Transition metal complexes of a tetradentat macrocyclic ligand 1,3,10,12-tetraazo-4,9,13,18-tetraoxo-2,11- dithiacyclo octadecane and bipyridine

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(Received 21 / 12 / 2009 , Accepted 9 / 9 / 2009)

Abstract

The research involve the preparation of some transition metal complexes of Mn (II),Fe(II),Co(II), Ni(II),Cu(II) and Zn(II) with tetradentate ligand 1,3,10,12-tetraazo-4,9,13,18-tetraoxo-2,11-dithiacyclo octadecane (L) and some adducts with some doner ligand such as bipyridine (bip) as a bidentate ligand .

These complexes and adducts were characterized by means of micro analysis (M),molar conductance measurements, magnetic measurements Infrared and electronic spectral techniques.

Introduction:

The coordination chemistry of macrocyclic ligands (with[N_4]) were an intensive area of study and numerous transition metal complexes of these groups of ligands have been investigated[1-3]. Nature prefers macrocyclic derivatives for biological fields such as photosynthesis and transport of oxygen in mammalian and other respiratory systems[4,5].Chandra and Gupta[6] reported the synthesis and spectroscopic characterization of Mn(II),Co(II),Ni(II) and Cu(II) complexes with a novel macrocyclic tatradentate nitrogen doner [N_4] ligand.They showed that the ligand and its complexes were also evaluated against the growth of bacteria and pathogenic fungi in vitro.

As a continuation of our interest to investigate interaction between some first transition series metal ions and several donating ligands[7,8,9] we reporte here a preparation of a tetradentate [N_4] ligand and some of its transition metal complexes.

Experimental

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

Treatment of bi(2-methylbenzoic acid)(2.12 g; 2 mol) and thiourea (7.6g; 2 mol) and a solution of sodium hydroxide.(2g) in (7 ml) of water. The mixture was stirred for 1/2h and refluxed at 110-112 ºC for 4h , then cooling to 60 ºC and acidifying it by adding conc. Hydrochloric acid drop by drop until the solution becomes acidic as indicated by comgo red paper turning blue. Cool the mixture in an ice bath until precipitate appears and complete. Filter the product by vacuum and recrystallize from water, the yield 85%,Fig (1).

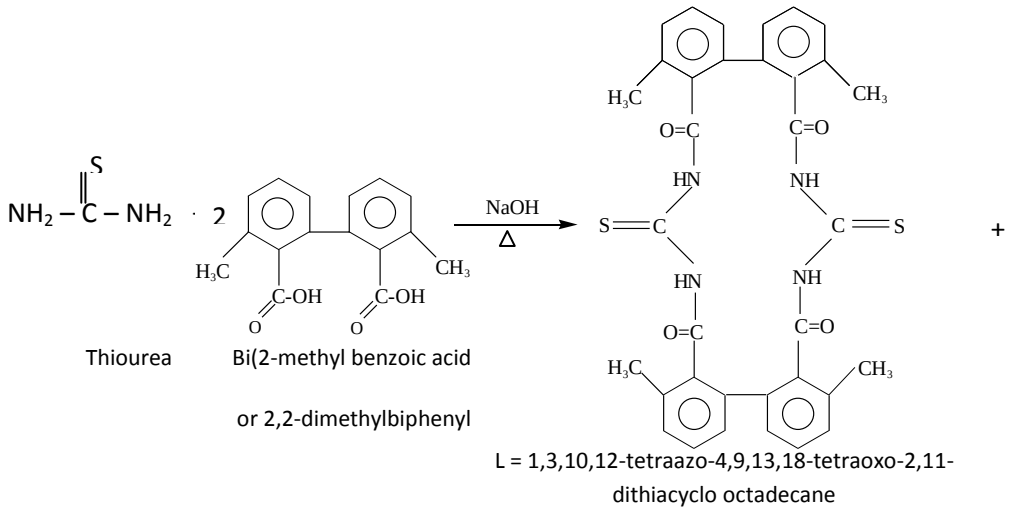

Fig 1: Preparation and structure of the ligand (L).

A: Preparation of the metal complexes:

A-1-[M(L)Cl_2]:

A hot ethanolic (20 ml) solution of the ligand (L) (0.5 g,0.001 mol) was added hot ethanolic (20 ml) solution of the corresponding, metal salts (table 1) (0.001 mol) with stirring.The mixture was refluxed for 5hr. Cooling gave complexes with different colour . They were filtered off washed with cold EtOH and dried in vacuum.

A-2-[M(L)(bip)]Cl_2

A hot ethanolic (20 ml) solution of the complexes [MCl_2](0.001 mol) was added to a hot ethanolic (20 ml) solution of bipyridyl ligand (0.16 g,0.001 mol) with stirring. A precipitate was formed immediately. The mixture was stirred for 2hr to ensure completation of the reaction. The solid, thus formed was filtered off washed with cold ethanol and dried under vacuum.

B: Physical measurements:

Analysis of ligand and complexes were carried out using standard gravimatric method. Infrared spectra were recorded on a FTIR brucker Tsncor 27 Co. Spectraphotometer in the (250-4000 cm^{-1}) range using CsI discs. Electronic spectra were obtained using Shimadzu UV/Vis, recording UV160 spectrophotometer at room temperature. The measurement were recorded using a concentration of 10^{-3} M solution of the complexes in DMF. Magnetic measurements were carried out at 25ºC on the solid complexes using Faraday method using Bruker B6. Instrument. Conductivities

were measured using a conductivity meter mode PCM3-JenWay. 10^{-3}M solution in DMF at 25ºC.

Results and discussion:

IR spectrum of the new ligand (m.p.184-185 ºC) (L) did not exhibit any band corresponding for the primary diamine and hydroxyl group. Four new bands appear in the spectrum of the free ligands (L) assignable 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[11,12]. Bands at 750 cm^{-1} and 1465 cm^{-1} may be due to the thioamides I and II respectively.A band observed at 3360 cm^{-1} may be assigned to [υ(N–H)] Table 3, M.Sharkir etal.[13].

The data in Table 3 ,show's that a downfield shift in the υ(N–H) absorption band by 35-110 cm^{-1} in the complexes as compared within free ligand. Further supported by the appearance of a medium intensity band in the rang of 433-499 cm^{-1} attributed to [υ(M – N)].

On the basis of M analysis, the complexes were assigned to posses the compositions show in Table 1 molar conductance measurements of the complexes in DMF shown to the nonelectrolyte nature in free bipyridyl complexes and gave a results consistent with a 1:2 electrolyte in the bipyridyl complexes.Thus these complexes may be formulated as $[M(L)Cl_2]$ and $[M(L)(bipy)]Cl_2$ (M = Mn(II),Fe(II), Co(II), Ni(II),Cu(II) and Zn(II)).

Manganese (II) complexes:

The magnetic moments of the two manganese complexes were 5.96 and 5.95 B.M corresponding to five unpaired electrons. Electronic spectra of these complexes exhibit, three absorption bands (18380, 21249 and 26042) , (18882, 22125 and 28246)cm^{-1} respectively Table 2. These band 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 band at 38759 and 36783 cm^{-1} may be due to charge transfer[11,12].

The magnetic moments values and the position of electronic spectral bands indicates that these complexes have octahedral geometry [11-13] Fig (2).

Fe(II) complexes:

The magnetic moments values 4.61,4.93 B.M of the Fe (II) complexes were well in accord with those having distorted octahedral structure[14,15]. Electronic spectra showed a band at 11200 cm^{-1} for the two complexes respectively, which 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[15,16].

Cobalt(II) complexes:

Cobalt complexes show magnetic moments at room temperature 4.61 and 4.93 B.M corresponding to three unpaired electrons Table (2). The electronic spectra of the two cobalt (II) complexes display absorption in the region 11210 and 10876,13540 and 1341,18780 and 19660,35510 and 36400 cm^{-1} respectively[16].

These bands may be assigned to the transitions $^3A_1g\ (F) \longrightarrow {}^4T_2g(F)(\upsilon_1)$, $^4T_1g \longrightarrow {}^4A_2g(\upsilon_2)$ and $^4T_1g\ (F) \longrightarrow {}^4T_1g\ (P)(\upsilon_3)$ respectively. It is difficult to give the assignments for the fourth band and it may be due to charge transfer. The position of these bands in dicates that the complexes have octahedral geometry Fig (2).

Nickel (II) complexes:

The Nickel complexes shows a magnetic moments 2.99 and 3.12 B.M 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.

The electronic spectrum of the two complexes shows three bands at 11222 and 10124,15625 and 14814,23278 and 23300 cm^{-1} correspond to the three spin- allowed transtion $^3A_2g\ (F) \longrightarrow {}^3T_2g(F)(\upsilon_1)$, $^3A_2g(F) \longrightarrow {}^3T_2g(F)(\upsilon_2)$ and $^3A_2g(F) \longrightarrow {}^3T_1g(P)(\ \upsilon_3)$ respectively. These bands indicates that the complexes have octahedral geometry[17] Fig (2).

Copper (II) complexes:

The magnetic moment of the two copper complexes at room temperature have the values 1.99 and 1.83 B.M corresponding to one unpaired electron.

Electronic spectra of the copper (II) complexes display bands at 12330 and 11870,19415 and 18520 cm^{-1}assigned to the $^2Eg \longrightarrow {}^2T_2g$ transition in distorted octahedral structure around the Cu(II) ions[18] 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 diamagnetic as expected .

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

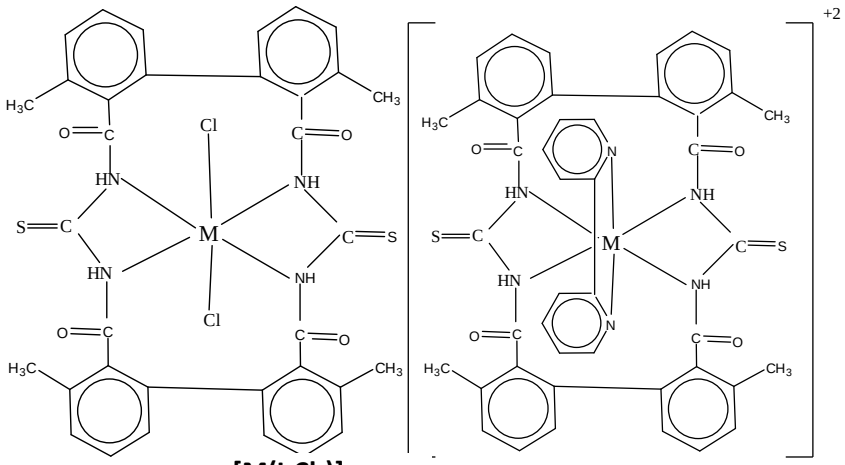

Fig. 2: Suggested structure of the complexes where M: Mn(II), Fe(II), Co(II), Ni(II),Cu(II) and Zn(II) L = 1,3,10,12-tetraazo-4,9,13,18-tetraxo-2,11-dithiacyclo octadecane bip= 2,2′-bipyridyl

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

No.	Compound	Colour	M.P (ºC)	Yield (%)	Molar conductaus (Ω^{-1} cm^2 mol^{-1})	Elemental analysis data found (calculated)(%)	
						N	Metal
L		White	184-185	85	---	10.91 (11.08)	---
1	$[Mn(L)Cl_2]$	Dark green	257-260	67	24.0	7.88(8.02)	7.7(7.79)
2	$[Mn(L)(bip)]Cl_2$	Brown	280-283	75	163.0	10.10(10.14)	6.6(6.7)
3	$[Fe(L)Cl_2]$	Brown	252-255	72	13.0	7.87(7.93)	7.8(7.82)
4	$[Fe(L)(bip)]Cl_2$	Red	262-263	68	167.0	10.09(10.12)	6.7(6.77)
5	$[Co(L)Cl_2]$	Dark green	304-305	85	14.0	7.85(7.89)	8.1(8.3)
6	$[Co(L)(bip)]Cl_2$	Green	278-280	80	154.0	10.05(10.08)	6.9(7.2)
7	$[Ni(L)Cl_2]$	Dark gray	273-275	84	20.0	7.84(7.87)	8.2(8.24)
8	$[Ni(L)(bip)]Cl_2$	Gray	290-293	69	168.0	10.07(10.10)	7.0(7.2)
9	$[Cu(L)Cl_2]$	Black	262-266	54	28.0	7.79(7.81)	8.7(8.8)
10	$[Cu(L)(bip)]Cl_2$	Dark green	255-256	43	153.0	10.01(10.02)	7.5(7.55)
11	$[Zn(L)Cl_2]$	White	291-293	73	16.0	7.7(7.73)	9.02(9.05)
12	$[Zn(L)(bip)]Cl_2$	White	309-310	70	173.0	9.98(9.11)	7.72(7.74)

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

No.	Compound	μ_{eff} B.M (25ºC)	λmax (cm^{-1})
L		----	29885,30897,38766
1	$[Mn(L)Cl_2]$	5.96	18380,21249,26042,38759
2	$[Mn(L)(bip)]Cl_2$	5.95	18882,22125,28246,36783
3	$[Fe(L)Cl_2]$	4.61	11200,26883,36762
4	$[Fe(L)(bip)]Cl_2$	4.93	10300,26440,36128
5	$[Co(L)Cl_2]$	4.83	11210,13540,18780,35510
6	$[Co(L)(bip)]Cl_2$	4.76	10876,13421,19660,36400
7	$[Ni(L)Cl_2]$	2.99	11222,15625,23278,30897
8	$[Ni(L)(bip)]Cl_2$	3.12	10124,14814,23300,30890

9	$[Cu(L)Cl_2]$	1.99	12330,19415,29900
10	$[Cu(L)(bip)]Cl_2$	1.83	11870,18520,30414
11	$[Zn(L)Cl_2]$	----	----------
12	$[Zn(L)(bip)]Cl_2$	----	----------

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

No.	C=O Amide I	***υ(C-N + δ N-H)*** ***amide II***	δ (N – H) III	Thioamid I and II		υ(N-H)	υ(M-N)
L	1610_S	1580_S	1355_S	750_w	1465_S	3360_b	---
1	1615_S	1557_S	---	759_w	1418	3290_b	477_S
2	1625_S	1524	1270_S	745	1440_S	3220_b	474_S
3	1614_S	1532_S	1288_S	752	1428	3275_b	499_S
4	1630_S	1563_S	1295	763	1442_S	3300_b	482_S
5	1652_S	1575	1275	718	1425_S	3295_b	475_S
6	1622_S	1530	1276	720	1425	3287_b	473_S
7	1620_S	1551	1249	739_w	1438	3235_b	460_S
8	1617_S	1580_S	1277	735	1445_S	3241_b	490_S
9	1647_S	1560	1238	710	1460	3270_b	433_S
10	1710_S	1526_S	1250_S	750_w	1405	3328_b	472_S
11	1660_S	1555	1232	730	1431	3285_b	486_S
12	1649_S	1600	1290	751_w	1435_S	3260_b	477_S

s = strong ,b = broad, w = weak.

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الملخص

حضرت معقدات العناصر الانتقالية لكل من Mn(II) و Fe(II) و Co(II) و Ni(II) و Cu(II) فضلاً عن Zn(II) مع ليكاند رباعي السن من نوع (١، ٣، ١٠ ،١٢ تترا ازو-٤،٩ ،١٣ ،١٨-تترا اوكسو ٢، ١١-ثنائي ثايا اوكتادكين الحلقي) وثنائي البريدين . شخصت المعقدات المحضرة بواسطة تقنيات التحليل الدقيق للعناصر (M) وقياسات التوصيلية المولارية والقياسات المغناطيسية والأشعة تحت الحمراء والطيف الالكتروني.