Characterization studies on Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with new ligand`s derived from thiourea

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الخلاصة

تم تحضير عدد من معقدات جديدة   من نوع [M(L₁)Cl₂] و [M(L₁)Cl₂] حيث كانت M = Mn(II) , Fe(II) , Ni(II) , Co(II) , Zn(II) , Cu(II) و L₁=(2,11-ثنائي ثايو اوكسو – 1,3,10,12-رباعي ازا اوكتا دكا الحلقي – 6,15-ثنائي اين – 4,9,13,18- رباعي أون) وL₂=(2,9-ثنائي ثا يو اوكسو – 1,3,8,10-رباعي ازا –رباعي دكين الحلقي – 4,7,11,14-رباعي أون) وقد درست هذه المعقدات وشخصت من خلال   التحليل الدقيق للعناصر (M) وقياسات التوصيلية المولارية والقياسات المغناطيسية   والأشعة تحت الحمراء والطيف الالكتروني للتوصل الى الصيغة المتوقعة لهذه المعقدات والتي يمكن ان تتخذ لها شكل ثماني السطوح.

Abstract

complexes of the type [M(L₁)Cl₂] and [M(L₂)Cl₂] (M=Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); L₁=(2,11-dithioxo-1,3,10,12-tetra azacyclo octa deca-6,15-diene-4,9,13,18-tetraone), L₂=(2,9-dithioxo-1,3,8,10-tetra aza cyclo tetra decane-4,7,11,14-tetraone) have been prepared and characterized by means of micro analysis (M) molar conductance measurements, magnetic susceptibility measurements, IR and electronic spectral. The prepared complexes may have an octahedral configuration.

Introduction

When macrocyclic ligands are used for synthesis, the size and shape of the ligand cavity are the most important factors which influence the host-guest (metal- ligand) stability relation[1]. The marocyclic ligands which have [N₄] cavity with NH group have intensive area of study with a numerous transition metals. This partially due to their wide rang of

different molecular topologies and sets of donor atoms [2,3,4,5]. In addition to their interesting ligational properties they had competence biological and industrial application in the field of anti-infammantry action and bacterial growth inhibitors[6,7]. Chandra and Gupta reported the synthesis and spectroscopic characterization of macrocyclic complexes containing [N_4], they were also evaluated against the growth of bacteria and pathogenic fungi in vitro [8,9,10].

In view of the above our interest turned toward the investigation and the interaction between some of the first transition metal ions and two donating ligands and studying a new class of tetradentate[N_4]ligand Fig.1.

Experimental

The ligand L_1 has been synthesized according to the following procedure[10].

2-Butene-1,4-dicarboxylic acid (14.4 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 refluxed at ~ 80°c for 9h 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. The same procedure was done in the preparation of L_2 use by succinic acid (118.1, 0.05 mol). Some of its physical properties are listed in table 1.
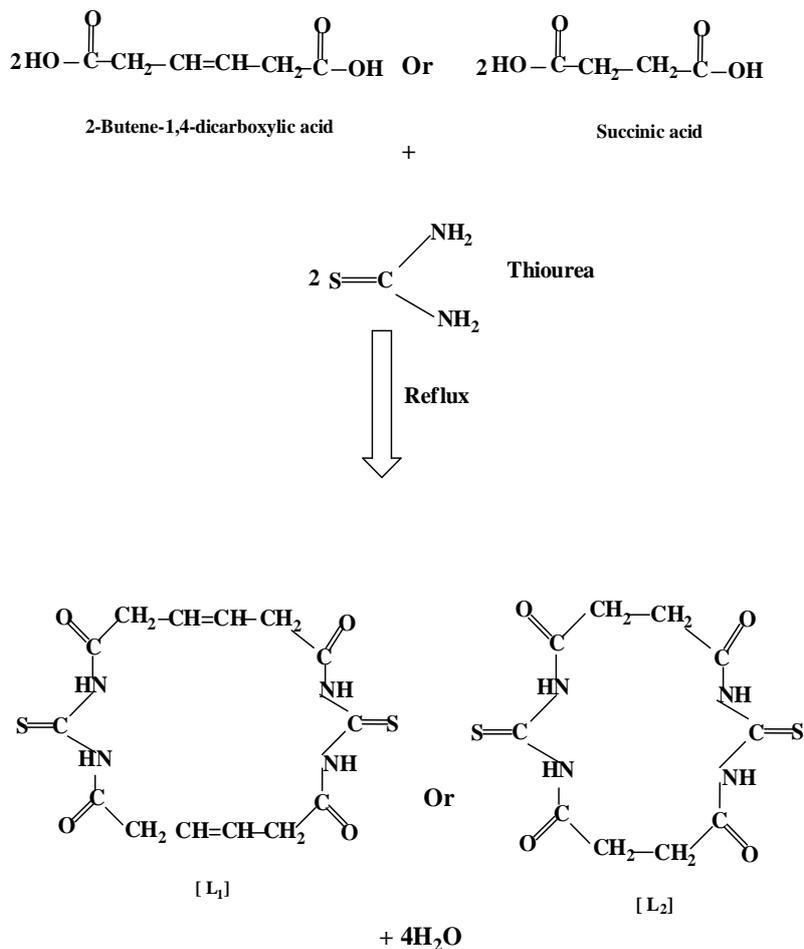

Fig. 1: Preparation and structure of the ligands L_1 and L_2.

A: Preparation of the metal complexes:

The hot ethanolic solution of ligands L_1 or L_2(0.001 mol/20 ml) (0.43, 0.32 g) respectively and ethanolic solution of the corresponding metal salt (0.001 mol/20 ml) were mixed together with stirring. The mixture was refluxed for 4h at ~80°c. On cooling gives a coloured precipitate (table 1) of the complexes. It was filtered off washed with cold EtOH and dried under vaccum.

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 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:

Four new bands appear in the spectrum of the free ligands (L_1 and L_2) assigned to amid I [υ(C=O), amide II [υ(C–N) + δ(N–H)], amide III [δ(N–H)] and amide IV [δ(C=O)] bands, respectively[11,12]. Bands at 730 cm^{-1} and ~1310 cm^{-1} are due to the thioamides I and II, respectively. A sharp band observed at 3205 cm^{-1} for L_1 and 3185 cm^{-1} for L_2 may be assigned to [υ(N–H)] of the secondary amino group Table 2[13].

IR spectrum of the two ligands does not exhibit any band corresponding for the free primary amine and hydroxyl group[11].

Complexes:

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

On complexes 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 419-477 cm^{-1} which attributed to [υ(M–N)].

Manganese (II)complexes:

The Manganese II complexes with L_1 and with L_2 have a magnetic moment values 5.93, 5.98 BM at room temperature respectively, these

values in accord with those having octahedral structure with five unpaired electrons[11, 12]. The electronic spectra exhibit bands at 3174 and 37735 and 31650, 36672 cm^{-1} are due to charge transfer[13, 14].

Iron(II) complexes:

The electronic spectra of iron at room temperature showed a band at 12250 and 10350 cm^{-1} which attributed to the ($^5T_2g \longrightarrow {}^5Eg$) transition and could be assigned to a distorted octahedral structure. The conductivity values of those two complexes were in accord with their tentative structure (table 1)[15, 16].

The magnetic moment values at room temperature are 4.76 and 4.90 BM for the Fe(II) complexes were well in accord with those having octahedral structure[15].

Cobalt(II) complexes:

The magnetic moment measurements of the two Co(II), these complexes are 4.98 and 4.80 BM corresponding to three unpaired electrons of octahedral structure higher value due to orbital contribution. Table 2.

The electronic spectra cobalt (II) complexes showed an absorption in the region 14792 and 14836 ,16500 and 16650, 19305 and 19480 and 32154, 31561 cm^{-1}. These bands may be assigned to the transitions: $^4T_1g(F) \longrightarrow {}^4T_2g(F)(\upsilon_1)$, $^4T_1g \longrightarrow {}^4A_2g(\upsilon_2)$ and $^4T_1g(F) \longrightarrow {}^4T_1g(p)(\upsilon_3)$ respectively[15]. It the assignments for the fourth band and may be due to charge transfer. The position of electronic spectral bands indicates that these complexes have octahedral geometry[11, 12, 14] .

Nickel (II) complexes:

The Ni(II) complexes shows a magnetic moments 2.97 and 2.96 BM at room temperature, these values are showed an octahedral environment around Ni(II) ions in the complexes [17] .

The electronic spectrum of the complexes shows three bands at (1) 13386 and 12658 (2)14619 and 15267, (3)24509 and 24807 cm^{-1} corresponding 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 in an octahedral geometry Fig (2).

Copper (II) complexes:

The magnetic moment of the Cu(II) complexes at room temperature lie in the 1.88 and 1.81 BM. These values are corresponding to the presence of one unpaired electron.

Electronic spectra of copper (II) complexes display bands assigned to the $^2E_2g \longrightarrow {}^2T_2g$ transition in distorted octahedral structure around the Cu(II)ions[9,18].Fig (2).

As the spectrum of Zn(II) complexes is not well resolved it is not interpreted but its µeff 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).
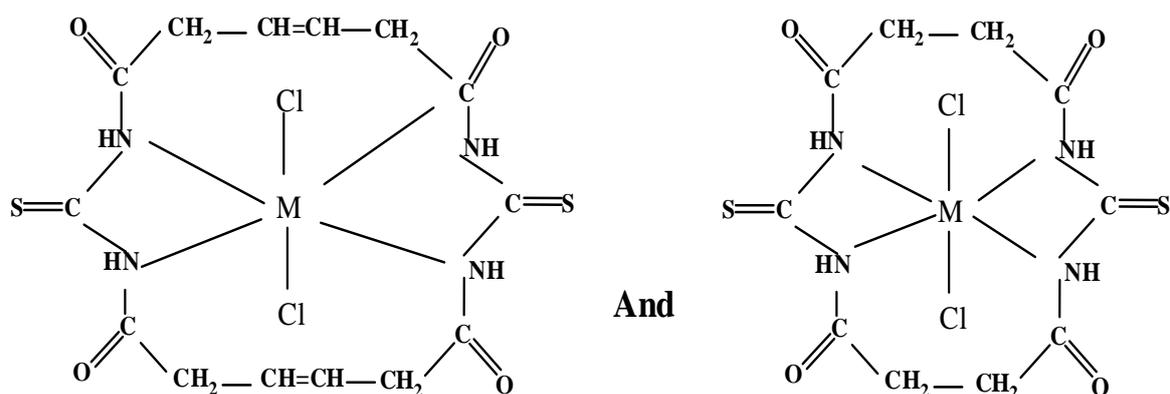

Fig. 2: Suggested structure of the complexes of [ML₁Cl₂] and [ML₂Cl₂] were M: Mn(II),Fe(II),Co(II),Ni(II), Cu(II) and Zn(II).

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

No.	Compound	Colour	M.P (ºC)	Yield (%)	Molar conductaus ($\Omega^{-1} cm^2 mol^{-1}$)	Metal analysis data found (calculated)(%)
	L_1	**White**	206-207	85	-----	-----
1	$[Mn(L_1)Cl_2]$	Brown	245-247	65	27	11.03(11.12)
2	$[Fe(L_1)Cl_2]$	Yellow-Brown	262-264	72	47	11.68(11.28)
3	$[Co(L_1)Cl_2]$	Green-blue	307-310	70	41	11.71(11.83)
4	$[Ni(L_1)Cl_2]$	Yellow	223-225	68	44	11.44(11.79)
5	$[Cu(L_1)Cl_2]$	Brown	290-292	63	42	12.28(12.64)
6	$[Zn(L_1)Cl_2]$	White	275-277	78	38	12.79(12.96)
	L_2	White	215-217	81	-----	-----
7	$[Mn(L_2)Cl_2]$	Green	323-325	67	47	12.14(12.42)
8	$[Fe(L_2)Cl_2]$	Orange	293-295	75	44	12.48(12.60)
9	$[Co(L_2)Cl_2]$	Gray	370-372	68	25	13.01(13.21)
10	$[Ni(L_2)Cl_2]$	Green	320-323	53	43	13.06(13.17)
11	$[Cu(L_2)Cl_2]$	Yellow	233-235	69	30	13.98(14.10)
12	$[Zn(L_2)Cl_2]$	White	288-290	84	38	14.35(14.45)

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$_2$]	5.93	14920,16660,22720,31740,37735
2	[Fe(L$_1$)Cl$_2$]	4.76	12250,24950
3	[Co(L$_1$)Cl$_2$]	4.98	14792,16500,19305,32154
4	[Ni(L$_1$)Cl$_2$]	2.97	13386,14619,24509,37593
5	[Cu(L$_1$)Cl$_2$]	1.88	10983,16824,38790
6	[Zn(L$_1$)Cl$_2$]	-----	-----------
7	[Mn(L$_2$)Cl$_2$]	5.98	14840,17140,22156,31650,36672
8	[Fe(L$_2$)Cl$_2$]	4.90	10350,25840
9	[Co(L$_2$)Cl$_2$]	4.80	14836,16650,19480,31561
10	[Ni(L$_2$)Cl$_2$]	2.96	12658,15267,24807,37676
11	[Cu(L$_2$)Cl$_2$]	1.81	10776,16358,37980
12	[Zn(L$_2$)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 − N)
	L$_1$	1614	1715	1426	730	8.25	1315	3205	-----
1	[Mn(L$_1$)Cl$_2$]		1603	1418				3145	477
2	[Fe(L$_1$)Cl$_2$]		1608	1404				3134	467
3	[Co(L$_1$)Cl$_2$]		1609	1417				3028	475
4	[Ni(L$_1$)Cl$_2$]		1604	1405				3162	472
5	[Cu(L$_1$)Cl$_2$]		1635	1418				-----	419
6	[Zn(L$_1$)Cl$_2$]		1653	1395				3125	465
	L$_2$	1610	1717	1416	730	803	1309	3185	----
7	[Mn(L$_2$)Cl$_2$]		1697	1400				3110	450
8	[Fe(L$_2$)Cl$_2$]		1698	1416				3100	460
9	[Co(L$_2$)Cl$_2$]		1698	----				3128	418
10	[Ni(L$_2$)Cl$_2$]		1622	1362				3100	425
11	[Cu(L$_2$)Cl$_2$]		1623	1403				3178	423
12	[Zn(L$_2$)Cl$_2$]		1621	1412				3085	410

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