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SYNTHESIS AND CHARACTERISATION OF MANGANESE(II) COMPLEXES WITH SEMICARBAZIDE AND THIOSEMICARBAZIDE BASED LIGANDS

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Keywords:

Mangenese(II) Complexes, Semicarbazones, Thiosemicarbazones

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ABSTRACT: Mn(II) complexes with four semicarbazide and thiosemicarbazide based ligands such as 2-formyl pyridine semicarbazone (L_1), 2-formyl pyridine thiosemicarbazone (L_2), 5-methyl 2-formyl pyridine semicarbazone (L_3) and 5-methyl 2-formyl pyridine thiosemicarbazone (L_4) have been synthesized and characterized. All the ligands were characterized by elemental analyses, IR, ^{1}HNMR and mass spectral studies. The complexes were characterized by using various physicochemical techniques such as elemental analysis, molar conductance, magnetic susceptibility measurements and spectral studies such as IR, UV-visible and EPR. The complexes were found to have general compositions $Mn(L)_2X_2$ [where L = L_1, L_2, L_3 & L_4, X = Cl^-, NO_3^-]. The molar conductance data of chloro and nitrato complexes of L_1, L_2, L_3 and L_4 suggest nonelectrolytic nature of the complexes. Therefore they may be formulated as $[Mn(L)_2X_2]$.Complexes show magnetic moment corresponding to five unpaired electrons. On the basis of IR electronic and EPR spectral data distorted octahedral geometry of complexes has been suggested.

INTRODUCTION: Metal complexes of semicarbazones and thiosemicarbazones were found to show more biological activities as compared to the free semicarbazone and thiosemicarbazone [1]. In addition, the complexes can exhibit bioactivities which are not shown by the free ligands. Owing to the wide range of medicinal properties of semicarbazones and thiosemicarbazones, their metal complexes are emerging as a new class of experimenral studies. A lot of work is going on the synthesis and characterisation of transition metal complexes with semicarbazones and thiosemicarbazones [2]. The transition metal complexes of these ligands were synthesised mainly due to their pharmacological activities.

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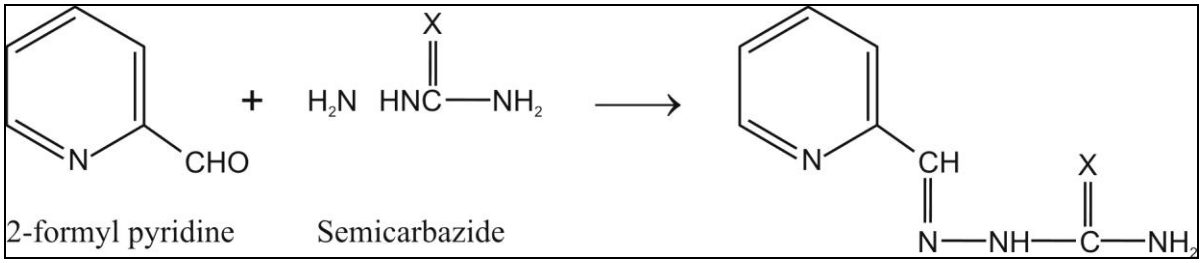
Another important aspect to synthesize such complexes is to compare the coordination behaviour of N⌒O and N⌒S donor ligands. The complexes of manganese(II) with sulphur containing ligands play an excellent role in catalytic property [3, 4]. Manganese and its compounds are widely used in analytical chemistry, metallurgical processes, paints and pigment industry.

Further, the coordination chemistry of manganese with a diverse range of ligands remains an area of considerable interest towards coordination compounds [5, 6, 7] in adsorption into soil because these are very abundant in soil and are essential for plant growth. In soil, these are formed by bio-degradation of lignin [8, 9, 10]. Mn(II) was found to be important for enzymatic systems with DNA. DNA and RNA polymerases [11, 18] catalyze the replication and transcription of DNA and have a specific requirements for Mn(II) [12 - 19]. In view of the above applications of Mn(II) the synthesis and characterization of the Mn(II) complexes with

semicarbazide and thiosemicarbazide based ligands are highly desirable. In this paper we repeat the synthesis and spectral studies of Mn(II) complexes with semicarbazide and thiosemicarbazide based ligands: 2-formyl pyridine semicarbazone (L_1), 2-formyl pyridine thiosemicarbazone (L_2), 5-methyl-2-formyl pyridine semicarbazone (L_3) and 5-methyl-2-formyl pyridine thiosemicarbazone (L_4). The ligands were synthesised by the reactions as shown in **Fig.1.**



(X = O or S in L_1 and L_2 respectively)

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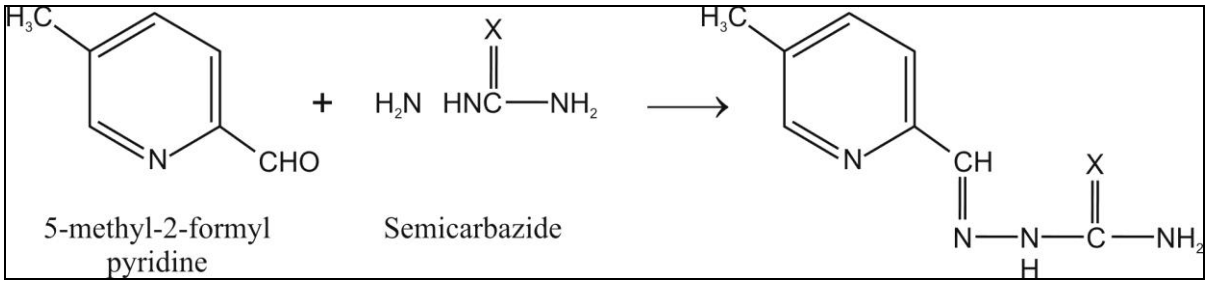


(X = O or S in L_3 and L_4 respectively)

FIG. 1: SYNTHESIS OF LIGANDS

MATERIALS AND METHODS:

Experimental procedure: All reagents and chemicals used were of Anala R grade. All solvents used were of standard/spectroscopic grade.

Preparation of Ligand: Ligand L_1 and L_3 were prepared by adding hot ethanolic solution (20 mL) of 2-formyl pyridine/5-methyl-2-formyl pyridine (0.02 mol) to a hot aqueous solution of semicarbazide hydrochloride and 0.02 g sodium acetate. Mixture was refluxed on water bath for an hour at around 80°C. On cooling at ≈0 °C compounds were precipitated out. They were filtered and washed with hot water and dried over P_4O_{10}.

Ligand L_2 and L_4 were synthesised by refluxing the mixture of thiosemicarbazide (0.02 mol) and 2-formyl pyridine (0.02 mol)/5-methyl-2-formyl pyridine in a round bottom flask at around 80 °C till clear solution is obtained. Ligand was precipitated out on cooling at 0 °C. It was filtered and washed with ethanol.

Preparation of Manganese (II) Complexes with ligands L_1 to L_4: The complexes were prepared by using semicarbazide and thiosemicarbazide based ligands and corresponding Mn(II) salts ($MnCl_2.4H_2O$ and $Mn(NO_3)_2.H_2O$).

A hot ethanolic (20 mL) solution of corresponding metal salts (0.001mol) was mixed with hot ehtanolic solution of the ligands L_1 to L_4 (0.002 mol). The mixture was refluxed for 3-4 h at 80°C (±5). The completion of the reaction was confirmed by Thin Layer Chromatography. On cooling the contents, coloured complexes were precipitated out. These were filtered, washed with 50% ethanol and dried in vacuum over P_4O_{10}. Purity of the complexes were checked by Thin Layer Chromatography.

Instrumentation: Carbon (C), Hydrogen (H) and Nitrogen (N) were analysed on a carlo-Erba 1106 elemental analyser. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gony balance using $CuSO_4.5H_2O$ as calibrant ^{1}HNMR spectra was recorded at room temperature on a Bruker Advance DPX-300 spectrometer using DMSO-d_6 as a solvent. IR spectra (KBr) were recorded in DMSO on a shimadza UV mini-1240 spectrophotometer.

EPR spectra were recorded as polycrystalline samples and in a DMSO solution at liquid nitrogen temperature (LNT) and room temperature (RT) on an E_4-EPR spectrometer using DPPH as a g-marker.

RESULTS AND DISCUSSION:

Characterization of ligands: The semicarbazide and thiosemicarbazide based ligands (L_1–L_4) have been characterized by elemental analysis, IR [20-26], UV, ^{1}HNMR and mass spectral studies.

Characterization of metal complexes: The formation of the complexes can be represented by the reaction :

$$L + CoX_2 \xrightarrow{\text{Reflux}} [Co(L)_2X_2]$$

Where, L=L_1, L_2, L_3 and L_4

X=Cl^-, NO_3^-, ½SO_4^{2-}

On the basis of elemental analysis the complexes were found to have general compositions $Co(L)_2X_2$. The molar conductance data suggest the non electrolytic nature of the complexes. Hence, the complexes may be formulated as $[Co(L)_2X_2]$. The results of elemental analysis and molar conductance data of complexes are shown in **Table 1.**

TABLE 1: ELEMENTAL ANALYSIS AND MOLAR CONDUCTANCE DATA OF Mn(II) COMPLEXES

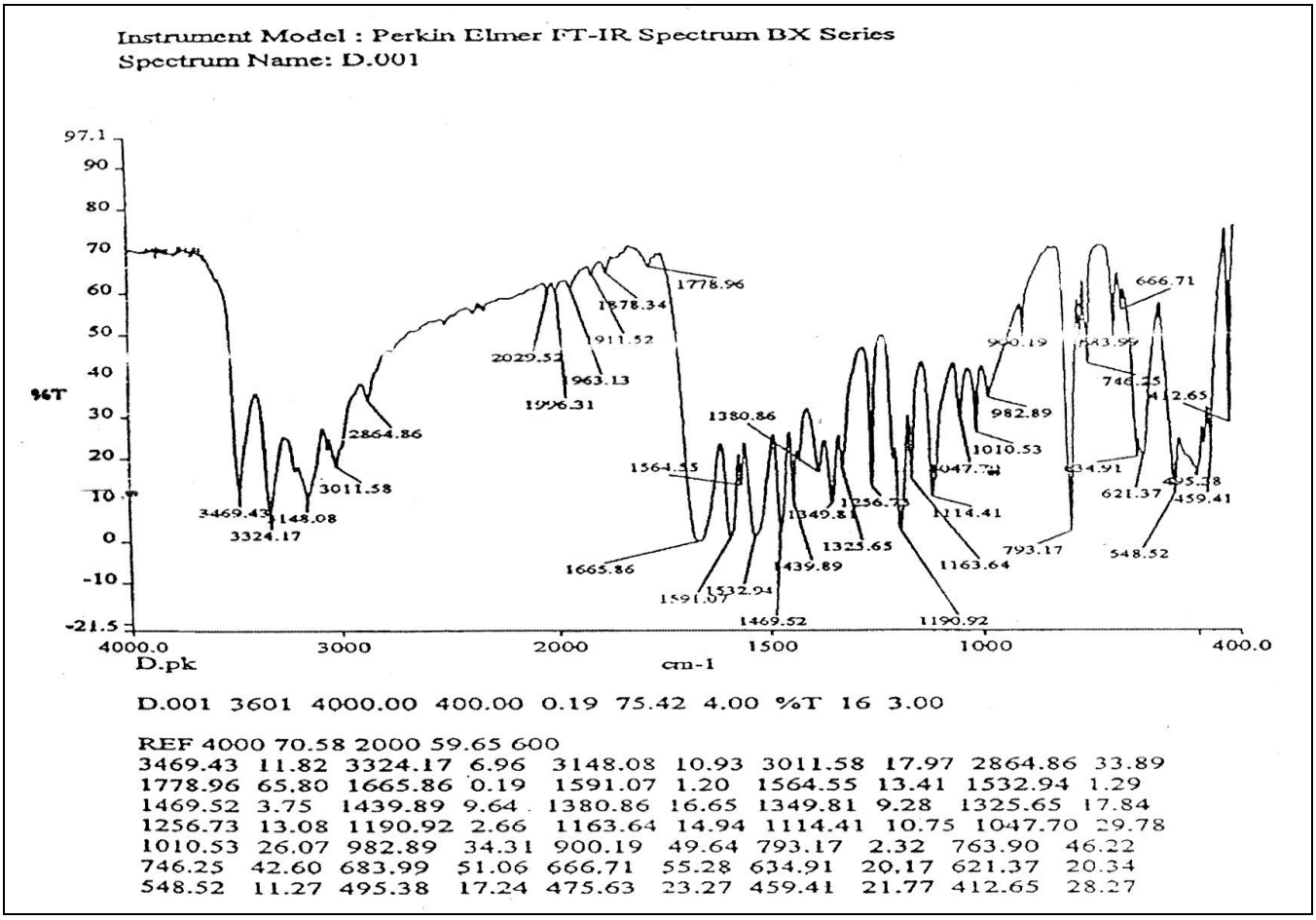
Complexes	Molar Conductance ν^{-1} cm^2 mol^{-1}	Colour	M.P. °C	Yield %	Elemental Analysis data calculated/ (found)			
					M	C	H	N
$[Mn(L_1)_2Cl_2]$	20.0	Yellow	242	58	12.10	37.01	3.52	24.67
$MnC_{14}H_{16}N_8O_2Cl_2$					(12.12)	(37.00)	(3.51)	(24.66)
$[Mn(L_1)_2 (NO_3)_2]$	19.0	Brown	260	62	10.83	33.14	3.15	27.61
$MnC_{14}H_{16}N_{10}O_8$					(10.81)	(33.10)	(3.12)	(27.64)
$[Mn(L_2)_2 Cl_2$	21.2	White	267	64	11.30	34.57	3.29	23.04
$MnC_{14}H_{16}N_8S_2Cl_2$					(11.32)	(34.59)	(3.24)	(23.03)
$[Mn(L_2)_2 (NO_3)_2$	21.9	White	255	65	10.50	32.12	3.05	26.77
$MnC_{14}H_{16}N_{10}S_2O_6$					(10.51)	(32.10)	(3.07)	(26.79)
$[Mn(L_3)_2Cl_2]$	11.5	Brown	240	60	11.39	39.83	4.14	23.23
$MnC_{16}H_{20}N_8O_2Cl_2$					(11.38)	(39.80)	(4.16)	(23.21)
$[Mn(L_3)_2 (NO_3)_2]$	16.0	Yellowish	266	66	10.26	35.89	3.73	26.17
$MnC_{16}H_{20}N_{10}O_8$		Brown			(10.25)	(35.88)	(3.70)	(24.16)
$[Mn(L_4)_2 Cl_2$	15.0	White	270	61	10.68	37.35	3.89	21.79
$MnC_{16}H_{20}N_8S_2Cl_2$					(10.66)	(37.36)	(3.88)	(21.82)
$[Mn(L_4)_2 (NO_3)_2]$	17.0	Dull	280	59	9.68	34.04	3.54	24.82
$MnC_{16}H_{20}N_{10}S_2O_6$		White			(9.66)	(34.03)	(3.55)	(24.80)

IR Spectra of complexes: The important IR bands and their assignments of semicarbazide and thiosemicarbazide based ligands and their Mn(II) complexes are shown in **Table 2**.

TABLE 2: IMPORTANT IR BANDS (cm^{-1}) AND ASSIGNMENTS OF SEMICARBAZIDE AND THIOSEMCARBAZIDE BASED LIGANDS AND THEIR Mn(II) COMPLEXES

Compound	ν (C=N)	ν (C=O)	ν (NH)	ν (C–S)	ν (M–N)	ν (M–O/ ν (M–S)
Ligand (L_1)	1582s	1687s	3371m	-	-	-
$[Mn(L_1)_2Cl_2)]$	1564m	1681vs	3350m	-	459w	412mw
$[Mn(L_1)_2(NO_3)_2]$	1542m	1665s	3324s	-	461sh	412mw
Ligand (L_2)	1540	-	3240	802	-	-
$[Mn(L_2)_2Cl_2)]$	1460s	-	3240s	765ms	492m	-
$[Mn(L_2)_2(NO_3)_2]$	1455m	-	3240m	760m	492m	-
Ligand(L_3)	1598s	1685	3304s	-	-	-
$[Mn(L_3)_2Cl_2]$	1543s	1653s	3247m	-	445sh	-
$[Mn(L_3)_2NO_3]$	1549m	1682s	3263m	-	455w	-
Ligand (L_4)	1533s	-	3374s	804m	-	
$[Mn(L_4)_2Cl_2]$	1425s	-	3259s	770ms	498m	-
$[Mn(L_4)_2NO_3]$	1426m	-	3248m	727m	490m	-

Abbreviations; s= strong, ms=medium strong, m = medium, mw=medium weak, w = weak, sh = sharp



D.001 3601 4000.00 400.00 0.19 75.42 4.00 %T 16 3.00

REF 4000 70.58 2000 59.65 600

3469.43	11.82	3324.17	6.96	3148.08	10.93	3011.58	17.97	2864.86	33.89
1778.96	65.80	1665.86	0.19	1591.07	1.20	1564.55	13.41	1532.94	1.29
1469.52	3.75	1439.89	9.64	1380.86	16.65	1349.81	9.28	1325.65	17.84
1256.73	13.08	1190.92	2.66	1163.64	14.94	1114.41	10.75	1047.70	29.78
1010.53	26.07	982.89	34.31	900.19	49.64	793.17	2.32	763.90	46.22
746.25	42.60	683.99	51.06	666.71	55.28	634.91	20.17	621.37	20.34
548.52	11.27	495.38	17.24	475.63	23.27	459.41	21.77	412.65	28.27

FIG. 1: IR SPECTRUM OF $[Mn(L_1)_2Cl_2)]$

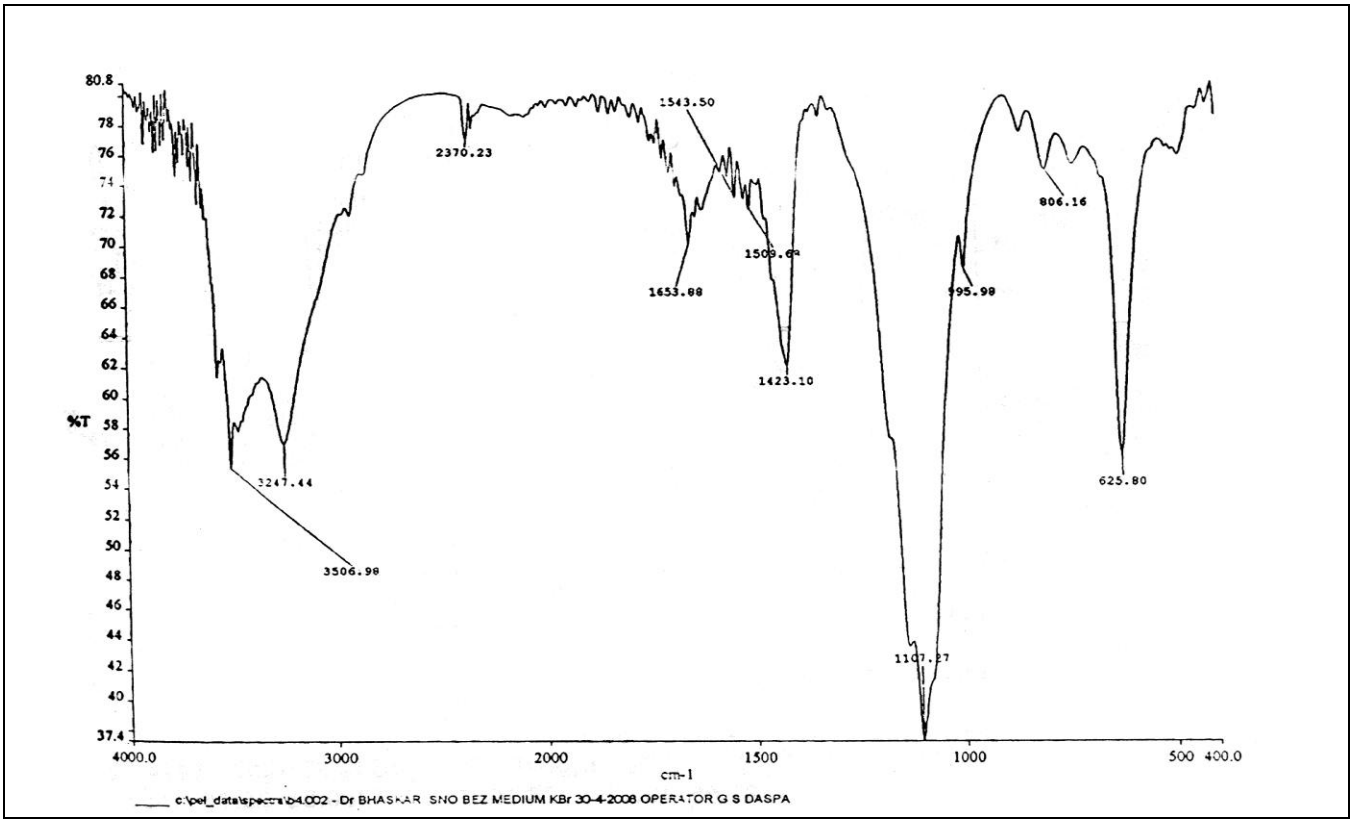


FIG. 2: IR SPECTRUM OF $[Mn(L_3)_2Cl_2]$

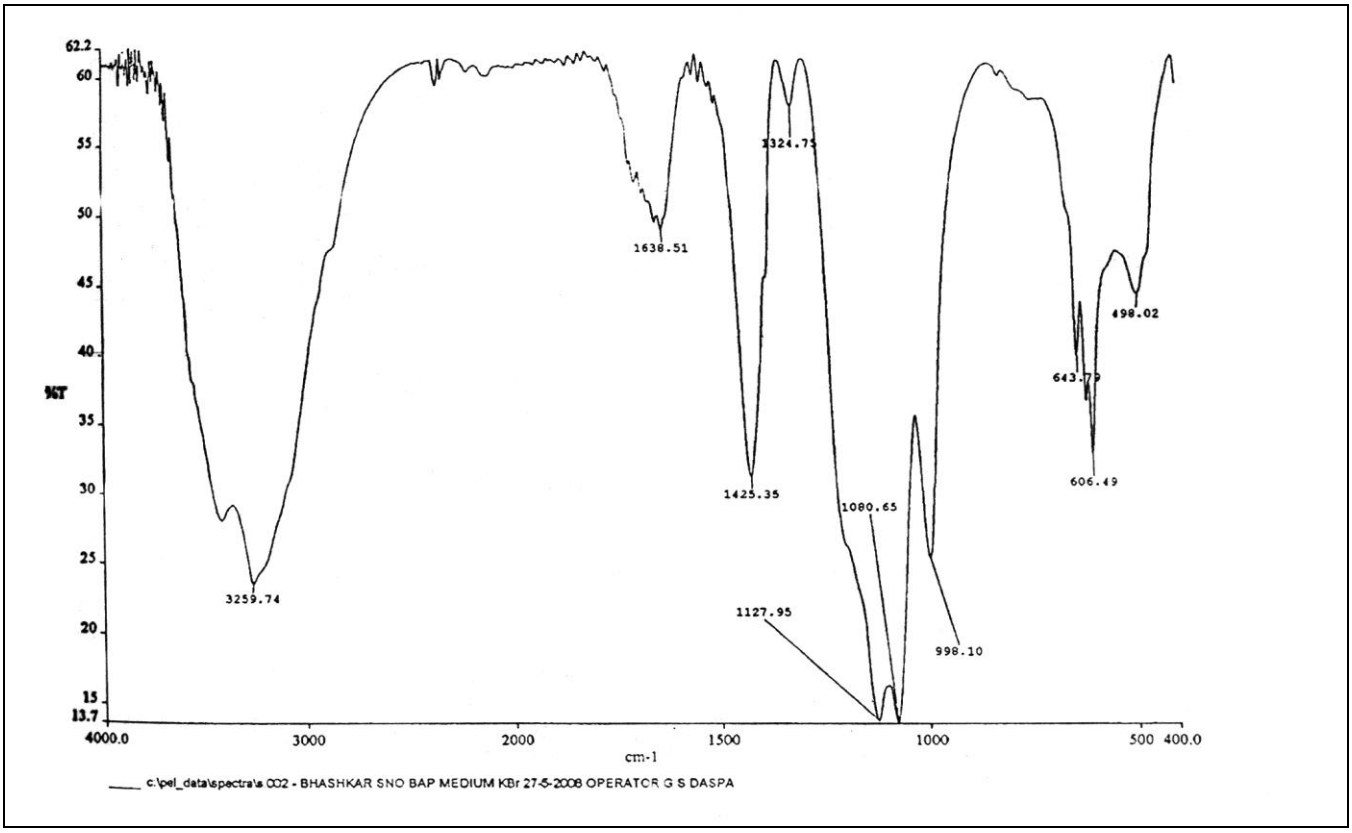


FIG. 3: IR SPECTRUM OF $[Mn(L_4)_2Cl_2]$

IR Spectral Bands due to Anions:

IR Spectra of Nitrato Complexes: The IR spectra of all the nitrato complexes show absorption bands in the region of 1464-1526 (ν_5) ν_a (NO_2, 1167-1199 (ν_1), $\nu_s(NO_2)$ and 778-806 cm^{-1} (ν_2) ν (NO). This indicates that the nitrate group coordinates in a unidentate manner.

Magnetic Moment: The magnetic moment [27-30] of all the Mn(II) complexes under study at room temperature lies in the range of 5.91 – 6.05 B.M., corresponding to five unpaired electrons (**Table 3**).

Electronic spectra of Mn(II) complexes of L1, L2, L3 and L4: The electronic spectra [31-52] of Mn(II) complexes were recorded using DMF/DMSO as a solvent and are depicted in (**Fig. 3.4-3.9**). The electronic spectral data of complexes are listed in **Table 3**.

Electronic spectra of complexes under study show bands in the region of 17637-18658 (ν_1), 18976-24652 (ν_2), 23211-29413 (ν_3), 32678-39372 (ν_4) cm^{-1} which are characteristic of distorted octahedral geometry. The assignments are obtained by fitting the observed spectra to the Tanabe-Sugano diagram. Thus these bands may be assigned to following transitions:

$^6A_1g \rightarrow {}^4T_{1g}$ (^4G) (ν_1)
$^6A_1g \rightarrow {}^4E_g$, ^4A_1g (^4G) (10B+5C) (ν_2)
$^6A_1g \rightarrow {}^4E_g$, ($^4D$) (17B+5C) ($\nu_3$)
$^6A_1g \rightarrow {}^4T_{1g}$, ($^4P$) ($\nu_4$) respectively [50-52].

TABLE 3: MAGNETIC MOMENT AND ELECTRONIC SPECTRAL DATA OF Mn(II) COMPLEXES

Complexes	μ_{eff} (B.M.)	λmax (cm^{-1})
$[Mn(L_1)_2Cl_2]$	5.92	18619, 21387, 25976, 35845
$[Mn(L_1)_2 (NO_3)_2]$	5.91	18346, 20459, 25126, 37310
$[Mn(L_2)_2Cl_2]$	5.93	18558, 21405, 26370, 36458
$[Mn(L_2)_2 (NO_3)_2]$	5.94	18385, 21349, 26793, 36539
$[Mn(L_3)_2Cl_2]$	5.98	18658, 24652, 29413, 39060
$[Mn(L_3)_2(NO_3)_2]$	5.95	18624, 22424, 27112, 39372
$[Mn(L_4)_2Cl_2]$	6.05	17642, 18976, 23211, 34723
$[Mn(L_4)_2(NO_3)_2]$	6.03	17637, 22470, 27337, 32678

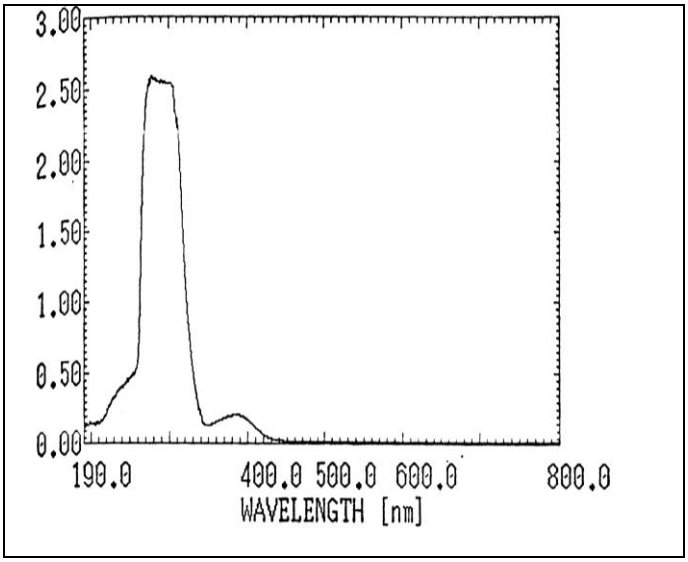


FIG. 4: ELECTRONIC SPECTRUM OF $[Mn(L_1)_2Cl_2]$

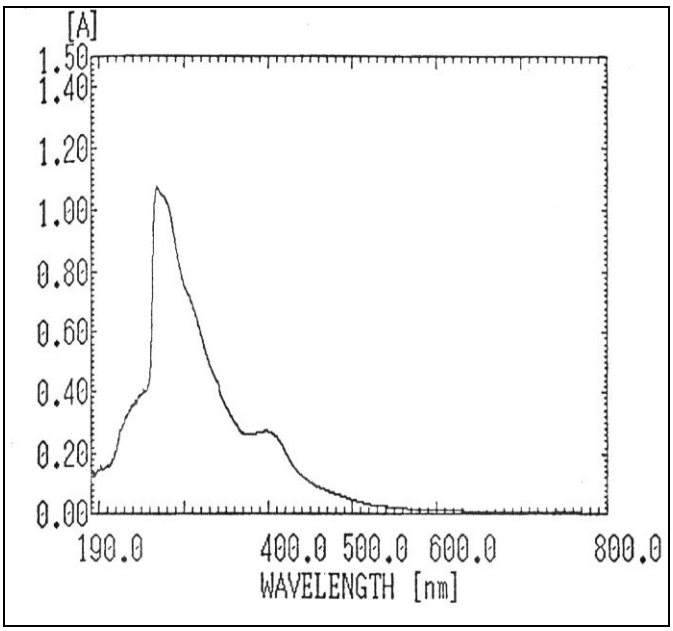


FIG. 5: ELECTRONIC SPECTRUM OF $[Mn(L_1)_2(NO_3)_2]$

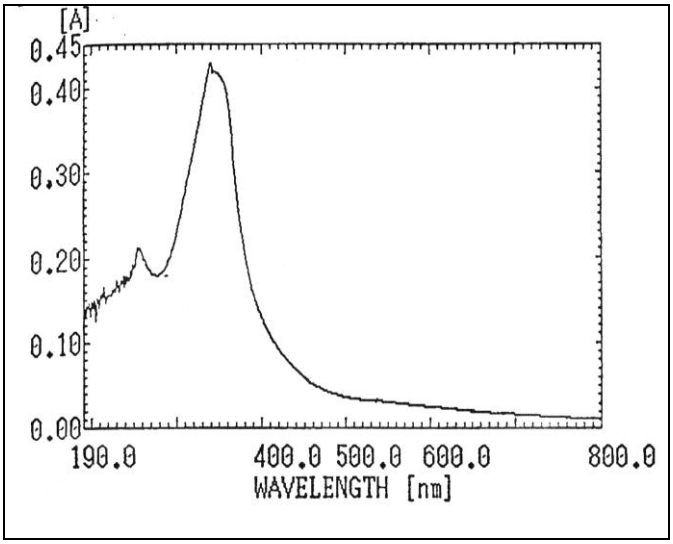


FIG. 6: ELECTRONIC SPECTRUM OF $[Mn(L_3)_2Cl_2]$

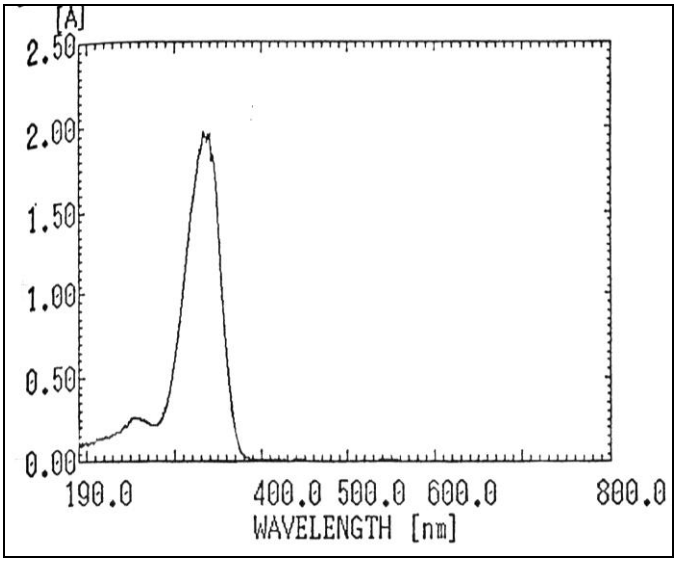


FIG. 7: ELECTRONIC SPECTRUM OF $[Mn(L_3)_2(NO_3)_2]$

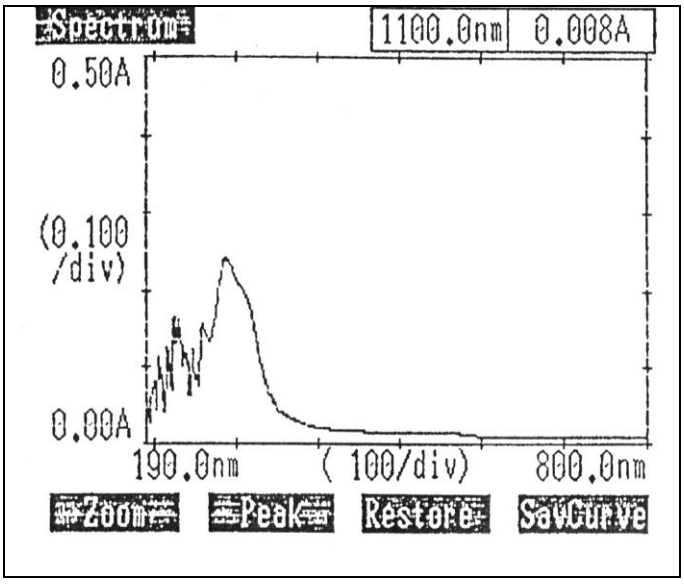


FIG. 8: ELECTRONIC SPECTRUM OF $[Mn(L_4)_2Cl_2]$

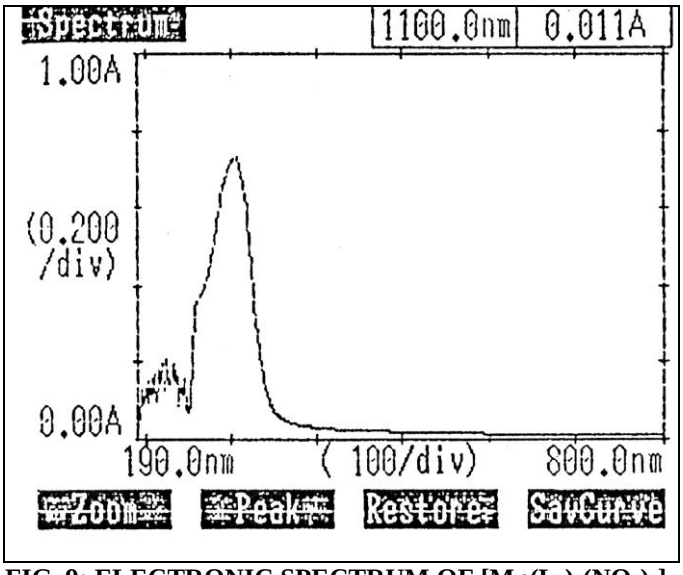


FIG. 9: ELECTRONIC SPECTRUM OF $[Mn(L_4)_2(NO_3)_2]$

Ligand Field Parameters: The experimentally observed transition energies are used to calculate the values of parameters B, C, Dq and β. The best set of values for parameters B and C could be obtained by using transitions.

6A1g → 4Eg, 4A1g (G) (10B+5C) (ν2)
6A1g → 4Eg, (4D) (17B+5C) (ν3)

This is due to the fact that the energies of these two transitions are independent of the crystal field splitting energy and depends only on parameters B and C [53]. The values for Dq could be evaluated with the help of the curve transition energy versus Dq, given by Orgel, using an energy level due to transition 6A1g → 4T1g. The value of Dq parameter could not be obtained from 6A1g → 4E1g 4A1g (4G) and 6A1g → 4Eg (4D) transition because, they have almost zero or negative slope. These transitions are independent of the Dq value (**Table 4**).

TABLE 4: LIGAND FIELD PARAMETERS OF Mn(II) COMPLEXES

Complexes	Dq	B	β	C	F_4	F_2	h_x
$[Mn(L_1)_2Cl_2]$	853	776	0.81	2725	78	1166	2.7
$[Mn(L_1)(NO_3)_2]$	840	764	0.79	2564	73	1126	3.0
$[Mn(L_2)_2Cl_2]$	850	773	0.80	2735	78	1163	2.8
$[Mn(L_2)(NO_3)_2]$	843	766	0.79	2737	78	1156	3.0
$[Mn(L_3)_2Cl_2]$	855	777	0.80	3376	96	1257	2.8
$[Mn(L_3)(NO_3)_2]$	853	776	0.80	2933	84	1196	2.8
$[Mn(L_4)_2Cl_2]$	810	736	0.76	2323	66	1066	3.4
$[Mn(L_4)(NO_3)_2]$	808	735	0.76	3024	86	1165	3.4

Racah and Slater Condon-Shortly parameters: The values of various parameters are listed in **Table 4**. Parameters B and C are linear combinations of certain coulomb's and exchange integral and are generally treated as empirical parameters obtained from the spectra of the free ions. Slater Condon-Shortly parameters F_2 and F_4 are related to the Racah parameters B and C as follows:

$$B = F_2 - 5F_4,\ C = 35F_4$$

The values of the parameters F_2 and F_4 are also listed in (**Table 4**). The electron-electron repulsion in the complexes is less than that in the free ion, resulting in an increased distance between electrons and thus an effective increase in the size of the orbitals. On increasing delocalization the value of β decreases and is less than 1 in the complexes. An estimate of β has been obtained from the nephelauxetic parameter for ligand (hx) and nephelauxetic parameters of the metal ion Km as ('1-β) = hx X Km. The values of the parameter of the metal (hx) for the complexes have been calculated using the covalency contribution of Mn(II) ions i.e. Km = 0.07, while the B corresponds to 960 cm^{-1} for the free Mn(II) ions has been used to calculate the values of β. The calculated value of β and hx indicate that the complexes under study have appreciable ionic character.

CONCLUSION: On the basis of elemental analysis, molar conductance measurements, magnetic moment, IR, electronic, and the subsequent discussion given above the following structure may be proposed for all the complexes (**Fig. 10 – 13).**

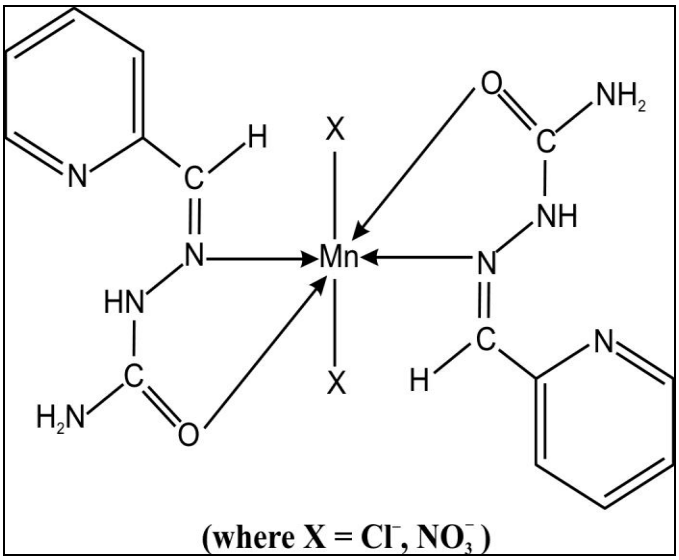


FIG. 10: Mn(II) COMPLEXES WITH LIGAND L_1

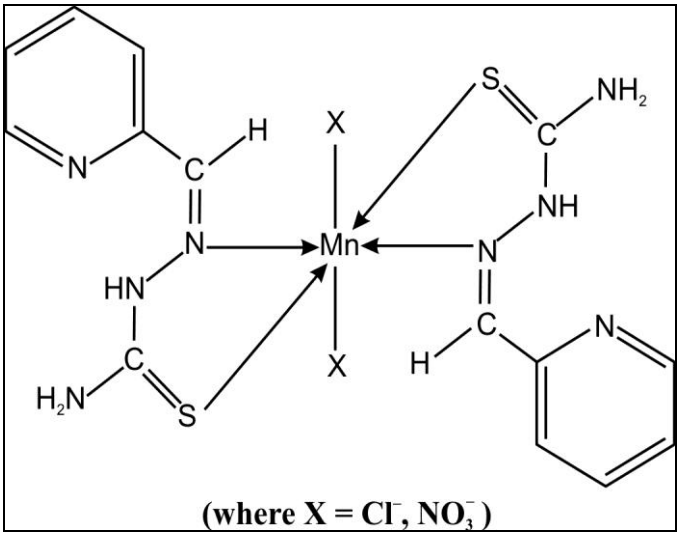


FIG. 11: Mn(II) COMPLEXES WITH LIGAND L_2

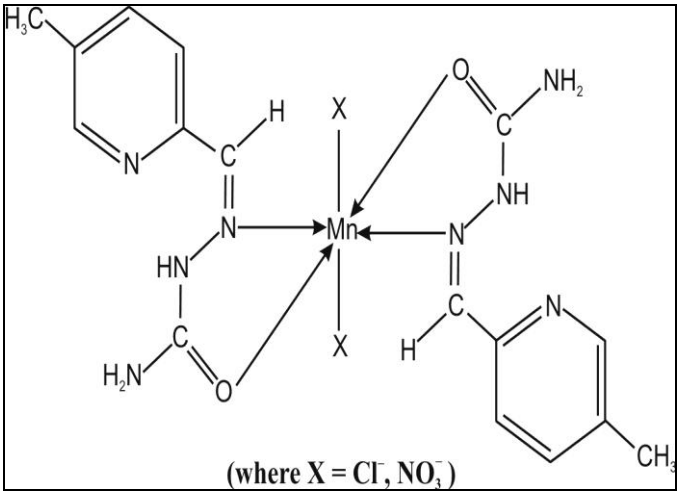


FIG. 12: Mn(II) COMPLEXES WITH LIGAND L_3

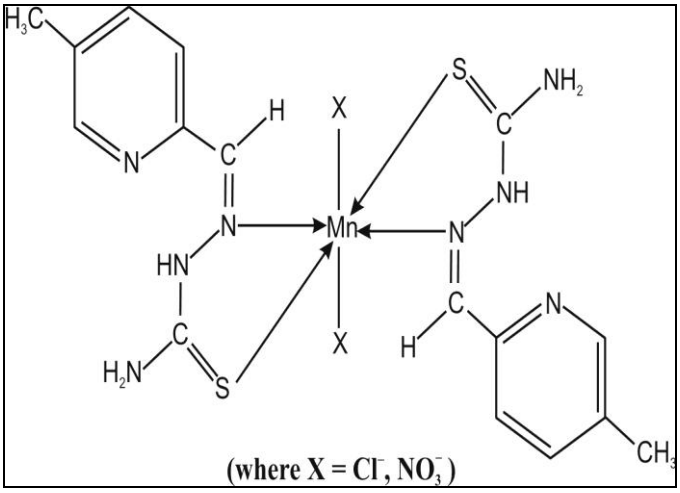


FIG. 13: Mn(II) COMPLEXES WITH LIGAND L_4

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