International Journal of Education and Science Research Review
ISSN 2348-6457
Volume-1, Issue-1
February- 2014
www.ijesrr.org
Email- editor@ijesrr.org

Spectral Studies Of Mn (II) Complexes with a New Tetraaza-Macrocyclic Ligand

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ABSTRACT
The complexes of Mn(II)) were synthesized with the new aza-macrocyclic ligand. The ligand [Ligand L: [2,6,12,16,21,22-hexaaza, 3,4,5,13,14,15-hexamethyltricyclo,[15,3,1,I^{7-11}] docosa1(2,10,2,5,7,9,11-(22), 12,15,17,19-decanene]was prepared by the reaction of 3-methyl-2,4-pentadione and 2,6diamino-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 WORDS
Spectroscopic, EPR, Mn(II), 2,6-diaminopyridine, 3-methyl-2,4-pentadione.

INTRODUCTION

Manganese is a constituent and an activator of several enzymes and proteins in plants, animals and humans**. Crowely et al [1]** reviewed Mn-containing and Mn-dependent enzymes and proteins, including their structures, functions and distribution. Mn^{n+} the active sites of enzymes can catalyze a wide variety of different reactions. Besides normal metabolic functions, numerous pathologies of this trace element can occur as a consequence of its deficiency or excess in plants, animals and humans. Thus manganese acts as an essential nutrient and as a toxicant. In humans, the range between deficiency and toxicity of manganese is narrow.
Manganese and its compounds are widely used in analytical processes, metallurgical processes paint and pigments industry. **[2-16]**.

In view of the above in the present paper we report the synthesis and spectroscopic characterization of Mn(II) with a nitrogen donor macro cyclic 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 legend 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^{0}C. On cooling, colored complex was precipitated out. It was filtered, washed with cold ethanol and dried under vacuum over P_4O_{10}.

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 $[Mn(L)X_2]$ [M = Mn(II), X = Cl^-, NO_3^- .]

The IR spectra of nitrato complexes with ligand L show absorption bands in the region 1414-1430 (ν_5), 1301-1316 (ν_1) and 1010-1038 cm^{-1} (ν_2). 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 18518- 20161 (ν_1)**,** 22573-24213 (ν_2)**,** 28011-28901 (ν_3) and 33003-36900 cm^{-1} (ν_4) 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 **.**

Acknowledgements

We are thankful to the UGC New Delhi for financial assistance and IIT Mumbai for recording EPR spectra.

Table – 1

Molar Conductance and Elemental Analysis

Complexes	Colour	Molar cond. $\Omega^{-1}cm^2mol^{-1}$	Yield (%)	M.P. (^0C)	Elemental analysis found (calculated) (%)			
					Mn	C	H	N
$[Mn(L)Cl_2]$ $MnC_{22}H_{26}N_6Cl_2$	Brown	09	64	282	10.88 (10.98)	52.79 (52.80)	5.18 (5.20)	16.71 (16.80)
$[Mn(L)(NO_3)_2]$ $MnC_{22}H_{26}N_8O_6$	Brown	12	60	278	9.94 (9.93)	42.72 (47.73)	3.81 (4.70)	15.13 (15.18)

Table 2.

Magnetic Moment and Electronic spectral data of the complexes

Complex	μ eff (B.M.)	λ max (cm^{-1})
$[Mn(L)Cl_2]$	5.92	18518,22573,28011,33003
$[Mn(L)(NO_3)_2]$	5.96	20161,24213,28901,36900

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

	g_{II}	$g_{\perp}$	g_{iso}
$[Mn(L)Cl_2]$	2.1102	2.2115	2.1439
$[Mn(L)(NO_3)_2]$	2.2190	2.2894	2.2424

Table4.

Ligand Field Parameters Of Mn(II) Complexes

Complexes	Dq (cm^{-1})	B (cm^{-1})	β	C (cm^{-1})	F_4	F_2	h_x
$[Mn(L)Cl_2]$	1851	776.85	0.9883	2961.00	84.60	1199.85	0.1657
$[Mn(L)(NO_3)_2]$	2016	669.71	0.8520	3503.18	100.09	1170.16	2.1142

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