

## MN (II) Complexes: Synthesis and Spectral Studies with Aza-Macrocyclic Ligand

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**ABSTRACT**

The complexes of Mn(II) were synthesized with the new aza-macrocyclic ligand. The ligand was prepared by the reaction of 3-ethyl-2,4-pentadione and 2,6-diamino-pyridine. All the complexes have been found to have general composition  $[M(L)X_2]$  [where  $M = Mn(II)$  and  $X = Cl, NO_3$ ]. All the complexes are characterized by the conductance measurements, magnetic susceptibility measurements, mass, I.R, EPR and electronic spectral studies. An octahedral geometry was assigned for Mn(II) complexes.

**Key word:** Mn(II), 2,6-diaminopyridine, 3-ethyl-2,4-pentadione, EPR, IR

**INTRODUCTION**

The chemistry of macrocyclic polyamine ligands having functional pendent arms has a great interest in research field in recent years. Mainly as the metal complex of such ligands are effective models for protein metal binding sites in metalloprotein in some biological system as potential therapeutic reagents or as multi electron catalysts. Manganese is a constituent and an activator of several enzymes and proteins in plants, animals and humans. Manganese is an essential trace element that occurs in the cells of all living creatures. Manganese and its compounds are widely used in analytical processes, metallurgical processes paint and pigments industry. [1-16].

In view of the above in the present paper we report the synthesis and spectroscopic characterization of Mn(II) with a aza- macrocyclic ligand.

**EXPERIMENTAL**

All the chemicals used were of AR grade and procured from Fluka and Sigma Aldrich. Metals salts were purchased from Emerck and were used as received.

**PREPARATION OF LIGAND**

Preparation of ligand has been discussed in previous paper [16].

**Preparation of Complexes**

A hot ethanolic solution of the manganese salt (0.002 mol) and hot ethanolic solution of corresponding ligand (0.001 mol) were mixed together with constant stirring. The mixture was refluxed for 5 to 7 hrs at

70-80°C. On cooling, coloured complex was precipitated out. It was filtered, washed with cold ethanol and dried under vacuum over P<sub>4</sub>O<sub>10</sub>.

## RESULT AND DISCUSSION

Characterization of ligand has been discussed in previous paper.

Characterization of the complexes On the basis of elemental analysis, the complexes were assigned to possess the composition as shown in Table 1. The molar conductance measurements of the complexes in DMSO, correspond to non-electrolyte nature. Thus these complexes are formulated as [Mn(L)X<sub>2</sub>] [M = Mn(II), X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>].

The IR spectra of nitrate complexes with ligand L show absorption bands in the region 1410-1430 (ν<sub>5</sub>), 1305-1315 (ν<sub>1</sub>) and 1010-1035 cm<sup>-1</sup> (ν<sub>2</sub>). This indicates that nitrate group is coordinated to the metal ion as an unidentate fashion].

## MAGNETIC MOMENT AND ELECTRONIC SPECTRAL STUDIES

Electronic spectra of Mn(II) complexes, under study show absorption bands in the range of 15798-19120 (ν<sub>1</sub>), 22573-23529 (ν<sub>2</sub>), 23310-28328 (ν<sub>3</sub>) and 27933-18167 cm<sup>-1</sup> (ν<sub>4</sub>) which is characteristics to an octahedral geometry.

The ESR spectra of the complexes were recorded as polycrystalline sample and in solution of DMSO. [Table 3] [17-37].

On the basis of elemental analysis, molar conductance measurements, magnetic moment susceptibility, IR, electronic and EPR spectral studies, all the complexes of Mn(II) under study were found to possess an octahedral geometry .

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**Table – 1**  
Molar Conductance and Elemental Analysis

Complexes	Colour	Molar cond. $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Yield (%)	M.P. ( $^{\circ}\text{C}$ )	Elemental analysis found (calculated) (%)			
					Mn	C	H	N
[Mn(L)Cl <sub>2</sub> ] MnC <sub>24</sub> H <sub>30</sub> N <sub>6</sub> Cl <sub>2</sub>	Light Brown	13	58	290	10.38 (10.40)	58.60 (54.54)	5.64 (5.68)	15.86 (15.90)
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ] MnC <sub>24</sub> H <sub>30</sub> N <sub>8</sub> O <sub>6</sub>	Light Brown	11	55	286	9.46 (9.93)	49.56 (49.73)	5.12 (5.16)	14.39 (14.45)

**Table 2**  
Magnetic Moment and Electronic spectral data of the complexes

Complex	$\mu$ eff (B.M.)	$\lambda$ max ( $\text{cm}^{-1}$ )
[Mn(L)Cl <sub>2</sub> ]	6.02	19120,23529,28328,38167
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	5.98	14970,15798,22573,23310,27933

**Table 3**  
EPR Spectral data of the Mn(II) Complexes

	$g_{\parallel}$	$g_{\perp}$	$g_{\text{iso}}$
[Mn(L)Cl <sub>2</sub> ]	2.0192	2.2115	2.2115
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	2.1458	2.2405	2.1458

**Table4**  
Ligand Field Parameters Of Mn(II) Complexes

Complexes	Dq ( $\text{cm}^{-1}$ )	B ( $\text{cm}^{-1}$ )	$\beta$	C ( $\text{cm}^{-1}$ )	F <sub>4</sub>	F <sub>2</sub>	$h_x$
[Mn(L)Cl <sub>2</sub> ]	1912	685.57	0.8722	3334.65	95.27	1161.94	1.8257
[Mn(L)(NO <sub>3</sub> ) <sub>2</sub> ]	1579	660.43	0.8402	3341.14	95.46	1137.74	2.2823