

# Spectral studies of transition metal complexes with 25, 26 dioxo1,6,12,17,23,24 hexaazacyclohexacosa 1,5,12,16 tetraene macrocyclic ligand (L)

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Received 14 June 2013; revised 14 July 2013; accepted 21 July 2013

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## ABSTRACT

**Mn(II), Co(II), Ni(II) and Cu(II) complexes with this ligand (L) i.e. 25, 26 dioxo1,6,12,17,23,24 hexaazacyclohexacosa1,5,12,16 tetraene have been prepared. All the complexes were characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, mass, i.r. electronic, and e.p.r. spectral studies. The molar conductance measurements in DMF indicate that the Mn(II), Co(II), and Cu(II) are non-electrolyte whereas the complexes of Ni(II) are electrolyte. Thus, these complexes may be formulated as  $[M(L)X_2]$  and  $[Ni(L)]X_2$  (where M = Mn(II), Co(II) and Cu(II) and X =  $Cl^-$  and  $NO_3^-$ ). All the complexes are of the high spin type expected Ni(II) complexes which are diamagnetic. On the basis of spectral studies, an octahedral geometry may be assigned of Mn(II) and Co(II). Square planar is for Ni(II) complexes, and tetragonal geometry for Cu(II) complexes.**

**Keywords:** Mass; IR; Magnetic Moment; Electronic EPR; X-Ray Diffraction Studies

## 1. INTRODUCTION

Schiff bases are widely studied because of increasing recognition in biological system [1] e.g. antimicrobial, antiviral, antifungal, antitumour and other biological activities particularly with first row of transition metal complexes [2-9]. Macrocyclic compounds are similar in structure and reactions to many naturally occurring compounds, Which are known to exhibit selective cation complexation [10,11]. The chemical properties of macrocyclic complexes can be turned to force metal ions

to adopt unusual coordination geometry. Transition metal macrocyclic complexes have received much attention as an active part of metalloenzymes [12] as biomimic model compounds [13] due to their resemblance with natural proteins like hemerythrin and enzymes. Synthesis of transition metal complexes of new aza macrocycles with different cavity sizes donor types, ring substituents etc. under different experimental conditions have resulted in a large number and variety of compounds [14,15]. Because of the numerous areas of chemistry where aza macrocyclic complexes have found a niche, the preparation of new macrocyclic ligands with ever more elaborate structures is also a vital area of research. In view of the above applications, the synthesis and characterization of transition metal complexes with such ligand is highly desirable. In this paper we report the synthesis and characterization of transition metal complexes with 25, 26 dioxo1,6,12,17,23,24 hexaaza cyclohexaneosa 1,5,12,16 tetraene macrocyclic ligand [L]. (Figure 1).

## 2. CHEMISTRY

All the chemicals used were of Anala R grade, and were purchased from Aldrich. Metal salts were purchased from E. Merck and were used as received. All solvents used were of standard/spectroscopic grade.

### 2.1. Synthesis of Complexes

All the complexes were prepared by template method. An ethanolic solution of diethylenetriamine [10 mL] and glutaricanhydride (10 mL) were mixed. To this solution the ethanolic solution of metal salt (0.001 mol) was added. The resulting solution was boiled under refluxed for six hours. The solution was then concentrated upto half of its volume under reduced pressure. On cooling

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the solution is precipitated out. It was filtered, washed with cold ethanol and dried over  $P_4O_{10}$  under vacuum.

## 2.2. Physical Measurements

The C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy-balance using  $CuSO_4 \cdot 5H_2O$  as a callibrant. Electron-impact mass spectra were recorded on JEOL, JMS, DX-303 mass spectrometer, IR spectra were recorded on a Perkin-Elmer 137 instrument in Csl pellets. EPR spectra of the complexes were recorded as polycrystalline sample and in the DMF solution, at liquid nitrogen temperature for Co(II) and at room temperature for Mn(II) and Cu(II) complexes on E4-EPR spectrometer using the DPPH as the g-marker.

## 3. RESULTS AND DISCUSSION

**Complexes:** On the basis of elemental analysis, the complexes were found to have the composition as shown in Table 1.

The molar conductance measurement of the complexes in DMF correspond to be nonelectrolytic nature for Mn(II), Co(II) and Cu(II) while 1:2 electrolytes for Ni(II) complexes. Thus, these complexes may be formulated as  $[M(L)X_2]$  and  $[Ni(L)]X_2$  (where M = Mn(II),

Co(II), and Cu(II) and X =  $Cl^-$  and  $NO_3^-$ ). In the IR spectra of complexes, the shifting in lower side of a band  $[v(N-H)]$  and the band of amides II and III, suggest the coordination through nitrogen of  $-NH$  group ( $N_4$ ).

### 3.1. i.r. Spectra of the Complexes

The presence of the absorption bands at 1410 - 1421, 1299 - 1319 and 1010 - 1031  $cm^{-1}$ , in the i.r. spectra **Figures 2(a)-(c)** of the Mn(II), Co(II) and Cu(II) of nitrate complexes suggest the both nitrate groups are coordinated to the central metal ion in a unidentate fashion [16-18]. The Ni(II) nitrate complex exhibits a sharp strong peak at 1387  $cm^{-1}$ , which is in favour of an un-coordinated nitrate group [16,17].

#### 3.1.1. Manganese(II) Complexes

The magnetic moment recorded at room temperature lies in the range 5.90 - 5.96 B.M. corresponding to five unpaired electrons. Electronic spectra of Mn(II) complexes in DMSO solution display four weak intensity absorption bands (**Table 2**) in the 15,870 - 16,743 region ( $\epsilon = 24 - 26 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ), 20,356 - 21,685 ( $\epsilon = 33 - 36 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ), 24,787 - 27,006 ( $\epsilon = 61 - 64 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). These bands may be assigned to the transitions,  ${}^6A_{1g} - {}^4A_{1g}$  ( ${}^4G$ ),  ${}^6A_{1g} - {}^4E_g$ ,  ${}^6A_{1g}$  ( ${}^4G$ ) ( $10B + 5C$ ),  ${}^6A_{1g} - {}^4E_g$  ( ${}^4D$ ) ( $17B + 5C$ ) and  ${}^6A_{1g} - {}^4T_{1g}$  ( ${}^4P$ ), respectively [19].

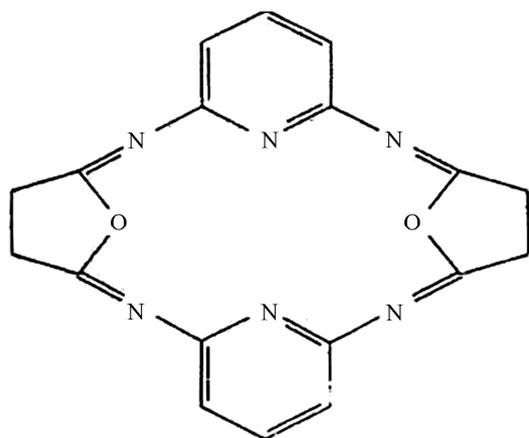
The e.p.r. spectra were recorded at room temperature

**Table 1.** Molar conductance and elemental analysis data of complexes.

Complex	Colour	Molar Conductance ( $\Omega^{-1}\cdot\text{cm}^{-1}\cdot\text{mol}^{-1}$ )	% Yield	Elemental Analysis Data				M. Pt ( $^{\circ}C$ )
				Calculated (Found) %				
				C	H	N	Metal	
$[Mn(L)Cl_2]$ $C_{20}H_{18}MnN_6S_2Cl_2$	Brown	02	69	45.0 (45.1)	3.3 (3.4)	15.6 (15.8)	10.5 (10.3)	280
$[Mn(L)(NO_3)_2]$ $C_{20}H_{18}MnN_8S_2O_6$	Light Brown	09	66	41.0 (40.8)	3.1 (3.0)	19.0 (19.1)	9.2 (9.4)	288
$[Co(L)(NO_3)_2]$ $C_{20}H_{18}CoN_6S_2Cl_2$	Pink	10	65	44.6 (44.4)	3.4 (3.3)	15.6 (15.7)	11.3 (11.0)	290
$[Co(L)(NO_3)_2]$ $C_{20}H_{18}CoN_8S_2O_6$	Pink	08	61	40.5 (40.7)	3.1 (3.2)	18.8 (19.0)	9.9 (10.0)	299
$[Ni(L)Cl_2]$ $C_{20}H_{18}NiN_2S_2Cl_2$	Red	158	64	44.6 (44.2)	3.4 (3.6)	15.5 (15.7)	11.2 (10.0)	298
$[Ni(L)(NO_3)_2]$ $C_{20}H_{18}NiN_2S_2O_6$	Orange	146	60	40.2 (40.5)	3.1 (3.5)	18.8 (19.0)	9.8 (10.0)	297
$[Cu(L)Cl_2]$ $C_{20}H_{18}CuN_6S_2Cl_2$	Blue	06	62	44.1 (44.5)	3.3 (3.2)	15.8 (15.5)	11.6 (11.8)	288
$[Cu(L)(NO_3)_2]$ $C_{20}H_{18}CuN_8S_2O_6$	Shiny Blue	09	61	40.2 (40.4)	3.0 (2.9)	18.8 (18.9)	10.9 (10.8)	290

**Table 2.** Magnetic moments and electronic spectral data of the complexes.

Complex	$\lambda$ Max (cm <sup>-1</sup> )	$\mu_{\text{eff}}$ (B.M.)	$\epsilon$ (L mol <sup>-1</sup> ·cm <sup>-1</sup> )
[Mn(L)Cl <sub>2</sub> ]	15,872, 21,685 24,785, 38,217	5.90	24, 36, 61, 135
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	16,743, 20,356, 27,006, 35,426	5.96	26, 33, 64, 128
[Co(L)Cl <sub>2</sub> ]	9896, 14,906, 17,341, 39,046	4.85	56, 67, 82, 157
[Co(L)(NO <sub>3</sub> ) <sub>2</sub> ]	9510, 14,285, 18,645, 38,819	4.76	55, 65, 84, 154
[Ni(L)Cl <sub>2</sub> ]	1651, 22,088, 30,114,	Diamagnetic	52, 92, 132
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ]	15,811, 20,983, 28,547,	Diamagnetic	51, 90, 128
[Cu(L)Cl <sub>2</sub> ]	9983, 15,991, 28,057	1.96	48, 58, 149
[Cu(L)(NO <sub>3</sub> ) <sub>2</sub> ]	10,560, 16,384, 29,514	1.90	49, 58, 151

**Figure 1.** Structure of ligand.

as polycrystalline samples and in DMSO solution. The polycrystalline spectra give an isotropic signal centered at 2.04 - 2.16. The spectra recorded in DMSO solution gives well-resolved six line spectra due to the hyperfine interaction between the unpaired electrons with the <sup>55</sup>Mn nuclear ( $I = 5/2$ ).

### 3.1.2. Cobalt(II) Complexes

At room temperature the magnetic moment measurements of cobalt(II) complexes lies in the range 4.76 - 4.85 B.M corresponding to three unpaired electron (**Table 2**). The electronic spectra of all the cobalt(II) complexes **Figure 3** exhibit absorption in the region 6510 - 9896 ( $\epsilon = 55 - 65 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ), 14,285 - 14,906 ( $\epsilon = 65 - 67 \text{ m}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ), 17341-18645 ( $\epsilon = 82 - 74 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ )

and 39,046 - 38,819 cm<sup>-1</sup> ( $\epsilon = 154 - 157 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). These bands may be assigned to the transitions: <sup>4</sup>T<sub>1g</sub> (F) - <sup>4</sup>T<sub>2g</sub> (F) ( $\nu_1$ ), <sup>4</sup>T<sub>1g</sub> - <sup>4</sup>A<sub>2g</sub> ( $\nu_2$ ) and <sup>4</sup>T<sub>1g</sub> (F) - <sup>4</sup>T<sub>1g</sub> (P) ( $\nu_3$ ), respectively [20].

It is difficult to make the assignments for the fourth band and it may be considered as a charge transfer band. The position of these suggests an octahedral environment around the cobalt (II) ion.

The e.p.r. spectra of the Co(II) complexes were recorded as polycrystalline samples and in DMSO solution at liquid nitrogen temperature (LNT).

The g-values were found to be almost the same in both cases in polycrystalline samples as well as in the solution, (**Table 3**).

It indicates that the complexes have the same geometry in the solid as well as in solution. The large deviation in g-values, in the e.p.r. spectra, from the spin only value ( $g = 2.0023$ ) is due to the large angular momentum contribution.

### 3.1.3. Nickel(II) Complexes

At room temperature these complexes show the diamagnetic behavior, indicating the square planar environment around the Ni(II) ion.

The electronic spectra of **Figure 4** the Ni(II) complexes, exhibit three absorption bands in the range 15,812 - 16,510 ( $\epsilon = 51 - 53 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ), 20,983 - 22,088 ( $\epsilon = 90 - 92 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) and 28,547 - 30,114 cm<sup>-1</sup> ( $\epsilon = 128 - 132 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). An examination of these bands indicates that the complexes have square planar geometry. These bands may be assigned to the three spin allowed

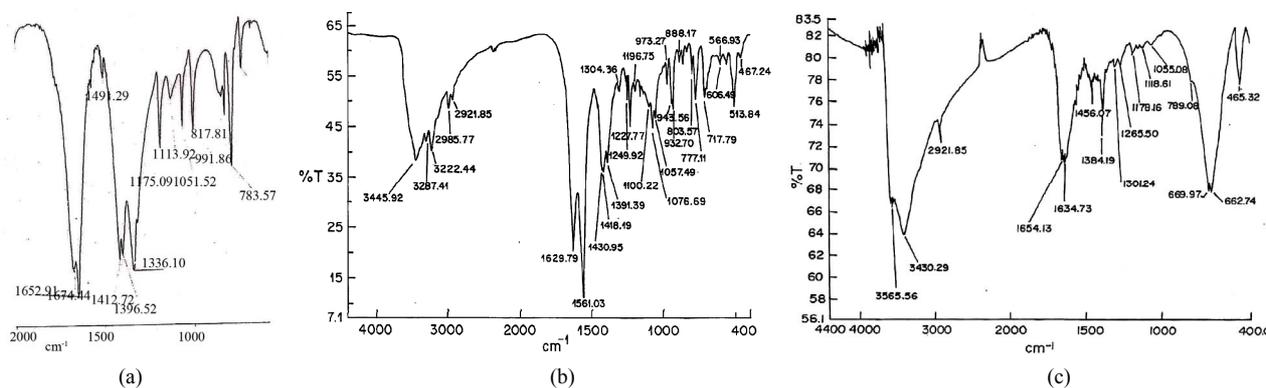


Figure 2. (a) IR Spectrum of [Co(L<sup>5</sup>)(NO<sub>3</sub>)<sub>2</sub>]; IR Spectrum of [Ni(L<sup>5</sup>)(NO<sub>3</sub>)<sub>2</sub>]; IR Spectrum of [Cu(L<sup>5</sup>)(NO<sub>3</sub>)<sub>2</sub>].

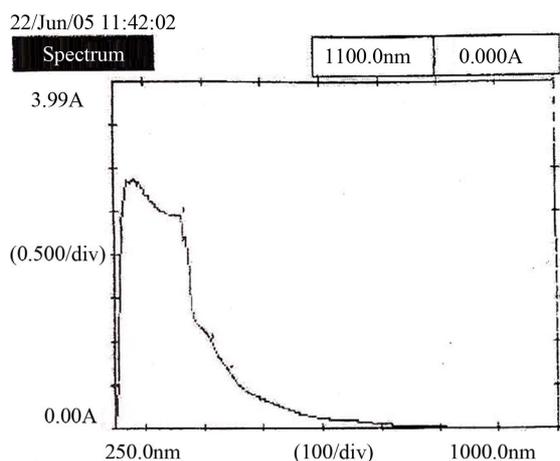


Figure 3. UV Spectrum of [Co(L<sup>5</sup>)(NO<sub>3</sub>)<sub>2</sub>].

transitions:  ${}^1A_{1g}(D)(v_1)$ ,  ${}^1A_{1g}(D) - {}^1B_{2g}(G)(v_2)$  and  ${}^1A_{1g}(D) - {}^1E_g(G)(v_3)$ , respectively [21].

### 3.1.4. Copper(II) Complexes

The magnetic moment of the Cu(II) complexes at room temperature lie in the range 1.90 - 1.96 B.M corresponding to one unpaired electron. The complexes may be considered to possess a tetragonal geometry.

The electronic spectra copper (II) complexes **Figure 5** display three bands (**Table 2**), in the 9987 - 10,560 ( $\epsilon = 48 - 49 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) 15,991 - 16,384 ( $\epsilon = 58 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) 28,057 - 29,514 ( $\epsilon = 149 - 151 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) ranges. These bands corresponding to the transitions  $B_{1g} - {}^2A_{1g}(d_x^2 - y^2 - d_z^2)v_1$ ,  ${}^2B_{1g} - {}^2B_{2g}(d_x^2 - y^2 - d_{xy})v_2$  and  ${}^2B_{1g} - {}^2E_g(d_x^2 - y^2 - d_{yz})v_3$ , respectively [22,23].

E.p.r. spectra of the Cu(II) complexes **Figure 6** were recorded, at room temperature, as polycrystalline samples and in DMSO solution, on the X-band at 9.3 GHz under the magnetic field strength 3400 G. Polycrystalline spectra show a well-resolved anisotropic broad signal [20].

The analysis of spectra give  $g_{\parallel} = 2.20 - 2.26$  and  $g_{\perp} = 2.06 - 2.10$  (**Table 3**). The trend  $g_{\parallel} > g_{\perp} > 2.0023$ , observed for the complexes, under study, indicate that the unpaired electron is localized in the  $d_x^2 - y^2$  orbital of the Cu(II) ion and the spectral figures and characteristic for the axial symmetry, Tetragonally elongated geometry is thus confirmed for the aforesaid complexes [24,25].

$G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ , which is the measurement of the exchange interaction between the metal centers in a solid sample of the complex has also been calculated. According to Hathaway and Billing [26] if  $G > 4$ , the exchange interaction is negligible but  $G < 4$  indicates the considerable exchange interaction in the solid complexes. The complexes reported here gives the 'G' value in the range 2.43 - 2.60, which is  $>4$ , indicating exchange interaction in the solid complexes.

### 3.2. Ligand Field Parameters

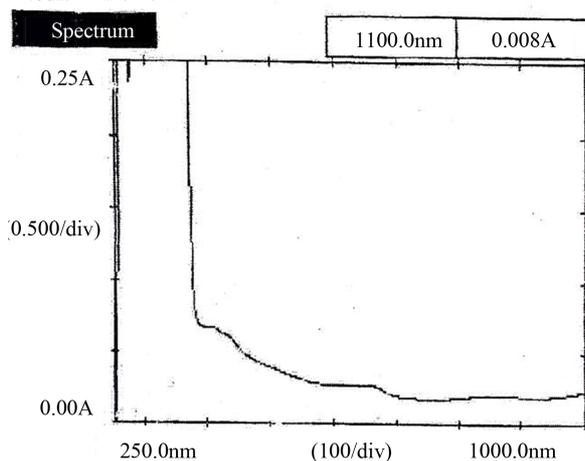
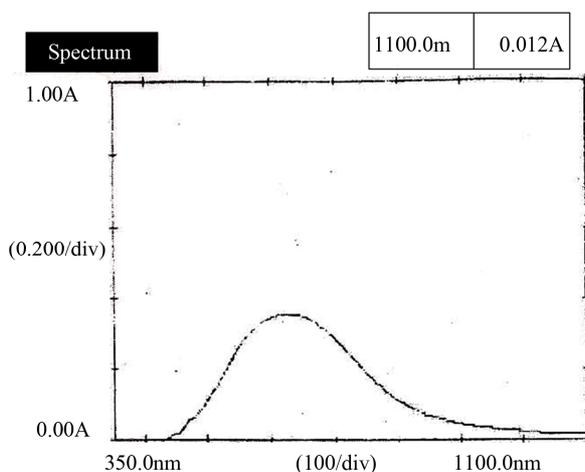
Various ligand field parameters were calculated for the complexes and are listed in **Table 4**.

The Values of Dq in Co(II) complexes were calculated from transition energy ratio diagram using the  $v_3/v_2$  ratio [27]. Our results are in agreement with the complexes reported earlier [28]. The Nephelauxetic parameter  $\beta$  was readily obtained by using the relation:  $\beta = B(\text{Complex})/B(\text{free ion})$ , where B (free ion) for Mn(II) is 786  $\text{cm}^{-1}$ , for Ni(II) is 1041 and for Co(II) is 1120  $\text{cm}^{-1}$  [29]. The values of  $\beta$  lie in the range of 0.46 - 0.070 range. The values of  $\beta$  and indicate the appreciable covalent character of metal ligand " $\sigma$ " bond. The graphical information contained in the Orgel energy leveldiagram [18,19]. Parameter B and C are a liner combination of certain Columb's exchange integral and are generally treated as empirical parameters obtained from the spectra of free ions. In Mn(II) the values of B and C are calculated from the second transition because and depend on B and C parameters. The calculated values of the ligand field parameters are given in **Table 4**. Slater condon shortly parameters  $F_2$  and  $F_4$  are related to the Rechah

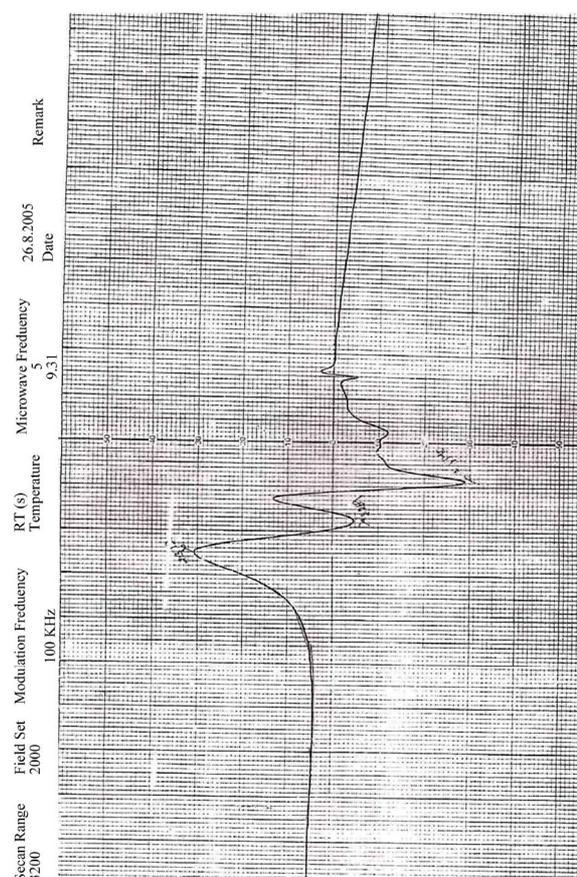
**Table 3.** EPR spectral data of the complexes.

Complex	Date as polycrystalline sample				Date in DMF solution				
	Temp.	$g_{11}$	$g_{\perp}$	$g_{iso}$	G	$g_{11}$	$g_{\perp}$	$g_{iso}$	G
[Mn(L)Cl <sub>2</sub> ]	RT	--	--	2.0052	--	--	--	2.0015	--
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	RT	--	--	2.0094	--	--	--	2.0018	--
[Co(L)Cl <sub>2</sub> ]	LNT	2.418	2.0098	3.75787	--	2.419	2.0178	3.7642	--
[Co(L)(NO <sub>3</sub> ) <sub>2</sub> ]	LNT	2.358	2.0175	3.70267	--	2.3396	2.0060	3.6793	--
[Cu(L)Cl <sub>2</sub> ]	RT	2.0930	2.0598	3.4662	0.87797	2.1345	2.0715	3.5155	0.8309
[Cu(L)(NO <sub>3</sub> ) <sub>2</sub> ]	RT	2.119	2.668	3.89767	0.63063	2.0810	2.6896	3.87407	0.6626

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**Figure 4.** UV Spectrum of [Ni(L<sup>5</sup>)(NO<sub>3</sub>)<sub>2</sub>].**Figure 5.** UV Spectrum of [Cu(L<sup>5</sup>)(NO<sub>3</sub>)<sub>2</sub>].

parameter B and C as:  $B = F_2 - 5F_4$  and  $C = 35F_4$ . The effect of covalence is to reduce the positive charge on the metal ion as consequence of the inductive effect to the ligand with reduced positive charge, the radial extension of the *d* orbital increases, this decreases the electron-electron repulsion, lowering the energy of the <sup>3</sup>P states.

**Figure 6.** EPR Spectrum of [Cu(L<sup>5</sup>)SO<sub>4</sub>].**Table 4.** Ligand field parameters of the complexes.

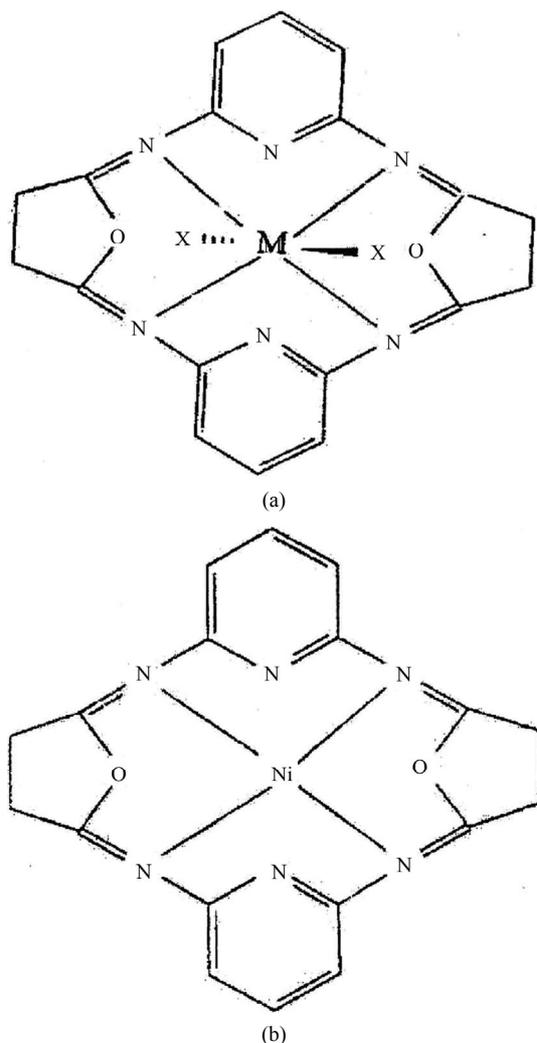
Complex	Dq (cm <sup>-1</sup> )	B (cm <sup>-1</sup> )	$\beta$	LFSE (kJ·mol <sup>-1</sup> )
[Mn(L)Cl <sub>2</sub> ]	1851.85	613.70	0.75	
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	1891.08	518.25	0.61	
[Co(L)Cl <sub>2</sub> ]	990	501	0.53	121.50
[Co(L)(NO <sub>3</sub> ) <sub>2</sub> ]	951	510	0.50	133.75
[Ni(L)Cl <sub>2</sub> ]	1650	750	0.66	231.90
[Ni(L)(NO <sub>3</sub> ) <sub>2</sub> ]	1581	718	0.80	237.23

#### 4. XRD

The XRD spectra have been recorded for all the complexes. For all the complexes the value of  $d$  is found to be same. This indicates that the complexes have same geometry. Hence on the basis elemental analyses, magnetic moment molar conductance, IR, EPR and X-ray diffraction pattern following structure of the complexes may be suggested **Figures 7(a)** and **(b)**.

#### 5. CONCLUSION

Complexes of Mn(II), Co(II), Cu(II) & Ni(II) with tetradentate macrocyclic ligand have been prepared and characterized. The proposed study revealed six coordinated octahedral geometry for Co(II), Mn(II) and square planer geometry for Ni(II) and tetragonal geometry for Cu(II) complexes. Various ligand fields and bonding parameters have been calculated and discussed.



**Figure 7.** (a)  $[M(L)X_2]X = Cl^{-1}, NO_3^{-}, CH_3COO^{-}$   
 $M = Mn(II), Co(II)$  and  $Cu(II)$ ; (b)  $[Ni(L)X_2]$ ,  $X = Cl^{-1}$ .

#### 6. ACKNOWLEDGEMENTS

Authors are thankful to UGC New Delhi for financial assistance and I.I.T. Bombay for recording EPR spectra.

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