes lie in 4.97, 5.15 and 4.72 BM corresponding to three unpaired electrons of octahedral structure high value due to orbital contribution. (Table 2).

The electronic spectra of all the cobalt (II) complexes showed an absorption in the region (1)(14235, 14204 and 14749 cm^{-1}),(2)(16966, 16447 and 16286cm^{-1}) , (3)(18233, 19286 and 19154 cm^{-1}), (4)(32313, 32679 and 32211 cm^{-1}). These bands may be assigned to the transitions: $^4T_1g(F) \longrightarrow {}^4T_2g(F)(\upsilon_1)$, $^4T_1\ g \longrightarrow {}^4A_2g(\upsilon_2)$ and $^4T_1g(F) \longrightarrow {}^4T_1g(p)(\upsilon_3)$ respectively[25]. 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 [19,20,24] .

Nickel (II) complexes:

The Ni(II) complexes shows a magnetic moments 3.04, 3.23 and 3.16 BM at room temperature, these values shows the presence of an octahedral environment around Ni(II) ions in the complexes [27].

The electronic spectrum of the complexes shows three bands at (1) 12101, 11655 and 11658 (2) 14450, 15641 and 14619, (3) 24393, 24585 and 23809 cm^{-1} correspond to the three spin-allowed transition $^3A_2g(F) \longrightarrow {}^3T_2g(F)(\upsilon_1)$, $^3A_2g(F) \longrightarrow {}^3T_1g(F)(\upsilon_2)$ and $^3A_2g(F) \longrightarrow {}^3T_1g(p)(\upsilon_3)$ respectively.

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

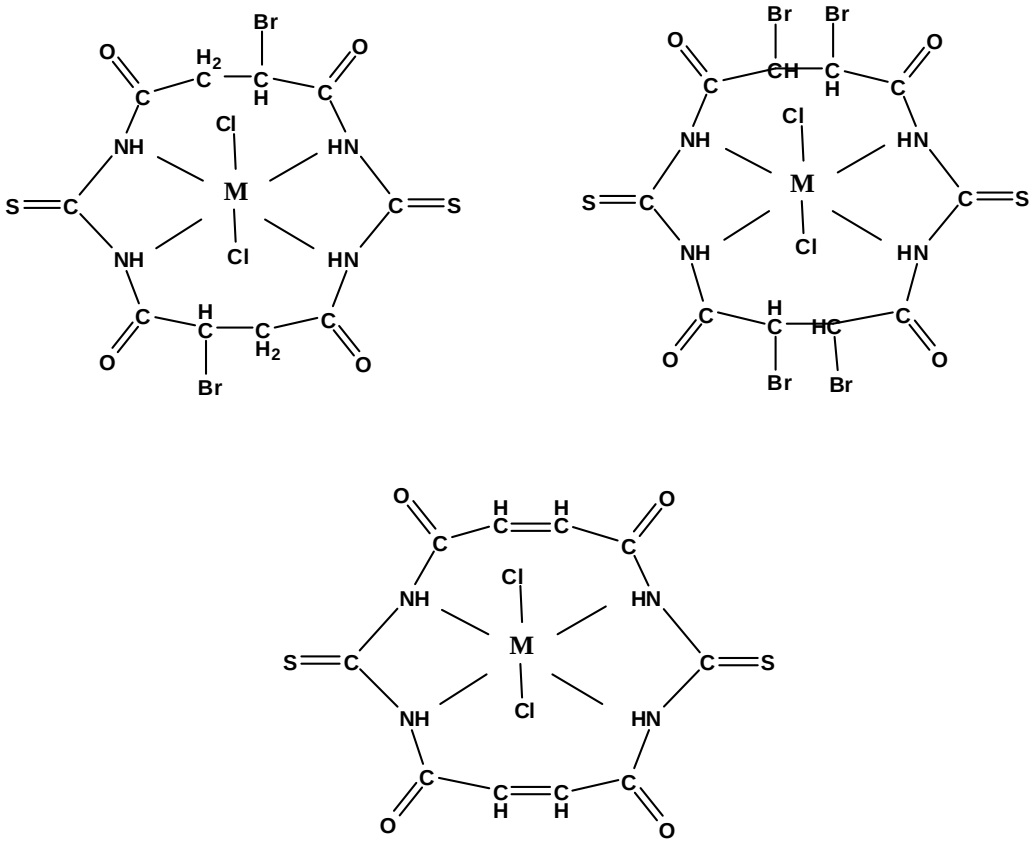
Copper (II) complexes:

The magnetic moment of the Cu(II) complexes at room temperature lie in the 1.83, 1.87 and 1.81 BM corresponding to one unpaired electron.

Electronic spectra of the copper (II) complexes display bands at (1)11658, 11185 and 11917 (2)16315, 16906 and 16437 cm^{-1}assigned to the $^2Eg \longrightarrow T_2g$ transition in distorted octahedral structure around the Cu(II) ions [28] (Fig.2).

As the spectrum of Zn(II) complexes is not well resolved, it is not interpreted but its μ_{eff} value show that they are diamagnatics as expected.

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



(where M= Mn(II),Fe(II),Co(II),Ni(II), Cu(II) and Zn(II))

Fig. 2: Suggested structure of the complexes.

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

No.	Compound	Colour	M.P (°C)	Yield (%)	Molar conductaus (Ω^{-1} cm^2 mol^{-1})	Metal analysis data found (calculated) (%)
	L_1	White	204	77	-----	-----
1	$[Mn(L_1)Cl_2]$	Pale green	248	69	28	9.15(9.19)
2	$[Fe(L_1)Cl_2]$	Yellow	218	75	44	9.29(9.37)
3	$[Co(L_1)Cl_2]$	Green	250	70	45	9.75(9.96)
4	$[Ni(L_1)Cl_2]$	Green	242	63	45	9.72(9.87)
5	$[Cu(L_1)Cl_2]$	Brown	226	57	42	10.44(10.71)
6	$[Zn(L_1)Cl_2]$	White	214	81	39	10.70(10.84)
	L_2	White	210	71	-----	-----
7	$[Mn(L_2)Cl_2]$	Yellow	216	78	33	7.24(7.55)
8	$[Fe(L_2)Cl_2]$	Yellow-brown	228	77	40	7.35(7.52)
9	$[Co(L_2)Cl_2]$	Green	219	88	37	7.73(7.91)
10	$[Ni(L_2)Cl_2]$	Yellow	224	70	40	7.70(7.89)
11	$[Cu(L_2)Cl_2]$	Brown	232	67	32	8.28(8.34))
12	$[Zn(L_2)Cl_2]$	White	220	63	39	8.50(8.58)
	L_3	White	102	86	-----	-----
13	$[Mn(L_3)Cl_2]$	Yellow	122	75	38	12.54(12.73)
14	$[Fe(L_3)Cl_2]$	Brown	134	79	42	12.72(12.86)
15	$[Co(L_3)Cl_2]$	Blue	190	80	47	13.33(13.51)
16	$[Ni(L_3)Cl_2]$	Yellow	140	71	47	13.29(13.54)
17	$[Cu(L_3)Cl_2]$	Brown	127	73	42	14.22(14.29)
18	$[Zn(L_3)Cl_2]$	White	120	83	27	14.57(14.66)

Table 2: Magnatic moment and electronic spectral data of the complexes

No.	Compound	*Meff* BM (25°C)	λmax (cm^{-1})
1	$[Mn(L_1)Cl_2]$	5.91	14380, 16760, 21097, 31777, 37167
2	$[Fe(L_1)Cl_2]$	4.78	12200, 24585
3	$[Co(L_1)Cl_2]$	4.97	14235, 16966, 18233, 32313
4	$[Ni(L_1)Cl_2]$	3.04	12101, 14450, 24393, 37764
5	$[Cu(L_1)Cl_2]$	1.83	11658, 16315, 38409
6	$[Zn(L_1)Cl_2]$	-----	----------
7	$[Mn(L_2)Cl_2]$	5.82	14324, 17447, 21455, 32051, 36847
8	$[Fe(L_2)Cl_2]$	4.87	11985, 25906
9	$[Co(L_2)Cl_2]$	5.15	14204, 16447, 19286, 32679
10	$[Ni(L_2)Cl_2]$	3.23	11655, 15641, 24585, 37847
11	$[Cu(L_2)Cl_2]$	1.87	11185, 16906, 37864
12	$[Zn(L_3)Cl_2]$	-----	----------
13	$[Mn(L_3)Cl_2]$	5.90	14619, 16339, 21638, 31820, 37460
14	$[Fe(L_3)Cl_2]$	4.82	11290, 24154
15	$[Co(L_3)Cl_2]$	4.72	14749, 16286, 19154, 32211
16	$[Ni(L_3)Cl_2]$	3.16	11658, 14619, 23809, 37460
17	$[Cu(L_3)Cl_2]$	1.81	11917, 16437, 37674
18	$[Zn(L_3)Cl_2]$	-----	

Table 3: Selected I.R bands and their assignment in cm^{-1}

No.	Compound	υ(C = O) amid I	υC – N+ δN–H amid II	δ(N–H) III	δ (C = O) IV	Thioamid I and II		υ(N – H)	υ(M–Cl)	υ(M – N)
	L_1	1662	1581	1388	738	750	1466	3182	----	----
1	$[Mn(L_1)Cl_2]$	1664	1520	1275	720	780	1406	3161	292	471
2	$[Fe(L_1)Cl_2]$	1612	1533	1323	677	756	1402	3165	293	492
3	$[Co(L_1)Cl_2]$	1643	1557	1375	716	756	1462	3149	320	492
4	$[Ni(L_1)Cl_2]$	1639	1535	1288	714	756	1450	3151	307	455
5	$[Cu(L_1)Cl_2]$	1658	1552	1288	710	771	1433	3120	299	445
6	$[Zn(L_1)Cl_2]$	1639	1554	1255	710	756	1414	2970	305	448
	L_2	1676	1573	1351	715	781	1427	3284	----	----
7	$[Mn(L_2)Cl_2]$	1658	1561	1275	715	766	1371	3257	306	492
8	$[Fe(L_2)Cl_2]$	1658	1531	1273	712	764	1427	3253	310	494
9	$[Co(L_2)Cl_2]$	1672	1550	1275	715	766	1421	3248	289	496
10	$[Ni(L_2)Cl_2]$	1658	1569	1273	710	764	1405	3292	311	494
11	$[Cu(L_2)Cl_2]$	1655	1550	1271	717	762	1375	3284	305	492
12	$[Zn(L_2)Cl_2]$	1631	1555	1277	705	779	1420	3280	300	496
	L_3	1649	1577	1341	725	775	1439	3284	----	----
13	$[Mn(L_3)Cl_2]$	1620	1500	1315	716	775	1441	3199	289	471
14	$[Fe(L_3)Cl_2]$	1641	1566	1313	710	777	1419	2954	305	426
15	$[Co(L_3)Cl_2]$	1628	1516	1315	710	775	1400	2962	283	474
16	$[Ni(L_3)Cl_2]$	1630	1524	1317	721	775	1447	2960	292	528
17	$[Cu(L_3)Cl_2]$	1637	1508	1319	716	777	1437	2954	281	480
18	$[Zn(L_3)Cl_2]$	1628	1523	1317	715	775	1402	2978	320	472

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تحضير وتشخيص ليكاندات رباعية السن حلقية ومعقداتها مع بعض ايونات العناصر الانتقالية

ثناء يعقوب يوسف

قسم الكيمياء ، كلية العلوم ، جامعة الموصل ، الموصل ، العراق

(تاريخ الاستلام: ٢٨ / ١١ / ٢٠١٠ ---- **تاريخ القبول:** ١٦ / ٣ / ٢٠١١ **)**

الملخص

تم تحضير عدد من معقدات جديدة من نوع $[M(L_1)Cl_2]$ و $[M(L_2)Cl_2]$ و $[M(L_3)Cl_2]$ حيث كانت M = Mn(II) ، Fe(II) ، Co(II) ، Ni(II) ، Cu(II)، Zn(II) وL_1= (٥،١٢-ثنائي بروموـ ٢،٩-ثنائي ثايو اوكسوـ ١،٣،٨،١٠-رباعي ازا رباعي دكان الحلقي-٤،٧،١١،١٤-رباعي أون) وL_2=(5,6,12,13-رباعي بروموـ ٢،٩-ثنائي ثايو اوكسوـ ١،٣،٨،١٠-رباعي ازا رباعي دكان الحلقي-٤،٧،١١،١٤-رباعي أون) وL_3=((5Z,12Z)- ٢،٩- ثنائي ثايو اوكسوـ ١،٣،٨،١٠-رباعي ازا رباعي دكا الحلقي-٥،١٢-داين ٤،٧،١١،١٤-رباعي أون) وقد درست هذه المعقدات وشخصت من خلال التحليل الدقيق للعناصر (M) وقياسات التوصيلية المولارية والقياسات المغناطيسية والأشعة تحت الحمراء والأطياف الالكترونية للتوصل الى الصيغة المتوقعة لهذه المعقدات والتي يعتقد بأنها لها شكل ثماني السطوح.