

## Synthesis and Characterization of some Complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with Bis-(2, 3-Dimethoxybenzylidene) thiosemicarbazone

Sahbaa Ali. Al-Sabaawi

Department of Chemistry, Lecture College of Science, University of Mosul

(NJC)

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### Abstract

A number of new complexes of the general formulae  $[ML_2Cl_2]$  and  $[ML_2(bip)]Cl_2$  {where L= bis-(2,3-Dimethoxybenzylidene)thiosemicarbazone ; M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II), bip = bipyridyl} were prepared and characterized by molar conductance, magnetic properties, infrared, electronic spectra, metal contents, and CHN analysis. The electronic spectra study and magnetic moments measurements indicated that the Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes have an octahedral geometry.

### الخلاصة

تم تحضير عدد من المعقدات الجديدة ذوات الصيغة العامة  $[ML_2Cl_2]$  و  $[ML_2(bip)]Cl_2$  حيث  $L = \text{ثنائي-}(2,3\text{-ثنائي ميثوكسي بنزليدين)}$  ،  $M = \text{ثايوسيميكارابازون}$  ،  $M = \text{Mn(II), Fe(II), Co(II), Ni(II), Cu(II) و Zn(II)}$  ،  $bip = \text{ثنائي البيريدائل}$  . تم تشخيص المعقدات المحضرة بواسطة قياسات التوصيلية الكهربائية والمغناطيسية وأطياف الأشعة تحت الحمراء والأطياف الالكترونية والتحليل الدقيق للعناصر CHN وتعيين المحتوى الفلزّي. وقد بيّنت دراسة الأطياف الالكترونية وقياسات العزوم المغناطيسية بان معقدات  $(\text{Mn(II), Fe(II), Co(II), Ni(II), Cu(II) و Zn(II)})$  تمتلك بنية تركيبية ثماني السطوح.

### Introduction

Thiosemicarbazones exhibit various biological activities and have attracted considerable pharmaceutical interests. They have been evaluated over the last 50 years as antibacterial, antifungal (1,2), antiviral,

antitubercular, antitumor and anticancer therapeutics (3-6). A variety of functional groups have been attached to the thiosemicarbazones entity in order to modify the physical, chemical and biological properties of the resulting metal complexes (7).

Thiosemicarbazide and thiosemicarbazones (TSC) behave as chelating ligands toward transition and non-transition metal ions, bonding through S and azomethine N atoms<sup>(8,9)</sup>. Two thiosemicarbazones, (E)-2-(2,4-dimethoxybenzylidene) thiosemicarbazone and (E)-2-(2,5-dimethoxybenzylidene) thiosemicarbazone derived from 2, 4-dimethoxybenzaldehyde and 2, 5-dimethoxybenzaldehyde, respectively, with thiosemicarbazide have been synthesized, compound (1) crystallized in the monoclinic system whereas compound (2) crystallized in the orthorhombic system<sup>(10)</sup>.

New Schiff bases ligands L have been synthesized from benzofuran-2-carbohydrazide and benzaldehyde or 3, 4-dimethoxybenzaldehyde complexes of the type  $[MLCl_2]$ , where M=Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II). Studies have shown that the imines ligands behave as bidentate coordinated through the azomethine nitrogen and oxygen of the carbonyl<sup>(11)</sup>.

The present paper describes the synthesis and characterization of bis-(2,3-Dimethoxybenzylidene) thiosemicarbazone, and its complexes with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II).

## Experimental

### Physical measurement :

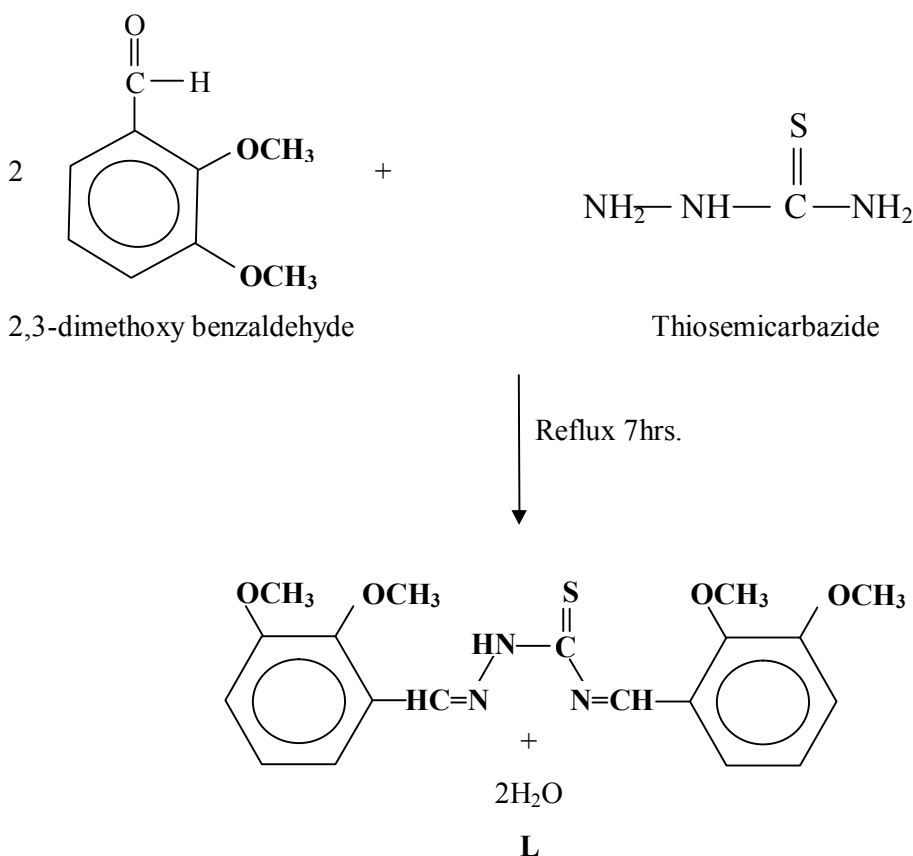
Electronic spectra were recorded on Shimadzu UV/Vis, Spectrophotometer UV-160 at room temperature in DMF solvent, The measurements were recorded using a concentration of  $10^{-3}M$  of the ligand and their complexes. Infrared spectra ( $4000-200\text{ cm}^{-1}$ ) were recorded on a FTIR Bruker Tensor 27 Spectrophotometer using KBr or CsI discs. Metal contents analyses were made on Shimadzu AA 670 atomic absorption Spectrophotometer. CHN analysis of the ligand and complexes was carried out using standard method and costech instruments elements combustion system model 4010. The magnetic moments were carried out at  $25^\circ\text{C}$  on the solid states Faraday method using Bruker BM6 instrument. The molar conductance of  $10^{-3}M$  solution of metal complexes in (DMF) were measured at  $25^\circ\text{C}$  using Jenway 4070 conductivity meter. Melting point were determined on a Buchi 510 melting point apparatus and were uncorrected. Metal salts 2,3-dimethoxybenzaldehyde, thiosemicarbazide were supplied by (Fluka).

**a. Preparation of the ligands :**

The ligand Lhas been synthesized according to the same procedure<sup>(12)</sup>.

A mixture of 2,3-dimethoxy benzaldehyde(3.32g, 0.02mol) in(10ml) ethanol ,thiosemicarbazide ( 0.91 g, 0.01mol) in (10 ml) ethanol, was refluxed for 7hrs. in presence and

2ml conc. HCl, to give apale yellow solid the mixture cooled to room temperature filtered off , washed with cold ethanol and dried in vacuum.The product was recrystallized from propanol (Scheme (1)).



**Scheme (1): Preparation and structure of the ligand L**

**b. Preparation of the complexes :**

A hot ethanolic solution of the ligand L (0.77g,0.02mol) and ethanolic solution of the corresponding metal salt {MnCl<sub>2</sub>.4H<sub>2</sub>O (0.19 g, 0.01mol) or

FeCl<sub>2</sub> (0.12 g, 0.01 mol) or CoCl<sub>2</sub>.6H<sub>2</sub>O (0.27 g , 0.01 mol) or NiCl<sub>2</sub>.6H<sub>2</sub>O (0.23 g , 0.01 mol) or CuCl<sub>2</sub>.2H<sub>2</sub>O (0.13 g, 0.01 mol)and ZnCl<sub>2</sub> (0.13g , 0.01 mol)} in (20 ml) of

ethanol were mixed together with stirring. The mixture has been refluxed for 4 hours, on cooling, a colored precipitate has been formed which was filtered off, washed with cold EtOH and dried under vacuum.

### c. Preparation of [Mn L<sub>2</sub>(bip)] Cl<sub>2</sub>:

An excess of bipyridyl (0.06 g, 0.01 mol) dissolved in ethanol (10 ml) was added to (0.36 g, 0.01 mol) complex [MnL<sub>2</sub> Cl<sub>2</sub>]. The mixture was refluxed for about 3 hours. On cooling a colored precipitate has been formed which was filtered off, washed with cold EtOH and dried under vacuum. The other complexes (4), (6), (8), (10) or (12) were prepared applying the same procedure.

## Results and Discussion

The complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with the ligand L=[bis-(2,3-dimethoxybenzylidene)thiosemicarbazone] were air stable solids and colored Table (1). The molar conductivities of the complexes in DMF indicated the presence of two types of complexes, a nonelectrolytic nature (15-30 ohm<sup>-1</sup>.cm<sup>2</sup>.mol<sup>-1</sup>)<sup>(13)</sup> for the (1), (3), (5), (7), (9) and (11) complexes, this complexes do not contain bipyridyl and contain chloride ions inside the coordination ball therefore this complexes are non

electrolytic, As 1:2 electrolytes (134-166 ohm<sup>-1</sup>.cm<sup>2</sup>.mol<sup>-1</sup>)<sup>(14)</sup> for the (2), (4), (6), (8), (10) and (12) mixed ligand complexes, this complexes contain bipyridyl and contain chloride ions outside the coordination ball these ions which responsible molar conductivities Table (1).

The important infrared spectral of the ligand and their complexes are listed in Table (2). The IR spectrum of the ligand L showed a band at 3147 cm<sup>-1</sup> assigned to  $\nu_{(NH)}$ , this band has been shifted to a lower frequency on complex formation<sup>(15)</sup>, this band however was remained unaltered in the complexes prepared indicating that there is no coordination through NH group and metal ion. The  $\nu_{(C=N)}$  was found to be splitted two bands at 1599 cm<sup>-1</sup> and 1576 cm<sup>-1</sup> as it is expected for the presence two types of C=N in the complex. The two bands were shifted to lower frequencies in the IR spectra of the complexes Table (2) indicating the participation of azomethine nitrogen in coordination<sup>(16,17)</sup>. The spectrum of the ligand showed a band at 1169 cm<sup>-1</sup> due to  $\nu_{(C=S)}$  this band undergo little shift in the spectra of some complexes and appears within the (1163-1174) cm<sup>-1</sup> range which indicate that this band does not involved in coordination<sup>(18)</sup>.

The other new bands in the range (418-443) $\text{cm}^{-1}$  range in the spectra of the complexes were assigned to  $\nu_{(M-N)}$ <sup>(19)</sup> while the  $\nu_{(M-N)}$  for (bipyridyl) ligand are in good agreement with the reported values of Nakamoto<sup>(14)</sup> which appeared within the (480-510)  $\text{cm}^{-1}$  range. The spectrum of the ligand showed  $\nu_{(N-N)}$  at (926-953) $\text{cm}^{-1}$  respectively<sup>(20,21)</sup>.

The electronic spectral bands of the two ligands and their complexes, and magnetic moment values for the complexes were listed in Table (3). The electronic spectra of the ligand as  $10^{-3}$  M solution DMF and the results were presented in Table (3), the bands observed at 35714  $\text{cm}^{-1}$  and 33112  $\text{cm}^{-1}$  are due to ligand which may be assigned as  $n-\pi^*$  and  $\pi-\pi^*$  transition respectively.

The electronic spectra exhibited band in the visible region at 21276, 27932  $\text{cm}^{-1}$  respectively for the two manganese (II) complexes these bands may be assigned to the transition  ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$  and  ${}^6A_{1g} \rightarrow {}^4T_{1g}(P)$  respectively, the bands appear at 32016, 33575  $\text{cm}^{-1}$  due to charge transfer<sup>(22)</sup>. The magnetic moment values 5.81, 5.92 B.M for two complexes were in accordance with

those having octahedral structure having five unpaired electrons.

The electron spectra of the two Fe(II) complexes showed a band in the visible region at 10245, 13089  $\text{cm}^{-1}$  respectively attributed to the  ${}^5T_{2g} \rightarrow {}^5E_g$  transition and could be assigned to octahedral structure<sup>(22)</sup>. The values of the magnetic moment were 4.62, 4.88 B.M have been in well accordance with those having octahedral geometry. The magnetic moment of Co(II) complexes were 4.22, 4.57 B.M indicating an octahedral geometry<sup>(22,23)</sup>. The electronic spectra showed band in the positions (1) 10204, 10706  $\text{cm}^{-1}$ , (2) 13089, 14970  $\text{cm}^{-1}$ , (3) 15197, 18796  $\text{cm}^{-1}$  respectively for the two cobalt (II) complexes these bands may be assigned to the transition  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(\nu_2)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$  respectively. The bands appear at 31654, 35842  $\text{cm}^{-1}$  due to charge transfer<sup>(22,23)</sup>.

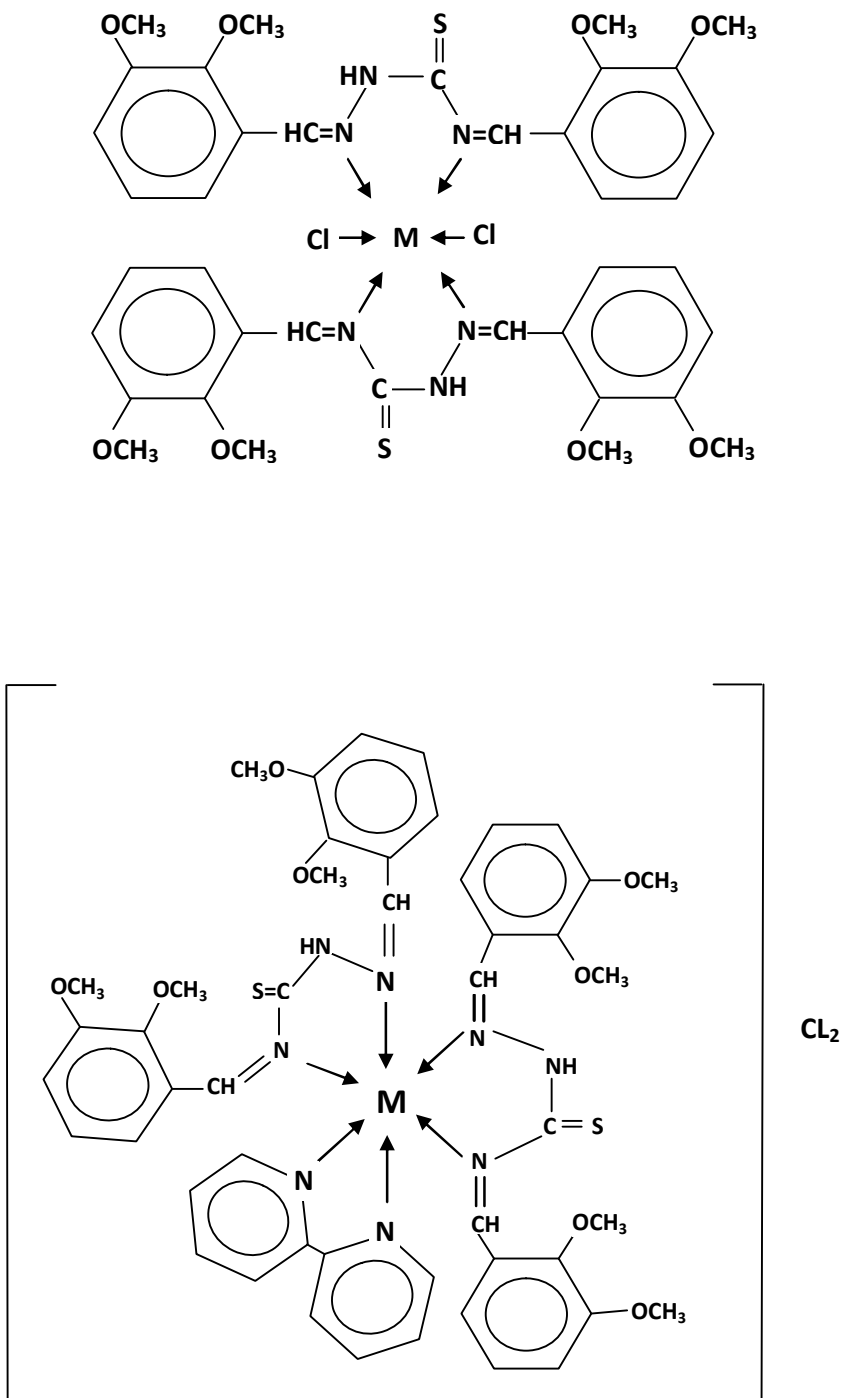
The two Ni(II) complexes exhibited magnetic moment values 2.87 and 2.92 B.M these values showed the presence of two unpaired electrons which lead to octahedral environment around Ni (II) ions<sup>(8)</sup>. The increases of magnetic moment values from 2.87 B.M are probably due to orbital contribution. The electronic

spectrum of the complexes showed three bands at (1) 10131-10204  $\text{cm}^{-1}$  (2) 13089-15364  $\text{cm}^{-1}$  and (3) 22624-26455  $\text{cm}^{-1}$  due to three spin allowed transitions  ${}^3A_2g(F) \rightarrow {}^3T_2g(F)(\nu_1)$ ,  ${}^3A_2g(F) \rightarrow {}^3T_1g(F)(\nu_2)$  and  ${}^3A_2g(F) \rightarrow {}^3T_1g(P)(\nu_3)$  respectively, indicating that the complexes had octahedral geometry<sup>(24,25)</sup>.

The magnetic moment of the Cu(II) complexes are 1.78 and 1.82 B.M which were due to the presence of one a broad unpaired electron. The

electronic spectra showed one a broadband at which assigned to the  ${}^2E_2g(F) \rightarrow {}^2T_2g$  transition in distorted octahedral structure around the Cu(II) ions<sup>(26,27)</sup>.

As the spectra of Zn(II) complexes were not well resolved, they were not interpreted but their  $\mu_{\text{eff}}$  values showed that they are diamagnetic as expected. On the basis of the above results the proposed structures for the metal (II) complexes were shown in Fig (1).



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

Fig. (1) Suggested structure of the complexes  $[ML_2 Cl_2]$  and  $[ML_2(bip)]Cl_2$

**Table (1) : Some analytical and physical properties of the complexes .**

No.	Compound	Colours	M.p °C	Yield %	Molar conductance Ohm <sup>-1</sup> .cm <sup>2</sup> .mol <sup>-1</sup>	Salts	Metal analysis found (calculated)%	Analysis found (calculated)%		
								C	H	N
	L	Pale yellow	194	58	----	----	----	58.91(59.10)	5.42(5.54)	10.85(10.96)
1.	[MnL <sub>2</sub> Cl <sub>2</sub> ]	Brown	288	86	15	MnCl <sub>2</sub> .4H <sub>2</sub> O	6.10 (6.22)	50.67(50.83)	4.66(4.84)	9.33(9.51)
2.	[MnL <sub>2</sub> (bip)]Cl <sub>2</sub>	Pale brown	262	64	166	MnCl <sub>2</sub> .4H <sub>2</sub> O	5.20 (5.33)	54.54(54.69)	4.73(4.89)	10.60(10.82)
3.	[FeL <sub>2</sub> Cl <sub>2</sub> ]	Brown	284	77	30	FeCl <sub>2</sub>	6.19 (6.26)	50.61(50.77)	4.66(4.91)	9.32(9.50)
4.	[FeL <sub>2</sub> (bip)] Cl <sub>2</sub>	Pale brown	253	51	157	FeCl <sub>2</sub>	5.28 (5.41)	54.50(54.73)	4.73(5.02)	10.59(10.84)
5.	[CoL <sub>2</sub> Cl <sub>2</sub> ]	Pale green	271	90	24	Co Cl <sub>2</sub> .6H <sub>2</sub> O	6.51 (6.69)	50.44(50.60)	4.64(4.86)	9.29(9.46)
6.	[CoL <sub>2</sub> (bip)]Cl <sub>2</sub>	Green blackish	277	56	161	Co Cl <sub>2</sub> .6H <sub>2</sub> O	5.56 (5.72)	54.34(54.52)	4.71(5.12)	10.56(10.78)
7.	[NiL <sub>2</sub> Cl <sub>2</sub> ]	yellow	269	82	21	NiCl <sub>2</sub> .6H <sub>2</sub> O	6.49 (6.56)	50.45(50.67)	4.64(4.91)	9.29(9.66)
8.	[NiL <sub>2</sub> (bip)] Cl <sub>2</sub>	Dark green	273	54	134	Ni Cl <sub>2</sub> .6H <sub>2</sub> O	5.54 (5.63)	54.35(54.76)	4.71(4.97)	10.56(11.03)
9.	[CuL <sub>2</sub> Cl <sub>2</sub> ]	Olive	291	85	19	Cu Cl <sub>2</sub> .2H <sub>2</sub> O	6.99(7.07)	50.19(50.63)	4.62(4.71)	9.24(9.62)
10.	[CuL <sub>2</sub> (bip)]Cl <sub>2</sub>	Pale green	300	63	152	Cu Cl <sub>2</sub> .2H <sub>2</sub> O	5.96(6.18)	54.10(54.64)	4.69(5.08)	10.52(10.74)
11.	[ZnL <sub>2</sub> Cl <sub>2</sub> ]	Pale yellow	256	70	23	Zn Cl <sub>2</sub>	7.18 (7.23)	50.08(50.36)	4.61(4.97)	9.22(9.36)
12.	[ZnL <sub>2</sub> (bip)] Cl <sub>2</sub>	White	289	61	147	Zn Cl <sub>2</sub>	6.13 (6.22)	54.01 (54.24)	4.68(4.81)	10.50(10.77)



**Table (2) : Selected I.R bands and their assignment in  $\text{cm}^{-1}$  .**

No.	Compound	$\nu$ (NH)	$\nu$ (C=N)	$\nu$ (C=S)	$\nu$ (N-N)	$\nu$ (M-N)	$\nu$ (M-N) for bip
	Ligand	3147	1599, 1576	1169	937	----	----
1.	[MnL <sub>2</sub> Cl <sub>2</sub> ]	3149	1577, 1545	1163	939	418	----
2.	[MnL <sub>2</sub> (bip)] Cl <sub>2</sub>	3153	1568, 1542	1169	937	425	500
3.	[FeL <sub>2</sub> Cl <sub>2</sub> ]	3151	1571, 1541	1174	953	418	----
4.	[FeL <sub>2</sub> (bip)] Cl <sub>2</sub>	3150	1564, 1547	1172	926	419	480
5.	[CoL <sub>2</sub> Cl <sub>2</sub> ]	3145	1579, 1553	1169	949	422	----
6.	[CoL <sub>2</sub> (bip)] Cl <sub>2</sub>	3147	1578, 1542	1167	939	436	507
7.	[NiL <sub>2</sub> Cl <sub>2</sub> ]	3155	1568, 1545	1169	937	420	----
8.	[ NiL <sub>2</sub> (bip)] Cl <sub>2</sub>	3154	1573, 1541	1168	928	443	501
9.	[CuL <sub>2</sub> Cl <sub>2</sub> ]	3145	1574, 1545	1171	942	420	----
10.	[CuL <sub>2</sub> (bip)] Cl <sub>2</sub>	3153	1578, 1542	1166	934	431	498
11.	[ZnL <sub>2</sub> Cl <sub>2</sub> ]	3149	1570, 1541	1168	932	424	----
12.	[ZnL <sub>2</sub> (bip)] Cl <sub>2</sub>	3152	1577, 1552	1172	945	419	510

**Table (3) : Magnatic moment and electronic spectral data of the complexes.**

No.	Compound	$\mu_{\text{eff}}$ B.M (25°C)	$\lambda$ max (cm <sup>-1</sup> )	Assignment	10Dq	$\beta^-$	$\beta^0$	$\beta$	15 $\beta^-$	C.F.S.E
				${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$						
6.	L [Co L <sub>2</sub> (bip)] Cl <sub>2</sub>	..... 4.57	10706, 11497, 18796, 35842, 36714	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ ${}^4T_{1g}(F) \rightarrow {}^4E_g$	10706	109.86	971	0.11	1648	19270.8
1.	[Mn L <sub>2</sub> Cl <sub>2</sub> ]	5.92	35842 21276, 32016	${}^6A_{1g}(F) \rightarrow {}^4T_{1g}(P)$ C.T	.....	.....	.....	.....	.....	.....
2.	[Mn L <sub>2</sub> (bip)] Cl <sub>2</sub>	5.81	10131, 10930, 13645, 30303	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ${}^6A_{1g} \rightarrow {}^4T_{3g}(P)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ C.T <sub>3</sub> ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	10131	610.06	1030	8.88	9151	1013.1
3.	[Fe L <sub>2</sub> Cl <sub>2</sub> ]	4.62	13089, 33333	${}^5T_{2g} \rightarrow {}^5E_g$ C.T	.....	.....	.....	.....	.....	.....
8.	[Ni L <sub>2</sub> (bip)] Cl <sub>2</sub>	2.92	10204, 15364, 22624, 4446	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3E_g(P)$ C.T	10204	491.73	1030	7.16	7376	12244.8
4.	[Fe L <sub>2</sub> (bip)] Cl <sub>2</sub>	4.88	10204, 15364, 22624, 4446	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3E_g(P)$ C.T	.....	.....	.....	.....	.....	.....
9.	[Cu L <sub>2</sub> Cl <sub>2</sub> ]	1.82	10204, 18860, 27624, 3197,	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^2E_g(F) \rightarrow {}^2T_{2g}$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ C.T	10204	155.06	971	0.15	2326	18367.2
5.	[Co L <sub>2</sub> Cl <sub>2</sub> ]	4.22	10204, 18860, 27624, 3197,	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^2E_g(F) \rightarrow {}^2T_{2g}$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ C.T	.....	.....	.....	.....	.....	.....
10.	[Cu L <sub>2</sub> (bip)] Cl <sub>2</sub>	1.78	10204, 30303	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ ${}^2E_g(F) \rightarrow {}^2T_{2g}$ C.T	.....	.....	.....	.....	.....	.....

				C.T						
11.	[Zn L <sub>2</sub> Cl <sub>2</sub> ]	Diamagnetic	30303, 32051	C.T	.....	.....	.....	.....	.....	.....
12.	[Zn L <sub>2</sub> (bip)] Cl <sub>2</sub>	Diamagnetic	31055, 33557	C.T	.....	.....	.....	.....	.....	.....

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