

SYNTHESIS, SPECTRAL CHARACTERIZATION OF Mn(II) AND Co(II) COMPLEXES WITH THIOSEMICARBAZONES AND SEMICARBAZONES DERIVED FROM PYRIDINE-2-CARBOXALDEHYDE

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ABSTRACT: Mn(II) and Co(II) complexes are synthesized with L₁(Pyridine-2-carboxaldehydethiosemicarbazones) and L₂ (Pyridine-2-carboxaldehydesemicarbazones). These complexes were characterized by elemental analysis, molar conductance measurements, magnetic susceptibility measurements, mass, IR, electronic and EPR spectral studies. The molar conductance measurement of the complexes in DMSO corresponds to non electrolytes nature with L₁ and formulated as [M(L)₂X₂] where M=Mn(II) and Co(II) complexes. The molar conductance measurements with L₂ lie in the range 208-217 Ω⁻¹cm²mol⁻¹ indicating the electrolytes nature of the complexes thus the complexes formulated as [M(L)₂]X₂ where M=Mn(II) and Co(II) complexes. On the basis of spectral studies an octahedral geometry has been assigned for Mn(II) and Co(II) complexes.

Keywords: Spectral studies, Manganese(II) complexes, Cobalt(II) complexes, Thiosemicarbazones and Semicarbazones.

INTRODUCTION

Schiff bases are regarded as “privileged ligands” due to their capability to form complexes with a wide range of transition metal ions yielding stable and intensely colored metal complexes. Some of them have been shown to exhibit interesting physical and chemical properties and potential biological activities (Chandra et. al; 2009). Thiosemicarbazones are very versatile ligands. They can coordinate to metal as neutral molecules or after deprotonation as anionic ligands and can adopt a variety of different coordination. Thio-semicarbazones and semicarbazones act as ligands because

1: They have better co-ordination tendency.

2: They form more stable complexes.

3: They have better selectivity.

4: They may form macrocyclic ligands.

5: They have the ability to produce some new and unique complexes with enhanced biological and analytical properties. Thiosemicarbazones usually act as chelating ligands with transition metal ion bonding through the sulphur and hydrazine nitrogen atom. Thiosemicarbazones and their complexes have received considerable attention because of their pharmacological activities (Kothari and Sharma, 2011). Thiosemicarbazones and their complexes have received considerable attention because of their antifungal (Prasad and Agarwal, 2007), antitumor (Ainscough et.al.,1998) antibacterial (Chandra et.al.,2009), antiamoebic, antimalarial, antiviral (Kolocouris et.al., 2002) radio protective and anti-inflammatory activities. Certain thiosemicarbazones are relatively specific inhibitors of ribonucleotide reductase, which is an important metabolic target for the development of chemotherapeutic agents against cancer (Sandercock et.al., 2007).

Metal complexes of Ni (II) are found to act as a sensor (R Aruna et.al., 2010) in many of the diseases states for which thiosemicarbazones have been shown to be effective. Thiosemicarbazones as chelating ligands with transition metal ions by binding through the thioketo sulphur and hydrazine nitrogen atoms and therefore this type of compounds can coordinate in vivo to metal ions. Because of such coordination, the thiosemicarbazones moiety undergoes a sterical reorientation that could favour its biological activity. The biological activity of thiosemicarbazones is also considered to involve the inhibition of ribonucleotide reductase, an obligatory enzyme in DNA synthesis. Ribonucleotide reductase is the enzyme that converts ribonucleotide to deoxy ribonucleotide, a vital enzyme in DNA synthesis and a key target for the development of antineoplastic agents. There is also consensus on the involvement of toxic oxygen species, such as superoxide and hydroxyl radicals, in many of the diseases states for which thiosemicarbazones have been shown to be effective. Semicarbazones are reported to possess versatile structural features and very good antifungal, antibacterial, antitrypanosomal (Cerecetto H et.al., 2000) and anticonvulsant properties (Dimmock J R et.al., 2010). Rhenium (V) and Ruthenium (II) complexes of 5-nitrofurylsemicarbazone were tested against the trypanocidal activity (Otero L et.al., 2006).

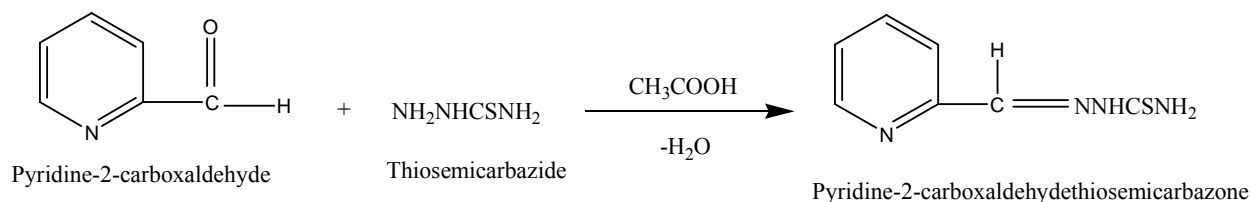
In present paper we report the synthesis and characterization of Mn(II) & Co(II) complexes with thiosemicarbazones (L_1) and semicarbazones (L_2) derived from pyridine-2-carboxaldehyde.

MATERIAL AND METHODS

All the chemicals used in the present work were of analytical grade and procured from Sigma Aldrich. Metal salts were purchased from E. Merck and used as received. The solvents used were either spectroscopic pure SRL/BDH or purified by the recommended methods (Vogel, 1962).

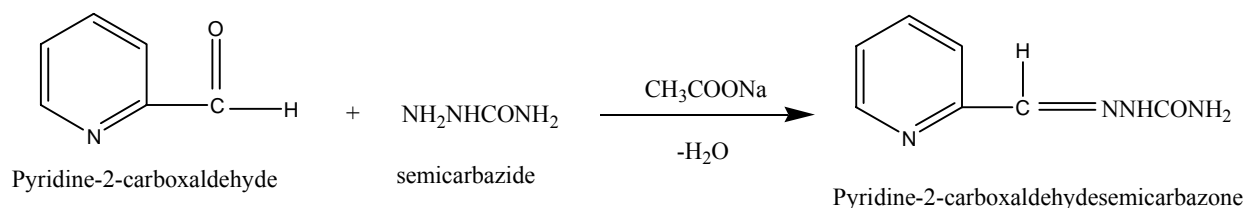
Synthesis of Schiff base ligand L_1 (Pyridine-2-carboxaldehyde thiosemicarbazone)

Hot ethanolic solution (50 mL) of thiosemicarbazide (4.55 g, 0.05 mol) and Pyridine - 2-carboxaldehyde (4.75 mL, 0.05 mol) mixed slowly with constant stirring in presence of acetic acid. This mixture was refluxed for 2 hours on a water bath. On cooling a cream colored compound was precipitated out. It was filtered, washed with cold ethyl alcohol and dried under vacuum over P_4O_{10} . This reaction is a type of condensation reaction which takes place between aldehyde and thiosemicarbazide with elimination of water molecules which form thiosemicarbazones. The reaction can be represented as below.



Synthesis of Schiff base ligands L_2 (Pyridine -2-carboxaldehyde semicarbazones)

An aqueous solution (50 mL) of semicarbazide hydrochloride (5.55 g, 0.05 mol) added in an ethanolic solution (50 mL) of corresponding aldehyde pyridine-2-carboxaldehyde (4.75 g, 0.05 mol) in the presence of sodium acetate (4.1 g, 0.05 mol). The reaction mixture was stirred vigorously for an hour in the magnetic stirrer. The crystalline product which formed was collected by filtration in each case washed several times with hot water and dried in vacuum over P_4O_{10} . This reaction is a type of condensation reaction which takes place between aldehyde and semicarbazide with elimination of water molecules which form semicarbazones. The reaction can be represented as below.



Synthesis of metal complexes

Hot ethanolic solution of metal salt (1mmol) e.g nickel chloride hexahydrate, nickel nitrate hexahydrate were mixed with ethanolic solution of the corresponding ligands (2mmol in 20mL of absolute ethanol) e.g L₁ (Pyridine-2-carboxaldehyde thiosemicarbazone (3.6 g, 0.02 mol) and L₂ (Pyridine-2-carboxaldehyde semicarbazone (3.28 g, 0.02 mol) were mixed together with constant stirring. The mixture was refluxed for 3-4 hour at 60-70^oc. On cooling solid colored complexes were precipitated out. The solid ppt. was filtered off, washed several times with ethanol and dried under vacuum over P₄O₁₀. Purity of the complexes was checked by the TLC color was noted, melting point was determined and yield of the complexes were calculated.

Table 1: Analytical data of ligands

Ligand	M.W	Color	M.P (^o C)	Yield (%)	Elemental analysis (%) found (Cal.)		
					C	H	N
C ₇ H ₈ N ₄ S(L ₁)	180	Shiny Yellow	178	68	46.68 (46.70)	4.46 (4.48)	31.14 (31.12)
C ₇ H ₈ N ₄ O(L ₂)	164	White	135	64	51.30 (51.26)	4.84 (4.91)	34.17 (34.16)

Physical Measurements

The C, H, N were analyzed on a carlo-Erba 1106 elemental analyzer. Molar conductance was measured on the Elico (CM82T) conducting bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO₄.5H₂O as a calibrant. A mass spectrum was recorded on JEOL, JMS.DX-303 mass spectrometer. IR spectra (KBr) were recorded on a FTIR spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer.

RESULT AND DISCUSSION

L₁ (Pyridine- 2-carboxaldehydethiosemicarbazone)

The IR spectra of ligands show band around 3433 cm⁻¹ and 3260 cm⁻¹ which may be assigned to -NH₂ and -NH group respectively. The band due to [ν(C=N)] of pyridine ring and [ν(C=N)] azomethane group appeared around at 620 and 1610 cm⁻¹ (Figure 1). The mass spectrum of the free ligands (L₁) confirms the proposed formula by showing a peak at 179 amu (calculated atomic mass-180 amu) corresponding to the molecular ions (M+⁺). It also show a peak corresponds to loss of (-CSNH₂) and various other fragments.

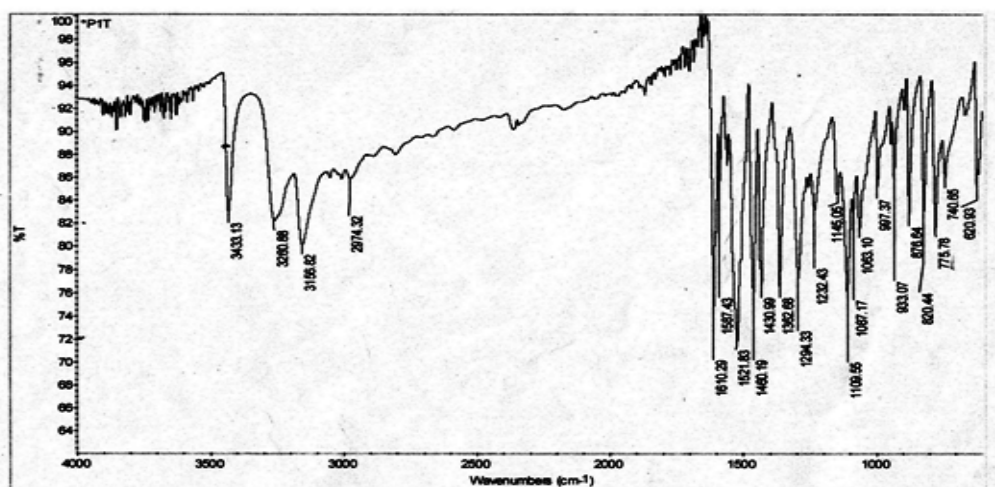


Figure 1: IR spectra of pyridine-2-carboxaldehydethiosemicarbazones

L₂ (Pyridine-2-carboxaldehydesemicarbazones)

The IR spectra of ligands show bands around at 3384 cm⁻¹ and 3235 cm⁻¹ which may be assigned to -NH₂ and -NH group respectively. The band due to [ν(C=N)] and [ν(C=O)] appeared at around 1668 cm⁻¹ and 1695 cm⁻¹ (Figure 2). The mass spectrum of the ligands L₂ confirm the proposed formula by showing a peak at 163 amu respectively corresponds to the molecular ions (M^{+ +1}). It also shows a peak corresponding to the molecular ion (M^{+ +1}).

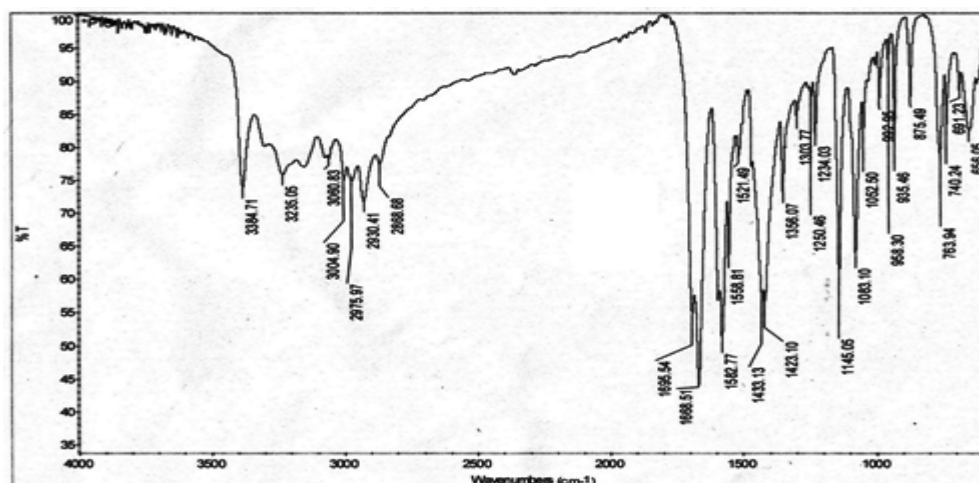


Figure 2: IR spectra of pyridine-2-carboxaldehydesemicarbazone

¹H NMR (δ, ppm) spectra of ligands pyridine-2-carboxaldehydesemicarbazones (PCT):

¹H NMR spectrum of ligands L₁ (PCT) in DMSO exhibit following signal.

11.61s, (s, 1H, N (3) H); 8.53 (d, 1H, C (1) H); 7.33 (t, 1H, C(2) H); 7.80 (t, 1H, C(3) H); 8.25 (s, 1H, C (4) H); 8.07 (s, 1H, C (6)); 8.31 (b, 2H, N (4) H)

¹H NMR (δ, ppm) spectra of ligands pyridine-2-carboxaldehydesemicarbazones (PCS):

¹H NMR spectrum of ligands L₂ (PCS) in DMSO exhibit following signal.

10.51s, (s, 1H, N (3) H); 8.52 (d, 1H, C (1) H); 7.32 (t, 1H, C(2) H); 7.79 (t, 1H, C(3) H); 8.13 (s, 1H, C (4) H); 7.87 (s, 1H, C (6)); 8.31 (b, 2H, N (4) H) Where s = singlet, d = doublet, t = triplet, b = broad

Complexes

The IR bands most useful for the determination of coordination between ligands and metal ion. On complexation with L₁(PCT) the bands corresponding to [ν(C=N)] shifted towards lower side while the pyridine rings vibration at around 620 cm⁻¹ shifted towards higher side due to increase in bond strength confirm the bidenting nature of the ligands coordinating through N of [ν(C=N)] azomethane and N atom of pyridine rings. Structure of metal complexes with ligands L₁ (PCT) represented as below (figure 3).

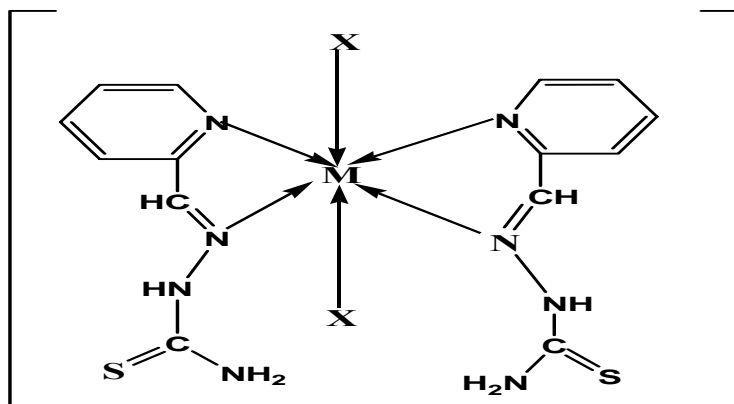


Figure 3: Suggested octahedral structure of the complexes [M(L₁)₂X₂] with L₁ where M= Mn(II) and Co(II) and X= Cl⁻, NO₃⁻

On complexation with metal/metal ion with L_2 (PCS) the band corresponding to $[\nu(C=N)]$ and $[\nu(C=O)]$ appeared at 1587 cm^{-1} and 1689 cm^{-1} shifted towards lower side but N atom of pyridine rings shifted towards higher side due to increase in bond strength indicate that L_2 (PCS) acts as a tridentate (three coordination side) ligands coordinating through the pyridine N, imine N and Oxygen atom. In the IR spectra of nitrate complexes with L_2 nitrate group is appeared at 1384 cm^{-1} suggest that nitrate group is uncoordinated and it is outside the coordination sphere. Structure of metal complexes with ligands L_2 (PCS) represented as below (figure 4).

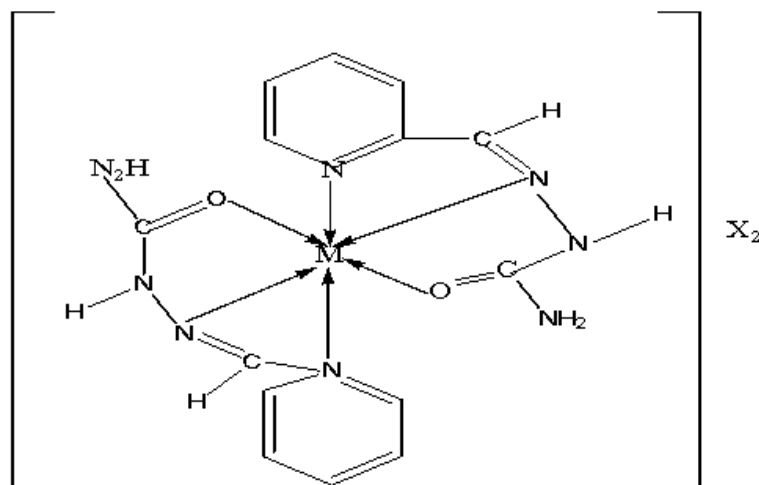


Figure 4: Suggested octahedral structure of the complexes $[M(L_2)_2] X_2$ with L_2 where $M = \text{Mn(II)}$ and Co(II) and $X = \text{Cl}^-, \text{NO}_3^-$

Table 2: Elemental analysis and molar conductance data of complexes

Complex	M.W	Mol. Conductance $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Color	MP ($^{\circ}\text{C}$)	Yield (%)	Elemental analysis (%) Found (calculated)			
						M	C	H	N
$[\text{Mn}(L_1)_2\text{Cl}_2]$	485.83	24	Green	275	63	11.26 (11.30)	34.53 (34.61)	3.28 (3.31)	23.00 (23.06)
$[\text{Mn}(L_1)_2(\text{NO}_3)_2]$	538.93	18	Yellow	280	64	10.14 (10.19)	31.15 (31.20)	2.86 (2.99)	25.85 (25.99)
$[\text{Mn}(L_2)_2\text{Cl}_2]$	454.17	217	Off white	276	63	12.08 (12.09)	37.00 (37.01)	3.54 (3.55)	24.69 (24.67)
$[\text{Mn}(L_2)_2](\text{NO}_3)_2]$	507.29	210	Off white	280	66	10.80 (10.82)	33.15 (33.14)	3.16 (3.17)	27.60 (27.61)
$[\text{Co}(L_1)_2\text{Cl}_2]$	490.29	17	Shiny Yellow	218	64	11.98 (12.01)	34.25 (34.29)	3.25 (3.28)	22.80 (22.85)
$[\text{Co}(L_1)_2(\text{NO}_3)_2]$	542.93	23	Brown	232	67	10.80 (10.85)	30.93 (30.97)	2.92 (2.97)	25.73 (25.79)
$[\text{Co}(L_2)_2\text{Cl}_2]$	458.17	208	Shiny Pink	218	68	12.84 (12.86)	36.68 (36.70)	3.49 (3.52)	24.40 (24.45)
$[\text{Co}(L_2)_2](\text{NO}_3)_2]$	511.28	213	Green	236	69	11.49 (11.52)	32.80 (32.88)	3.11 (3.15)	27.35 (27.39)

Manganese (II) complex

Magnetic moment of all the Mn(II) complexes at room temperature lie in the range 5.43-5.68 BM corresponding to five unpaired electron (table 3). Electronic spectra of Mn (II) complexes display four weak intensity absorption bands in the range 16,620-17,006; 24,630-24,875; 28,409-29,069 and 30,762-31,250, these bands may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$, ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^4A_{1g}({}^4G)$ (10B+5C), ${}^6A_{1g} \rightarrow {}^4E_g$, (4D) (17B+5C) and ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4P)$ (7B+7C) respectively. The position of these bands suggest an octahedral geometry around the Mn (II) ion.

Cobalt (II) complexes

Magnetic moment of all the Co (II) complexes at room temperature lie in the range 4.21-4.85 BM (table 3). The electronic spectra of Co (II) recorded in DMSO solution, exhibit absorption in the range 9,276-9,478; 17,331-17,857 and 20,408-20,618 cm^{-1} . These bands may be assigned to ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$, ${}^4T_{1g} \rightarrow {}^4A_{2g}$, and ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ transition respectively. The position of these bands suggest an octahedral geometry around the Co (II) ion.

Electronic Paramagnetic Spectra of Mn (II) complexes

The EPR spectra of Mn(II) complexes were recorded at room temperature as polycrystalline samples and in DMSO solution. EPR spectra of Mn(II) complexes were recorded as polycrystalline sample on X-band at frequency 9.1 GHz under the magnetic field strength 3000 Gauss. The polycrystalline spectra give an isotropic signal centered at 1.96-2.07 ($A^0 = 109-112$). The spectra recorded in DMSO solution gives well resolved six line spectra due to the hyperfine interaction between the unpaired electrons with the ${}^{55}\text{Mn}$ nuclear ($I = 5/2$).

Electronic Paramagnetic Spectra Co (II) complexes

EPR spectra of Co (II) complexes were recorded as polycrystalline sample in DMSO solution at liquid nitrogen temperature on X-band at frequency 9.1 GHz under the magnetic field strength 3000 Gauss. The 'g' values were found to be almost same in both cases in polycrystalline sample as well as in the solution. This indicates that the complexes have same geometry in solid as well as in the solution. All the complexes show anisotropic EPR spectra. The g value has been calculated by Kivelson's method by using formula $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, which measure the exchange interaction between cobalt centers in the polycrystalline solid sample of the complex. According to Hathway (Hathway and Billing, 1970) if $G > 4$ the exchange interaction is negligible. If however the value of $G < 4$ than it indicates considerable exchange interaction in the solid complexes. In the complexes reported here the G value are less than 4 indicating the exchange interaction in solid complexes.

Table 3: Magnetic moment and electronic spectral data of complexes

Complexes	μ (B.M)	Electronic spectral data (cm^{-1})		
		ν_1	ν_2	ν_3
[Mn(L ₁) ₂ Cl ₂]	5.68	16,722	24,630	28,735
[Mn(L ₁) ₂ (NO ₃) ₂]	5.62	17,006	24,875	28,571
[Mn(L ₂) ₂ Cl ₂]	5.67	16,620	24,813	28,409
[Mn(L ₂) ₂](NO ₃) ₂	5.43	16,720	24,640	29069
[Co(L ₁) ₂ Cl ₂]	4.84	9,467	17,391	20,408
[Co(L ₁) ₂ (NO ₃) ₂]	4.21	9,276	17,857	20,576
[Co(L ₂) ₂ Cl ₂]	4.82	9,478	17,331	20,577
[Co(L ₂) ₂](NO ₃) ₂	4.85	9,319	17,667	20,618

Ligands fields Parameters of Co (II) complexes

Various field parameters are calculated for Co (II) complexes. The nephelauxetic parameter $\beta = B(\text{complex})/B(\text{free ion})$ where B free ion for cobalt (II) is 1120 cm^{-1} . The value of β lies in the range 0.55-0.63 (table 4). These values indicate the appreciable covalent character of metal ligands sigma bond.

Table 4: Ligands field parameters of Co (II) complexes

Complexes	LFSE (kJ/mol)	Dq (cm^{-1})	β
[Co(L ₁) ₂ Cl ₂]	90	946	.55
[Co(L ₁) ₂ (NO ₃) ₂]	88	927	.63
[Co(L ₂) ₂ Cl ₂]	90	947	.56
[Co(L ₂) ₂](NO ₃) ₂	89	931	.61

CONCLUSION

Mn(II) and Co(II) complexes of Schiff base derived from pyridine-2-carboxaldehyde were synthesized and characterized using various spectral techniques. The IR result demonstrate the coordinating side of the ligands with metal through shifting of the band. Electronic spectra demonstrate the octahedral geometry of the complexes. Magnetic measurements exhibit the paramagnetic nature of the complexes.

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