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Original Research Article

Spectral and Biological Studies of Manganese Complexes with Macrocyclic Ligand

Dr. Neelam Kumari[1*], Pratibha[2]
[1]Associate Professor, Department of Chemistry, Meerut College, Near Commissioner Office, Western Kutchery Rd, Meerut, Uttar Pradesh, India
[2]Department of Chemistry, Mewar University, NH - 79, Gangarar, Rajasthan, India

***Corresponding author:** Dr. Neelam Kumari
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Abstract

A novel family of macrocyclic complexes with tetra aza macro cyclic ligand and ($X=Cl^-$, NO_3^-) have been synthesized and characterized by elemental analysis, IR, electronic, and EPR spectral studies. The molar conductance measurements of the complex in Dimethyl sulphoxide (DMSO)/dimethyl form amide corresponds to non-electrolytes for all the Mn(II) complexes except the complex with ligand LA which are 1:2 electrolyte. The spectra are consistent with the formula [$MnLx_2$] and [Mn (LA) $(H_2O)_2$] X2 and distorted octahedral geometry. The biological activity of these complexes was evaluated against different species of bacteria and plant pathogenic fungi and compared with different ligands.
Keywords: Macrocyclic complex, IR, magnetic moment, antibacterial antifungal activity.

INTRODUCTION

Manganese and its compounds are widely used metallurgical processes and paint, pigments industry and in analytical chemistry. Manganese complexes (II) with macrocyclic Schiff base ligands play an excellent role in catalytic property [1-4]. Adsorption of organic matter into soil such as lignin is an important process that influences transport and toxicity of metals in natural systems [5-8]. The great interest towards the manages (II) co-ordination compounds in adsorption into soil is because these are very abundant in soil and are essential for plant growth. In soil, these are formed by bio-degradation of lignin [9], Manganese [10] metal has a well-established importance in the field of biology and medicine. A lot of articles are available on the physiology and biochemistry of manganese [11]. Ruminants manganese is present in the serum of blood as manganese (III) β-globulin and in erythrocytes as manganese porphyrin ring. DNA and RNA polymerases [12] catalyze the replication and transcription of DNA and have a specific requirement for Mn(II). The binding of Mn(II) ions in these enzymes has been characterized by the EPR studies. Under certain conditions, manganese ions mediate the degradation of DNA, in the presence of O2, in vitro [13]. In view of the above applications, it is highly desirable to synthesize and characterize Mn (II) complexes of multidentate macrocyclic ligands.

MATERIALS AND METHODS

All the chemicals were used of Anala R grade and received from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and used as received.

Synthesis of Ligands
Ligand LA

Hot ethanolic solution (50 mL) of diethyloxalate (7.30 g, 0.05 mol) and a hot ethanolic solution (50 mL) of 1,3-diaminopropane (3.70 g, 0.05 mol) were mixed slowly with constant stirring. This mixture was refluxed at 80°C (+-5°C) for 6h in the presence of few drops of concentrated hydrochloric acid. On cooling, white coloured precipitate was formed. It was filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10} Yield 78%, m.p. 240°C.

Ligand LB

Hot ethanolic solution (50 mL) of diethyloxalate (7.30 g, 0.05mol) and a hot ethanolic solution (50 mL) of 2, 6-diaminopyridine (5.46 g, 0.05 mol) were mixed slowly with constant stirring. This mixture was refluxed at 75^0C (+_30C) for 9h in the presence of few drops of concentrate hydrochloric acid. On cooling, dull white colored precipitate was formed. It was filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10}- Yield 75%, m.p. 269°C.

Ligand LC

Hot ethanolic solution (50 mL) of ethylcinnamate (8.80 g, 0.05 mol) and a hot ethanolic solution (50 mL) of 1,3-diaminopropane (3.70 g, 0.05 mol) were mixed slowly with constant stirring. This mixture was refluxed at 72^0C for 6h in the presence of few drops of concentrated hydrochloric acid. On cooling, cream coloured precipitate was formed. It was filtered, washed with cold EtOH, and dried under vacuum over $P4O_{10}$. Yield 80%, m.p.271°C.

Synthesis of complexes

A hot ethanolic solution (20 mL) of the ligand L (0.002 mol; L = LA: 0.512g; LB: 0.652g; LC; 0.816g;) and hot ethanolic solution (20 mL) of corresponding Mn(II) salt (0.001 mol) were mixed together with constant stirring. The mixture was refluxed for 5-8h at 75-85°C. On cooling, colored complex was precipitated as filtered, washed with cold EtOH and dried under vacuum over P_4O_{10}. The mixture was refluxed for 20h at 40^0C. On cooling colored complex was precipitated out. Which was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10}

Results and Discussion

Composition of complexes were assigned as per data obtained from elemental analysis. The molar conductance measurements of the complexes in dimethylsulphoxide (DMSO) / dimethylformamidc (DMF) correspond to non-electrolytic nature of all Mn(II) complexes, except the complexes with the ligand LA, which are shown to be 1:2 electrolytes. Thus these complexes may be formulated as [Mn(L)X2] and [Mn(LA)(H2O)2]X2, respectively. [Where L – LB, LC, X = $Cl^-$and $NO3^-$].

Mass Spectra of the Ligands

The electron impact mass spectra of the ligands (LA, LB and LC) have been recorded.

Ligand LA

The electron impact mass spectrum of ligand LA shows a molecular ion peak at 255 amu, corresponding to the macrocyclic moiety $(C_{10}H_{16}N_4O_4)$+ and a series of peaks, due to different fragments, at 42, 56, 72, 128, 184 and 200 amu.

Ligand LB

The electron impact mass spectrum of ligand LB shows a molecular ion peak at 326 amu, corresponding to the macrocycle [$(C_{10}H_{16}N_6O_4)$, atomic mass 326 amu] and a number of peaks at 32, 56, 107, 163 and 270 amu, corresponding to the various fragments of the ligand LB.

Ligand LC

Presence of a peak at 409 amu, in the electron impact mass spectrum of the ligand LC, confirms the proposed formula for LC [$(C_{24}H_{32}N_4O_2)$, atomic mass 408 amu]. The peaks due to other fragments appear at 72, 77, 104, 132, 190, 204, 232 and 276 amu.

Magnetic Moments

The complexes show magnetic moment, at room temperature, corresponding to five unpaired electrons (5.89-6.03 B.M.).The values of magnetic moment are close to the spin only value i.e. 5.92 B.M.

Infrared Spectra

Infrared Spectra of the Ligands

The IR spectra of the ligands LA, LB and LC do not show any band around 3400 cm-1 indicating the absence of free primary diamine and hydroxyl group, which suggests the complete condensation of keto group with amino group Appearance of three new bands in the IR spectra of the ligands, in the region 1635-1651, 1518, 1226, 762-779 cm-1, which are corresponding to amide I [v(C=O)], amide II [v(C-N) + δ(N-H)] and amide III [δ(N-H)], respectively [14-15]. Another band, which appears in the IR spectrum of ligand LB at 1456 cm-1 is due to the pyridine ring, supporting the macrocyclic nature of the ligand. Non-shifting of this band, on complex formation, suggests the non-involvement of pyridine nitrogen atom in co-ordination. In the IR spectra of ligands LC the bands at 730-770 is due to the presence of phenyl ring in the macrocycle [16].

IR Spectral Bands due to Anions

Infra-red spectra of all the nitrate complexes with ligands LB and LC display three (N-O) stretching bands in the range 1418-1434 cm-1 (v5), 1302-1315 cm-1 (v1) and 1004-1016 cm-1 (v2). The separation of two highest frequency bands (v5-v1) is 116-119 cm-1, suggests that both nitrate groups are coordinated to the central metal ion as an unidentate manner. However, the IR spectrum of Mn(II) nitrate complex, with ligand LA, display a sharp strong band at 1383 cm-1, which suggests that both nitrate groups in this complex are uncoordinated [17]. In the complexes of ligand LA appearance of a broad band ~3415-3447cm -1 appears, which is a characteristic of-OH group, indicates that the water molecules are coordinated to the metal ion. Thus, the general formula of the complexes with LA ligand may be postulated as $[Mn(LA)(H_2O)_2]X_2$. The presence of water molecules in these complexes has been confirmed by the mass spectra and microanalysis.

Electronic spectra

In the high-spin octahedrally coordinated Mn(II) complexes, the lowest configuration (t2g)3 (eg)2 gives rise to the ground state 6A1g. Since this is the only sixtet level present, all the absorption bands must, therefore, be spin forbidden transitions. Electronic spectra of Mn(II) complexes gives four weak intensity bands in the range -18051-20132 cm-1 (V1), ~22553-24631 cm-1 (v2), ~27993-29975 cm-1 (v3) and ~33003-38610 cm-1 (v4). These bands are characteristic of an octahedral environment around

Mn(II) ion. These bands may be assigned to the following transitions

6A1g → 4T1g v1
6A1g → 4Eg
4A1g (4G) (10B + 5C) v2
6A1g → 4Eg (4D) (17B + 5C) v3
6A1g → 4T1g (4P) (7B + 7C) v4, respectively.

The experimentally observed transition energies and calculated values for various ligand field parameters are shown in Table-4 The value of parameter B and C were calculated from the transition 6Alg → 4Eg 4A]g (4G) and 6A1g -> 4Eg (4D), because these transitions are free from the crystal field splitting and depend on B and C parameters, only [18]. The values of Dq were obtained with the help of curve, transition energies vs. Dq, as given by Orgel [15] using the energy due to the transition 6A1g → 4T1g (4G). Parameters B and C are linear combinations of certain coulombs and exchange integral and are generally treated empirical parameters obtained from the spectra of the free ions. Slater Condon-shortly repulsion parameters F2 and F4 are related to Racah parameters [19] B and C as B = F2 - 5F4 and C = 35F4 The electron- electron repulsion in the complexes is more than in the free ion, resulting in an increased distance between electrons and thus affects the size of the orbital. On increasing delocalization, the value of p decreases up to less than one in the complexes. The value of p can be calculated from the Nephelauxetic parameter for the ligand (hx) and the Nephelauxetic parameter for the metal ion (km) as (1 - β) = hx X km. The value of the parameter hx for Mn(II) complexes have been calculated by using the co-valency contribution of Mn(II), while for the calculation of β, we used the numerical value of B for Mn(II) free ion which is 786 cm-1 [20].

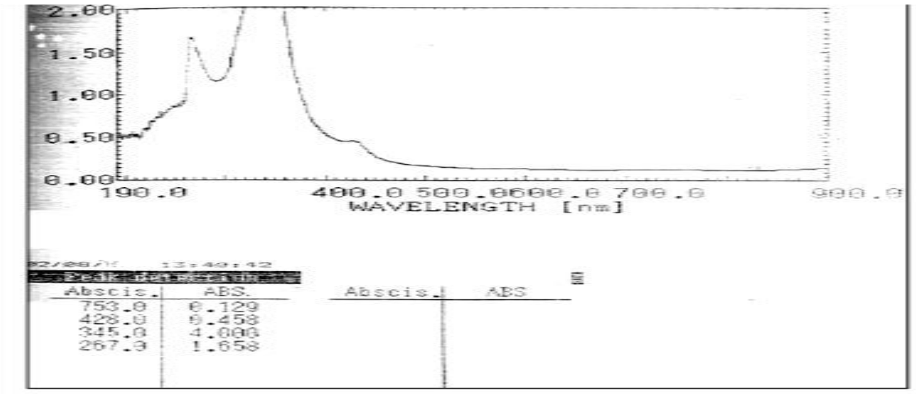

Fig-1: Electronic spectrum of $[Mn(LA)(H_2O)_2]Cl_{l2}$
X=Cl^- and NO_3^-

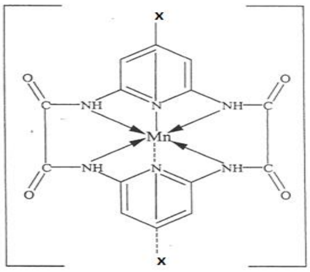

Fig-2: Complexes with the ligand LA

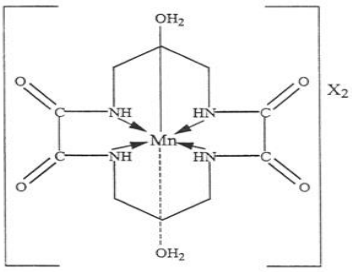

Fig-3: Complexes with the ligand LB

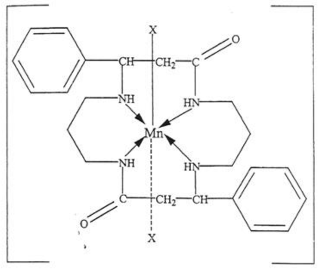

Fig-4: Complexes with the ligand LC

Table-1: molar conductance and elemental analysis of the ligand

Complexes	M.W. amu	Molar Cond. Ω⁻¹cm² mol⁻¹	Color	Yield %	M.P. (°C)	Elemental analyses %, Found (Calculated %)			
						Cr	C	H	N
LA $C_{10}H_{16}N_4O_4$	256	-	White	78	240	-	46.78 (46.86)	6.19 (6.25)	21.79 (21.88)
LB C14$H_{10}N_6O_4$	326	-	Dull white	75	269	-	51.62 (51.53)	3.16 (3.07)	25.65 (25.77)
LC $C_{24}H_{32}N_4O_2$	408	-	Cream	80	271	-	70.49 (70.59)	7.72 (7.84)	13.63 (13.72)

Table-2: molar conductance and elemental analysis of the complexes

Complexes	M.W. amu	Molar Cond. Ω⁻¹cm₂mol⁻¹	Colour	Yield %	M.P. (°C)	Elemental analyses % Found (Calculated %)			
						Mn	C	H	N
$[Mn(LA)(H_2O)_2]Cl_2$ $MnC_{10}H_{20}N_4O_6$Cl2	418	229	Light pink	78	269	13.09 (13.16)	28.65 (28.71)	4.70 (4.78)	13.33 13.33 (13.40)
$[Mn(LA)(H_2O)_2](NO_3)_2$ $MnC_{10}H_{20}N_6O_{12}$	471	235	Pale pink	68	265	11.61 (11.68)	25.37 (25.48)	4.19 (4.25)	17.91 (17.83)
$[Mn(LB)Cl_2]$ $MnC_{14}H_{10}N_6O_4Cl_2$	452	12	Light brown	71	277	12.27 (12.17)	37.27 (37.17)	2.19 (2.21)	18.52 (18.58)
$[Mn(LB)(NO_3)_2]$ $MnC_{14}H_{10}N_8O_{10}$	505	10	Light gray	65	281	10.97 (10.89)	33.22 (33.27)	1.96 (1.98)	22.10 (22.18)
$[Mn(LC)Cl_2]$ $MnC_{24}H_{32}N_4O_2Cl_2$	534	11	Brown	64	291	10.38 (10.30)	54.00 (53.93)	5.90 (5.99)	10.56 (10.49)
$[Mn(LC)(NO_3)_2]$ $MnC_{24}H_{32}N_6O_8$	587	13	Brown	59	285	9.28 (9.37)	48.98 (49.06)	5.36 (5.45)	14.41 (14.31)

Table-3: Magnetic moment of the complexes

Complexes	μ_{eff}.(B.M.)
$[Mn(LAXH_2O)_2]Cl_2$	5.89
$[Mn(LA)(H_2O)_2](NO_3)_2$	5.93
$[Mn(LB)Cl_2]$	5.96
$[Mn(LB)(NO_3)_2]$	5.89
$[Mn(LC)Cl_2]$	5.95
$[Mn(LC)(NO_3)_2]$	5.97

Table-4: Electronic spectra of the complexes

Complexes	$\lambda_{max}(cm^{-1})$
$[Mn(LA)(H_2O)_2]Cl_2$	18349, 22883, 28329, 38462.
$[Mn(LA)(H_2O)_2](NO_3)_2$	19685, 23474, 28011, 38610.
$[Mn(LB)Cl_2]$	20018, 24102, 28860.
$[Mn(LB)(NO_3)_2]$	20132, 24198, 28678.
$[Mn(LC)Cl_2]$	18051, 24155, 32680.
$[Mn(LC)(NO_3)_2]$	18587, 24570, 29412, 33003.

Table-5: ligand field parameter of the complexes

Complexes	Dq (cm^{-1})	B	β	C (cm^{-1})	F_4	F_2	h_x	v_2/v_1
$[Mn(LA)(H_2O)_2]Cl_2$	1835	778	0.98	3020.10	86.30	1209.50	0.29	1.25
$[Mn(LA)(H_2O)_2](NO_3)$	1968	648	0.82	3398.50	97.10	1133.65	2.57	1.19
$[Mn(LB)Cl_2]$	2002	680	0.86	3460.98	98.88	1174.11	2.00	1.20
$[Mn(LB)(NO_3)_2]$	2013	640	0.81	3559.60	101.70	148.50	2.71	1.20
$[Mn(LC)Cl_2]$	1805	-	-	-	-	-	-	1.34
$[Mn(LC)(NO_3)_2]$	1859	672	0.85	3570.58	102.02	1181.72	2.14	1.32

Table-6: EPR spectra of the complexes

Complexes	Recorded as polycrystalline Sample g_{iso}	Recorded in DMF Solution A^0
$[Mn(LA)(H_2O)_2]Cl_2$	1.9656	109.5760
$[Mn(LA)(H_2O)_2](NO_3)_2$	1.9992	102.5000
$[Mn(LB)Cl_2]$	1.9986	121.6667
$[Mn(LB)(NO_3)_2]$	2.0014	119.6667
$[Mn(LC)Cl_2]$	2.0739	112.1678
$[Mn(LC)(NO_3)_2]$	2.0080	105.0000

Antimicrobial screening

The ligands LA, LB and LC and their Mn(II) complexes were evaluated against different species of bacteria and plant pathogenic fungi [21-27]

Antibacterial Activity

The antibacterial action of the ligands and the complexes of Mn(II) was checked by the disc diffusion technique [28]. This was done on *Sarcina lutea* (Gram positive) and *Escherchia coli* (Gram negative) bacteria at 38°C. The disc of filter paper no. Whatman-4, with the diameter 6 mm, were shocked in the solution of compounds in DMSO/DMF (1.0 mg/cm-1). After drying, it was placed on nutrient agar plates. The inhibition areas were observed after 48h. DMSO/DMF was used as a control and Gentamycin as standard drug.

The bacterial growth inhibition capacity of the ligands and Mn(II) complexes follow the order LC>LB>LA, given in the Table7 100% growth of bacteria which is represented as +, 50% growth by ++, less than 50% by +++ and noble inhibition by ++++ .

Antifungal Activity

The antifungal activity of the macrocyclic ligands and its Mn(II) complexes, reported here, was checked by agar plate technique [29] for *Aspergillus niger* and *Aspergillus glaucus* fungi. The compounds were directly mixed with medium in different concentrations. The fungus 124 was placed in the medium with the help of an inoculums needle. The pattri dishes were wrapped in polythene sheets, containing few drops of EtOH and kept in incubator at 32°c ± 3°c for 75-90 hours. The growth of fungus was measured by the recording of diameter of fungal colony. The following relation calculate the fungal growth inhibition.

Table-7: Antibacterial activity of the complexes

Complexes	Bacterial growth inhibition in %	
	Sarcina luteea	*Escherchia coli*
$[Mn(LA)(H_2O)_2]Cl_2$	+	++
$[Mn(LA)(H_2O)_2](NO_3)_2$	+	+
$[Mn(LB)Cl_2]$	++	+
$[Mn(LB)(NO_3)_2]$	+	++
$[Mn(LC)Cl_2]$	++	++
$[Mn(LC)(NO_3)_2]$	++	++

Table-8: Antifungal activity of the complexes

Complexes	Antifungal growth inhibition in %	
	A. niger	*A. glaucus*
$[Mn(LA)(H_2O)_2]Cl_2$	**	*
$[Mn(LA)(H_2O)_2](NO_3)_2$	*	**
$[Mn(LB)Cl_2]$	**	*
$[Mn(LB)(NO_3)_2]$	*	*
$[Mn(LC)Cl_2]$	**	**
$[Mn(LC)(NO_3)_2]$	***	***
$[Mn(LD)Cl_2]$	***	***
$[Mn(LD)(NO_3)_2]$	**	***
$[Mn(LE)Cl_2]$	**	**
$[Mn(LE)(NO_3)_2]$	**	**

Fungal growth inhibition % = (A-B) X 100/A,

Where,
A = Diameter of fungal colony in control plate,
B = Diameter of fungal colony in test plate.

The results of antifungal activity are shown in Table8 100% growth of fungus which is represented as, 50%growth by, less than 50% growth by *** and * excellent inhibition by ****. The complexes show the fungal inhibition in the order LC>LA>LB.

Conclusion

On the basis of elemental analysis, molar conductance measurements, magnetic moment susceptibility, infra-red, electron impact mass, electronic and EPR spectral studies, all the complexes of Mn(II), under study were found to possess an octahedral geometry. The assigned structures of the complexes.

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