

# Synthesis, Physicochemical Studies and Structure Determination of Some Novel Manganese (III) Complexes of Azo Dyes Derived from 4-Aminoantipyridine

M. L. Harikumaran Nair, K. P. Lalitha

Department of Chemistry, University College, Thiruvananthapuram- 695 034, Kerala, India

**Abstract-** Some novel manganese(III) complexes with the ligand 2,3-dimethyl-1-phenyl-4-(3-methoxy-2-phenyl azo)5-pyrazolone, GAAP, guaiacol azoantipyridine, L, having the formulae  $[Mn(L)_2(X)_3]$ ,  $[Mn(L)_2(Y)_2Cl]$ , where  $X = Cl^- / NO_3^- / ClO_4^-$ ;  $Y = NCS^-$  were synthesized and characterized by elemental analysis, molar conductance and magnetic susceptibility measurements and spectral (IR, UV-Visible, FAB-mass) studies. The ligand was characterized by elemental analysis and spectral (IR, UV-Visible,  $^1H$ NMR,) studies. The X-ray diffraction study of the complex  $[Mn(L)_2(Cl)_3]$  indicated that it is not perfectly crystalline. The electrochemical properties of the complex  $[Mn(L)_2(Cl)_3]$  was investigated by cyclic voltammetry. Based on elemental analyses, thermo gravimetric and FAB-mass studies of the complexes a seven coordinate structure is tentatively proposed for the complexes.

**Index Terms-** Manganese (III), azo dye, thermal analysis, FAB-mass

## I. INTRODUCTION

There has been considerable interest in the coordination chemistry of manganese involving nitrogen and oxygen donor ligands due to increasing recognition of the role of this metal in biological systems. Manganese often plays an important role in numerous biological process associated with utilization or generation of hydrogen peroxide or dioxygen. At least five functions of these types are known, viz., manganese superoxide dismutase, manganese catalase, manganese peroxidase, manganese rib nucleotide reductase and oxygen evolving complex in photosystem-II. This has prompted recent attempts to understand the coordination chemistry of Mn(III) ions, which are believed to play a role in at least three of the above enzymes: manganese superoxide dismutase[1], manganese catalase and oxygen evolving complex in photosystem-II. These The ground state for manganese(III) is  $t_{2g}^3e_g^1$  or  $^5E_g$  and has a term symbol  $^5D$ . Because of the odd electron in  $e_g$  in octahedral surrounding manganese(III) is subject to Jahn-Teller distortion. Considerable elongation of the two trans bonds with little difference in the length of the other four has been observed in many Mn(III) complexes[2]. For a  $d^4$  state, only one spin allowed transition is to be expected. The transition is  $^5E_g \rightarrow ^5T_{2g}$  and is in the visible region. This usually appears as a broad band near  $20000\text{ cm}^{-1}$  which accounts for the red brown color of manganese(III) complexes Mn(III) forms a wide range of geometries – 6,4,5,7 or

even 8 coordinated complexes. Azo dyes play an important role in fabrication.

In view of these we have prepared and characterized few new complexes of an azo dye derived from 2,3-dimethyl-1-phenyl-4-(3-methoxy-2-phenyl azo)5-pyrazolone, GAAP, guaiacol azoantipyridine, L.

## II. RESEARCH ELABORATIONS

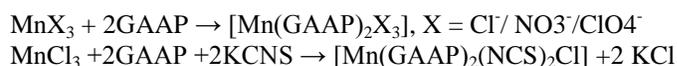
4-Aminoantipyridine (Fluka, Switzerland), Guaiacol (Lobochemie, Mumbai) were used as supplied.

$MnAc_3 \cdot 2H_2O$  was prepared by Christensen's method[3]. Methanol was purified by standard method. All other chemicals were of A.R. grade.

**Synthesis of the ligand:** The ligand GAAP, L was synthesized by diazotization of 4-aminoantipyridine followed by coupling with guaiacol, 2-methoxy phenol below  $5^\circ C$ , washed with cold water, dried and kept in a desiccator[4].

### Synthesis of the Complexes

Metal : Ligand (milli molar) ratio was kept 1:2 with metal salt in slight excess. The solvent used was methanol. Refluxed for 6 hrs. Transferred in a beaker, crystallized by slow evaporation, washed with aqueous methanol, benzene and finally with ether, dried and kept in a desiccator (yield 65%).



The metal, halogen and perchlorate were estimated by standard methods[5]. Microanalysis (CHNS) were performed on VarioEL III CHNS Elemental Analyzer. The IR spectra of the ligand and its Mn(III) complexes were recorded in the region,  $4000-400\text{ cm}^{-1}$  on a JASCO FTIR 430 and on SHIMADZU spectrophotometers using KBr pellets. The  $^1H$  NMR spectra of the ligand were recorded in  $CD_3OD$  on a 300 MHz (Bruker Advance dPx-300) FTNMR instrument using TMS as reference. The electronic spectra were recorded in the solid state by reflectance method on a Varian Cary 5E UV-Vis-NIR spectrometer.

Magnetic susceptibilities of the complexes at room temperature ( $300 \pm 3K$ ) were measured on a magnetic susceptibility balance, Sherwood Scientific, Cambridge, UK. Diamagnetic corrections ( $\chi_{Dia}$ ) for various atoms and structural units were computed using Pascal constants Thermal analysis of

the complex  $[\text{Mn}(\text{L}_2)_2(\text{NCS})_2\text{Cl}]$  was carried on Perkin Elmer Diamond TG/DTA. Cyclic voltammetric profile of the complex  $[\text{Mn}(\text{L}_2)_2\text{Cl}_2]$  was run on BAS-CV-50W Voltammetric analyzer, using glassy carbon as working electrode. X-ray powder diffraction patterns of the complex  $[\text{Mn}(\text{L}_2)_2\text{Cl}_3]$  was carried out on Philips X-ray diffractometer (PW1710) using  $k\alpha$  radiation with  $\lambda = 1.5405 \text{ \AA}$  and was indexed using Hesse and Lipson's procedure.

### III. RESULTS AND DISCUSSIONS

#### 3.1. Analytical measurements and magnetic susceptibilities

All the complexes are dark brown colored, non-hygroscopic solids and nonelectrolytes (Table I) [6]. They are soluble in nitrobenzene and acetonitrile and sparingly soluble in other organic solvents. The analytical data are in agreement with the proposed seven coordinate[22] structure. The magnetic susceptibility measurement shows that the magnetic moments of the complexes are much greater than that of the pure octahedral complexes and suffers Jahn-Teller distortion and spin orbit coupling confirming that they are paramagnetic[5]. Diamagnetic corrections[6],  $\chi_{\text{Dia}}$  were computed using Pascal's constants ( $\chi_{\text{Dia}} = -10.0 \times 10^{-6}$  C.G.S. units for  $\text{Ni}^{2+}$ ).

#### 3.2. Spectral Characterization

##### 3.2.1. The $^1\text{H}$ NMR spectrum

The  $^1\text{H}$  NMR spectrum of the ligand GAAP, L shows three singlets[7] at  $\delta$  (2.7-2.98) ppm,  $\delta$  (3.05-3.39) ppm and  $\delta$  (3.83-3.91) ppm corresponds to methyl protons of  $>\text{C}-\text{CH}_3$ ,  $>\text{N}-\text{CH}_3$  and  $-\text{OCH}_3$  respectively. The signal due to five aromatic protons of the antipyrine phenyl ring appear as multiplet between  $\delta$  (7.38-7.59) ppm and those due to protons of phenyl ring of phenol moiety are observed as multiplet between  $\delta$  (6.85-6.88) ppm. The signal due to phenolic  $-\text{OH}$  proton appears as a hump[8] at  $\delta$  5.56 ppm.

##### 3.2.2 Infra Red spectrum

The infra-red spectrum of the ligand possess a broad band of medium intensity  $\sim 3103 \text{ cm}^{-1}$  is assignable to hydrogen bonded  $-\text{OH}$  group[9]. This band is replaced by a new band  $\sim 3400 \text{ cm}^{-1}$  indicating the non-participation of the  $-\text{OH}$  group in the complex formation[10]. The  $\text{C}=\text{O}$  stretching frequency occurring at  $1637 \text{ cm}^{-1}$  in the spectrum of the ligand shows a downward shift to  $(1620 - 1599) \text{ cm}^{-1}$  in all the complexes showing the evidence of participation of  $\text{C}=\text{O}$  group in complexation[11]. Similarly a band of medium intensity observed  $\sim 1458 \text{ cm}^{-1}$  in the spectrum of the ligand shows a red shift to  $\sim (1427 - 1411) \text{ cm}^{-1}$  in the spectra of all the complexes is suggesting the participation of azo group in coordination[12] with the metal ion. The evidence suggests the neutral bidentate nature of the ligand in all the complexes.

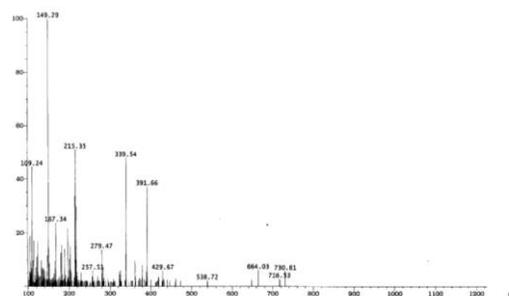
The nitrate complex shows bands at  $1317 \text{ cm}^{-1}$  and  $1022 \text{ cm}^{-1}$  assignable to  $\nu_1$  and  $\nu_2$  modes respectively of unidentately coordinated nitrate[13] group. The N- coordinated nature of the thiocyanate group[14] in its complex is indicated by  $\nu_{\text{C-N}}$  ( $\sim 2061 \text{ cm}^{-1}$ ),  $\nu_{\text{C-S}}$  ( $\sim 758 \text{ cm}^{-1}$ ) and  $\delta_{\text{NCS}}$  ( $\sim 507 \text{ cm}^{-1}$ ). The perchlorate complex shows bands at  $1108 \text{ cm}^{-1}$ ,  $1015 \text{ cm}^{-1}$ ,  $925 \text{ cm}^{-1}$  and

$625 \text{ cm}^{-1}$  are assignable to  $\nu_4$ ,  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  modes respectively of unidentate[15] coordination of perchlorate group.

**3.2.3 Electronic Spectra:** The electronic spectrum of the ligand shows an intense band at 380 nm is attributed to  $n \rightarrow \pi^*$  transition. The electronic spectra of the present complexes are similar and characterized by absorption band  $\sim 380 \text{ nm}$  and  $\sim 500 \text{ nm}$  is characteristics of  $n \rightarrow \pi^*$  and d-d transitions[16].

##### 3.2.4 FAB Mass Spectrum

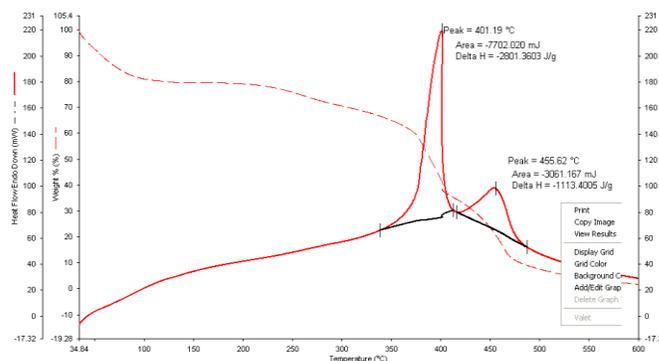
The FAB mass spectrum of the complex (Figure.1)  $[\text{Mn}(\text{L}_2)_2(\text{NCS})_2\text{Cl}]$ , shows the molecular ion peak devoid of One  $-\text{CH}_3$  group with  $m/z$  867.61.



**Figure 1: The FAB mass spectrum of the complex  $[\text{Mn}(\text{L})_2(\text{NCS})_2\text{Cl}]$ ,**

The important peaks [17] are that of  $m/z = 730.86$ ,  $[\text{Mn}(\text{L})_2]^+$ ;  $m/z = 392.59$ ,  $(\text{MnL})^+$ , the base peak;  $m/z = 149.32$ ,  $(\text{C}_3\text{H}_3\text{N}_2\text{OMn})^+$ .

#### 3.3 Thermo gravimetric analysis



**Figure 3: TG-DTACurve of the Complex  $[\text{Mn}(\text{L})_2(\text{NCS})_2\text{Cl}]$**

The decomposition stages are represented as at  $50^\circ\text{C}-75^\circ\text{C}$  the mass loss due to  $(1\text{NCS} + 1\text{Cl})$  which occurs at lower temperature due to the steric factors of seven[18] coordinate system. The stage II occurs at  $250^\circ\text{C} - 390^\circ\text{C}$  which is due to 31.44% mass loss is that of second NCS and part of the first ligand. The stage III occurs at  $390^\circ\text{C} - 510^\circ\text{C}$  which is due to the mass loss of the remaining[19] part of the first ligand and part of

the second ligand. The final residue is that due to the formation of  $Mn_2O_3$ , 17.80 % (expected 17.90 %).

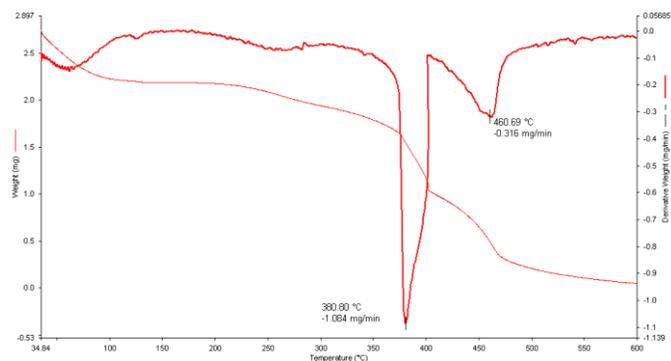


Figure 2: TG-DTG Curve of the Complex  $[Mn(L)_2(NCS)_2Cl]$

### 3.4 Electrochemical Analysis

The redox process  $Mn(III) / Mn(II)$ , with quasi reversible peaks,  $E_{pc} = 1102$  mV, indicating [20] covalent nature of the metal-ligand linkage.

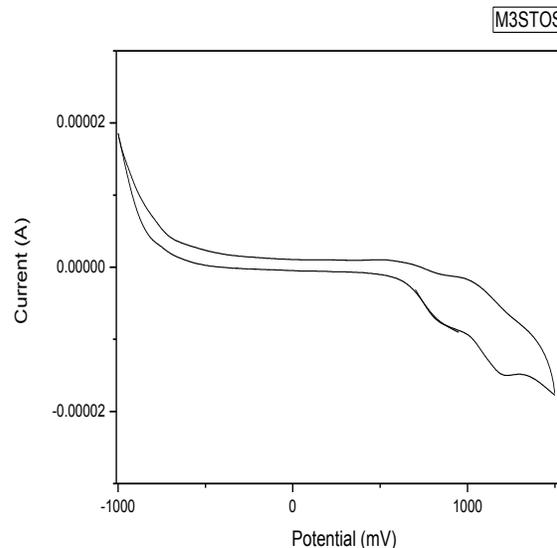


Figure 4: Cyclic Voltammogram of  $[Mn(L)_2Cl_3]$

### 3.5 X- Ray Diffraction Studies

The powder XRD of the complex  $Mn(L)_2(NO_3)_3$  shows that (Figure 5) the complex [21] behaves as it is not a perfectly crystalline substance.

Table I : Analytical and Physical Data of GAAP, L and Mn(III) Complexes

Ligand /Complex	Analytical data (%): Found (calcd.)						Molar conductance in Nitrobenzene $\Omega^{-1} cm^2 mol^{-1}$	$\mu_{eff}$ $\mu_B$ .
	Metal	Cl/Br	C	H	N	S		
GAAP, L	-	-	63.6 (63.9)	5.3 (5.3)	16.5 (16.5)	-	-	-
$[Mn(L)_2Cl_3]$	6.5 (6.5)	12.8 (12.7)	51.6 (51.5)	4.2 (4.2)	13.5 (13.7)	-	3.6	4.1
$[Mn(L)_2(NCS)_2Cl]$	6.2 (6.2)	4.0 (4.0)	51.7 (51.6)	4.1 (4.0)	15.7 (15.8)	7.1 (7.2)	8.6	5.0
$[Mn(L)_2(ClO_4)Cl_2]$	6.5 (6.5)	11.7 (11.8)	48.0 (47.9)	3.9 (3.9)	16.5 (16.7)	-	2.2	3.9
$[Mn(L)_2(NO_3)_3]$	5.8 (5.9)	-	47.0 (47.1)	3.9 (3.9)	16.4 (3.9)	-	1.3	3.4

Table II : Decomposition Parameters of  $[Mn(L)_2(NCS)_2Cl]$  –as per Coats- Red fern Equation

Decomposition Stage	Order of the Reaction	Correlation Coeft., R	Arrhenius Parameters/ $Sec^{-1}$	$E_a / KJ mol^{-1}$	$\Delta S / JK^{-1} mol^{-1}$	Transition Temp. / $^{\circ}C$
I	1.4	-0.9982	$3.54 \times 10^8$	75.76	- 86.48	65
II	1.3	-0.9917	$1.98 \times 10^{14}$	202.92	19.63	380.80
III	1.4	-0.9805	$1.42 \times 10^6$	137.01	134.57	460.69

#### IV. CONCLUSION

The ligand behaved as a neutral bidentate in nature and Mn(III) ion exhibits seven coordination in its [22] complexes. The structure of the ligand is as shown in (Fig. 6)

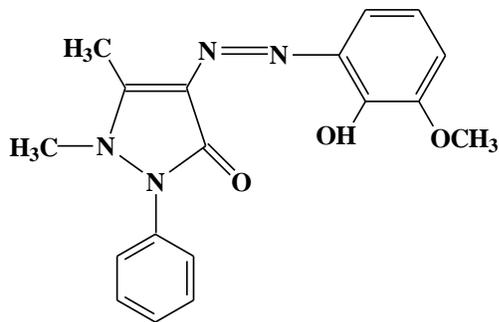


Figure 6: GAAP, L

The complexes are having highly distorted pentagonal bipyramidal structure.

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#### AUTHORS

**First Author** – M. L. Harikumar Nair, M.Sc., Ph.D, FICS, Department of Chemistry, University College, Thiruvananthapuram- 695 034, Kerala, India, E-mail id: drmlhnair@gmail.com

**Second Author** – K. P. Lalitha, M. Sc, M.Phil., Department of Chemistry, University College, Thiruvananthapuram- 695 034, Kerala, India, E-mail id: lalitha.chem08@gmail.com

**Correspondence Author** – M. L. Harikumar Nair, drmlhnair@gmail.com, Alternate email address: lalitha.chem08@gmail.com, +919446550668