

Synthesis and Characterization of Tetradentate Macrocyclic Ligands and its Complexes with Mn(II),Fe(II),Co(II),Ni(II) and Cu(II) Metal Ions

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الخلاصة

تم تحضير عدد من معقدات جديدة لبعض العناصر الانتقالية مثل Mn(II) و Fe(II) و Co(II) و Ni(II) و Cu(II) مع ليكاندات رباعية السن من نوع (1,3,7,9-رباعي أزا - 12,10,6,4 - رباعي أوكسو-8,2 - ثنائي ثايا دودكين الحلقي) L₁ و (5,11-ثنائي ميثيل - 9,7,3,1 - رباعي أزا - 12,10,6,4 - رباعي أوكسو - 8,2 - ثنائي ثايا دودكين الحلقي) L₂ و (13,12,6,5 - رباعي هيدروكسي-10,8,3,1 - رباعي أزا - 14,11,7,4 - رباعي أوكسو - 9,2 - ثنائي ثايا تترادكين الحلقي) L₃ ، وشخصت هذه المعقدات بالتحليل الدقيق للعناصر (M,N) واستخدام التوصيلية المولارية والقياسات المغناطيسية وتحت الحمراء والطيف الإلكتروني للتوصل الى الصيغة المتوقعة لهذه المعقدات.

ABSTRACT

A new complexes of Mn(II),Fe(II),Co(II),Ni(II) and Cu(II) are synthesized with a new tetradentate ligand (1,3,7,9-tetraaza-4,6,10,12-tetraoxo-2,8-dithiacyclododecane) L₁, (5,11-dimethyl-1,3,7,9-tetra aza-4,6,10,12-tetraoxo-2,8-dithiacyclododecane) L₂, (5,6,12,13-tetra hydroxy-1,3,8,10-tetraaza-4,7,11,14-tetraoxo-2,9-dithiacyclotetradecane) L₃ and characterized by microanalysis (N and M), molar conductance measurements, magnetic susceptibility measurements, IR, electronic spectral studies.

INTRODUCTION

A good deal of work has been reported on the synthesis and structural investigation of macrocyclic ligands with $[N_4]$ group and their transition metal complexes⁽¹⁻³⁾. This is partially due to their capability of acting as multidentate N_4 donor with the formation of mono-nuclear complexes.

Nature prefers macrocyclic derivatives for biological fields such as photosynthesis and transport of oxygen in mammalian and other respiratory system^(4,5). Sulkh Chandra et al.⁽⁶⁾ 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 series metal ions and several donating ligands⁽⁷⁾ we have prepared in the present work a new class of tetradentate $[N_4]$ ligand Fig 1.

EXPERIMENTAL

The ligands have been synthesised according to the following procedure⁽⁶⁾.

Malonic acid (14.40 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 this mixture at $\sim 80^\circ C$ 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 EtOH and dried under vacuum Fig 1. The same procedure was carried out with methyl malonic acid (15.8 g, 0.05 mol) and tartaric acid (19.0 g, 0.05 mol) to prepare L_2 and L_3 ligands. Some of their physical properties are listed in Table 1.

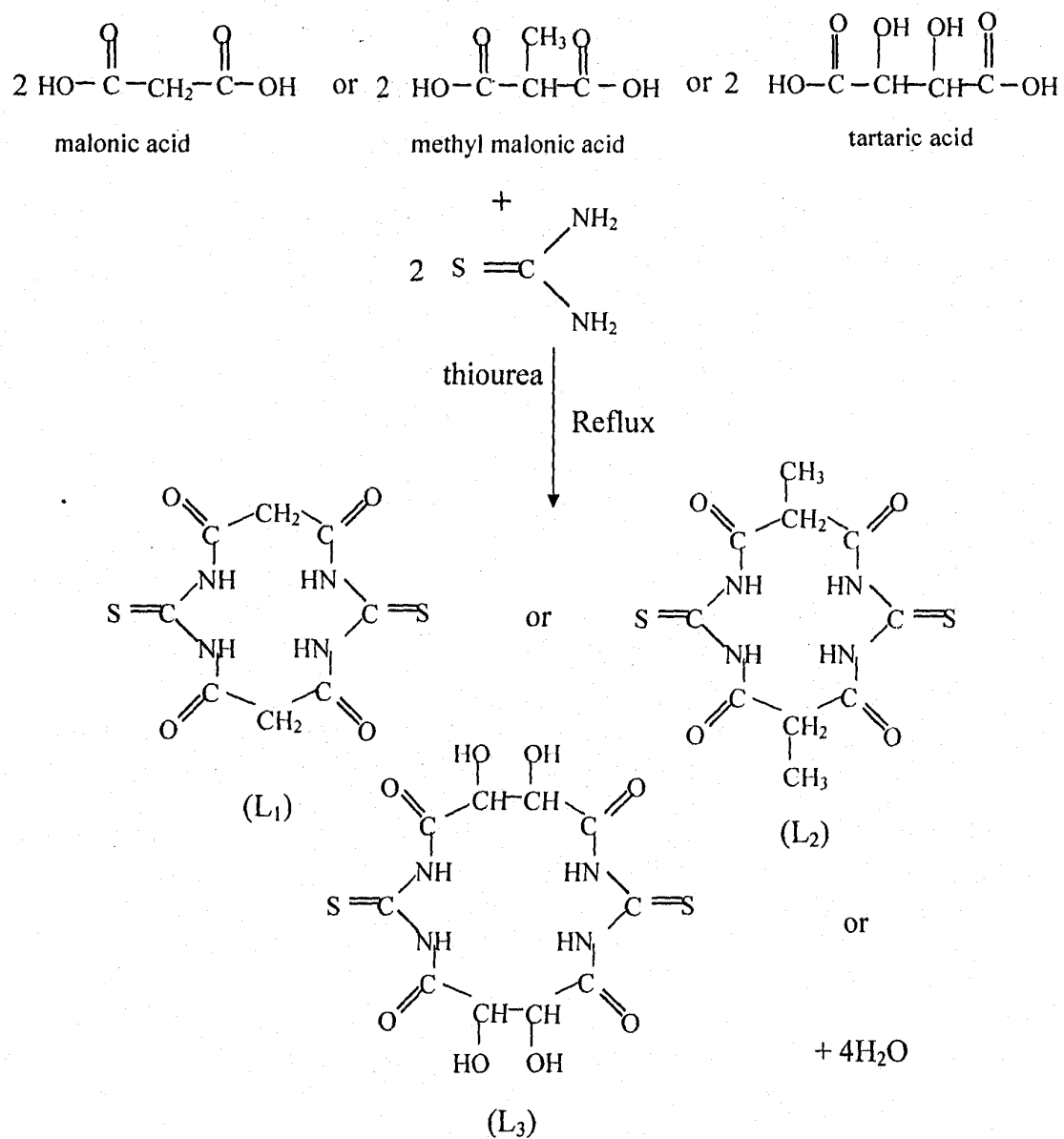


Fig 1: Preparation and structure of the ligands

A: Preparation of the metal complexes:

The hot ethanolic solution of ligands (0.001 mol/20 ml) and hot 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 standard method of analysis. Infrared spectra in the range 4000-400 cm^{-1} 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^{-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 over concentration of 10^{-3} 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[8]. Four new bands appear in the spectrum of the free ligands (L_1, L_2, L_3) 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^(8,9). Bands at 780-785 cm^{-1} and 1308-1481 cm^{-1} may be due to the thioamides I and II, respectively.

A sharp band observed 3328-3367 cm^{-1} , may be assigned to [$\nu(\text{N}-\text{H})$] of the secondary amino group Table 2⁽¹⁰⁾.

Complexes:

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

On complex formation the shifting toward lower side of [$\nu(\text{N}-\text{H})$] 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 range 472-500 cm^{-1} attributed to [$\nu(\text{M}-\text{N})$].

Manganese (II) complexes:

The magnetic moment values at room temperature in the range 5.87-5.96 BM for the Manganese (II) complexes were well in accord with those having octahedral structure with five unpaired electrons^(8,9). The electronic spectra exhibit bands in the range 26767-37238 cm^{-1} may be due to charge transfer.

Iron(II) complexes:

The magnetic moment values at room temperature 4.61-4.71 BM for the Fe(II) complexes were well in accord with those having distorted octahedral structure⁽¹²⁾. The electronic spectra showed a band at 1019-11866 cm^{-1} which attributed to the (${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$) transition and could be assigned to a distorted octahedral structure. The nonelectrolytic nature of those complexes were in accord with their tentative structure^(12,13).

Co(II) complexes:

The magnetic moment measurements of cobalt (II) complexes lie in the range 4.67-4.98 BM corresponding to three unpaired electrons. Table 2.

The electronic spectra of all the cobalt (II) complexes showed an absorption in the region 10355-10994, 13978-15276, 18784-19141 and 35348-3766 cm^{-1} . These bands may be assigned to the transitions: ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})(\nu_1)$, ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\nu_2)$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{p})(\nu_3)$ respectively⁽¹³⁾. 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^(8,9,11) Fig (2).

Nickel (II) complexes:

The Ni(II) complexes shows a magnetic moments 2.93-3.30 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⁽¹⁴⁾.

The electronic spectrum of the complexes shows three bands at 10207-10762, 15384-15748 and 24752-26042 cm^{-1} correspond to the three spin-allowed transition ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})(\nu_1)$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})(\nu_2)$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{p})(\nu_3)$ 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 rang 1.84-1.96 BM corresponding to one unpaired electron.

Electronic spectra of copper (II) complexes display bands in the range 10986-11122 and 17822-18522 cm^{-1} assigned to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition in distorted octahedral structure around the Cu(II)ions⁽¹⁵⁾.Fig (2).

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

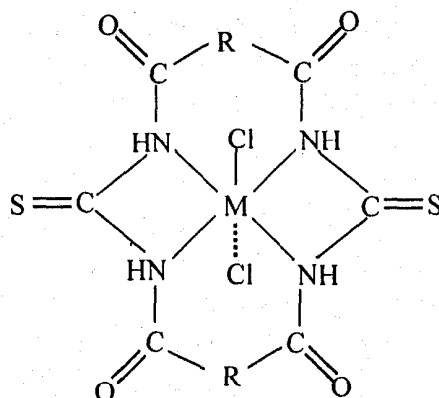


Fig 2: Suggested structure of the complexes
(where M: Mn(II),Fe(II),Co(II),Ni(II) and Cu(II) and R:-CH₂;CH₂CH₃

and $\begin{matrix} \text{OH} & \text{OH} \\ | & | \\ -\text{CH} & - & \text{CH}- \end{matrix}$ for L₁,L₂ and L₃ ligand respectively)

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

No.	Compound	Colour	MP (°C)	Yield (%)	Molar conductans ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	Elemental analysis data found (calculated)(%)	
						N	Metal
	L ₁	White	171-173	63	-----	19.21(19.44)	-----
1	[Mn(L ₁)Cl ₂]	Yellow	193-194	55	8	13.23(13.56)	13.19(13.29)
2	[Fe(L ₁)Cl ₂]	Gray	202-204	70	5	13.40(13.53)	13.22(13.48)
3	[Co(L ₁)Cl ₂]	Blue	193-194	71	11	13.25(13.43)	14.03(14.12)
4	[Ni(L ₁)Cl ₂]	Palegreen	182-183	68	4	13.38(13.43)	13.95(14.12)
5	[Cu(L ₁)Cl ₂]	Blue	190-191	48	5	13.10(13.28)	14.98(15.06)
	L ₂	White	132-135	75	-----	17.53(17.72)	-----
6	[Mn(L ₂)Cl ₂]	Green	284-285	66	12	12.68(12.70)	12.33(12.45)
7	[Fe(L ₂)Cl ₂]	Brown	240-242	80	11	14.69(14.78)	14.70(14.73)
8	[Co(L ₂)Cl ₂]	Green	166-168	69	9	12.52(12.58)	13.18(13.23)
9	[Ni(L ₂)Cl ₂]	Green	176-179	71	16	12.49(12.59)	13.05(13.19)
10	[Cu(L ₂)Cl ₂]	Yellow	230-232	75	14	12.34(12.45)	14.01(14.12)
	L ₃	Redish white	208-209	54	-----	14.59(14.73)	-----
11	[Mn(L ₃)Cl ₂]	Gray	227-229	74	9	11.02(11.09)	10.81(10.87)
12	[Fe(L ₃)Cl ₂]	Dark green	275-277	73	10	11.02(11.07)	10.89(11.03)
13	[Co(L ₃)Cl ₂]	Pink	265-267	78	13	10.92(11.00)	11.38(11.57)
14	[Ni(L ₃)Cl ₂]	Dark green	236-239	71	14	10.88(11.00)	11.45(11.53)
15	[Cu(L ₃)Cl ₂]	Brown	220-223	64	16	10.56(10.90)	12.10(12.36)

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

No.	Compound	M_{eff} BM (25°C)	λ_{max} (cm ⁻¹)
1	[Mn(L ₁)Cl ₂]	5.95	17697,23143,26767,37037
2	[Fe(L ₁)Cl ₂]	4.61	11806,26783
3	[Co(L ₁)Cl ₂]	4.97	10355,14243,19083,37666
4	[Ni(L ₁)Cl ₂]	3.01	10762,15384,26042,36133
5	[Cu(L ₁)Cl ₂]	1.84	11083,17822,28937
6	[Mn(L ₂)Cl ₂]	5.87	23788,26868,37238
7	[Fe(L ₂)Cl ₂]	4.66	10190,27112,35572
8	[Co(L ₂)Cl ₂]	4.67	10445,13978,19141,35348
9	[Ni(L ₂)Cl ₂]	3.3	10207,15748,24752,35348
10	[Cu(L ₂)Cl ₂]	1.94	10986,18522,27400
11	[Mn(L ₃)Cl ₂]	5.96	17990,22519,36128
12	[Fe(L ₃)Cl ₂]	4.71	11866,26540,37414
13	[Co(L ₃)Cl ₂]	4.98	10994,15276,18784,37345
14	[Ni(L ₃)Cl ₂]	2.93	10207,15748,24752,37092
15	[Cu(L ₃)Cl ₂]	1.96	11122,18418,27981

Table 3: Selected IR bands and their assignment in cm^{-1}

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_1	1615 _s	1589 _s	1350 _s	725	750 _w	1468 _s	3367 _s
1	$[\text{Mn}(\text{L}_1)\text{Cl}_2]$	1614 _s	1481 _s	-----	715 _s	750 _w	1396	3281
2	$[\text{Fe}(\text{L}_1)\text{Cl}_2]$	1635 _s	1557 _s	1200 _w	710 _w	805 _w	1418	3295
3	$[\text{Co}(\text{L}_1)\text{Cl}_2]$	1610 _s	1524 _s	1275 _s	710 _w	780 _w	1424 _s	3250 _s
4	$[\text{Ni}(\text{L}_1)\text{Cl}_2]$	1614 _s	1510 _s	1250 _w	715 _w	780 _w	1481 _s	3281 _s
5	$[\text{Cu}(\text{L}_1)\text{Cl}_2]$	1620 _s	1520 _s	1300 _w	698 _s	710 _s	1474 _s	3283 _s
	L_2	1635 _s	1575 _s	1348 _s	720 _s	740 _s	1450 _s	3355 _s
6	$[\text{Mn}(\text{L}_2)\text{Cl}_2]$	1625 _s	1505 _s	1225 _s	718 _s	760 _s	1395 _s	3280 _s
7	$[\text{Fe}(\text{L}_2)\text{Cl}_2]$	1652 _s	1490 _s	1274 _s	718 _s	750 _s	1405 _s	3157 _s
8	$[\text{Co}(\text{L}_2)\text{Cl}_2]$	1626 _s	1541 _s	1394 _s	709 _s	-----	1394 _s	3298 _s
9	$[\text{Ni}(\text{L}_2)\text{Cl}_2]$	1614 _s	1481 _s	1396 _s	715 _s	710	1405	3281
10	$[\text{Cu}(\text{L}_2)\text{Cl}_2]$	1622 _s	1541 _s	1307 _s	715 _w	694 _s	1397 _s	3277
	L_3	1733 _s	1550 _s	1305 _s	789 _s	680	1420	3328
11	$[\text{Mn}(\text{L}_3)\text{Cl}_2]$	1720	1497	1250	748	720	1405	3178
12	$[\text{Fe}(\text{L}_3)\text{Cl}_2]$	1557	1400	1113	739	653	1390 _w	3178
13	$[\text{Co}(\text{L}_3)\text{Cl}_2]$	1607 _s	1417 _s	1175	744	640	1400	3225
14	$[\text{Ni}(\text{L}_3)\text{Cl}_2]$	1600 _s	1417 _s	1200 _s	821 _s	723	1308	3189
15	$[\text{Cu}(\text{L}_3)\text{Cl}_2]$	1623 _s	1410 _s	1205 _w	730	714	1398	3177

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