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### **Synthesis, Characterization, Structural Elucidation and Reactivity Studies of Two New Mononuclear Schiff base Complexes of Manganese(III)**

**Nath Bhowmik Kanti Ranjan**

Department of Chemistry, Ramthakur College, Agartala 799 002, Tripura, India

#### **ABSTRACT**

Two new mononuclear Schiff base complexes viz.  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$  and  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ , have been synthesized by reacting manganese(III) acetate with the corresponding Schiff base in methanol solution. Complexes have been characterized based on elemental analyses, molar conductance measurements, FTIR, room temperature magnetic susceptibility measurements and electronic spectroscopic studies. The redox behaviour of the synthesized complexes was ascertained from cyclic voltammetric studies. The results of the above studies suggest that in  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ , 1, Schiff base ligand  $\text{H}_2\text{L}^1$  is coordinated to the metal center in tridentate fashion through azomethine nitrogen, phenolic and carboxylate oxygen atoms, whereas in  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ , 2, Schiff base ligand  $\text{H}_2\text{L}^2$  is ligated to manganese(III) center in bidentate manner involving its azomethine nitrogen and carboxylate oxygen atoms respectively. Schiff base complexes, have demonstrated their catalytic potentials in oxidizing selective organic substrates viz. cyclohexene by hydrogen peroxide as the oxidizing agent. The oxidized products have been ascertained as trans-cyclohexane-1, 2- diol.

**KEYWORDS:** Mn(III) Schiff base complexes, synthesis, characterization, reactivity.

#### **\*Corresponding author**

**Dr. Kanti Ranjan Nath Bhowmik**

Department of Chemistry, Ramthakur College, Agartala, 799002, INDIA

Email: [kantinathbhowmik@gmail.com](mailto:kantinathbhowmik@gmail.com); telephone: +917005711456.

## **INTRODUCTION**

Metal complexes with Schiff base ligands have been the subject of intense investigations for the past several years<sup>1-3</sup>. The instant and enduring property of Schiff base ligands undoubtedly stems from the ease with which they can be synthesized, their versatility and also due to their wide-ranging complexing ability. The survey of the literature reveals that the study of this diverse ligand system is linked with many of the key advances in inorganic chemistry and has played a seminal role in the development of modern coordination chemistry<sup>4</sup>, inorganic biochemistry<sup>5</sup>, catalysis<sup>6, 7</sup> and optical materials<sup>8</sup> etc. Manganese(III) Schiff base complexes though well known, continue to generate interest due to their potential application in fields as diverse as homogeneous catalysis and magnetic materials<sup>9-11</sup>. Mn(III) Schiff base complexes are also studied widely due to their important role in several metalloenzymes, redox and non-redox proteins<sup>12, 13</sup>. A contemporaneous field of work is concerned with the study of salen and salicylaldimine type of ligands containing redox active metal centers such as manganese(III). Tridentate and tetradentate salen-type Schiff bases are capable of forming complexes with metal ions which can exhibit unusual coordination, high thermodynamic stability and kinetic inertness. The salen-type Schiff bases, formed by a condensation of an amine with an aldehyde<sup>14</sup>, usually coordinate to metal through the imine nitrogen and another group usually oxygen, nitrogen or sulphur situated on the original aldehyde. Condensation of one of the carbonyl function of a  $\beta$ -diketone with an amine also produces a tridentate Schiff base ligand. These group of tridentate ligands have been used exclusively for the synthesis of mono, di and polynuclear complexes with first row transition elements<sup>15-17</sup> and also as precursors for the synthesis of unsymmetrical tridentate Schiff base complexes<sup>18, 19</sup>. In view of the enhanced interest and considering the importance of metal-schiff base complexes, studies related to the chemistry of manganese(III) Schiff base complexes were undertaken. The present report deals with studies involving syntheses, characterization and structural elucidation of mononuclear Mn(III) complexes with tridentate phenyl-salicylalden-imine type of ligand as well as Schiff base derived from condensation of a carbonyl function of  $\beta$ -diketone with aminobenzoic acid. An additional goal of the present investigation was also to explore the catalytic potentials of some of the synthesized complexes towards the oxidation of selective organic substrates. A brief discussion of the redox properties of the synthesized complexes has been also included.

## **EXPERIMENTAL**

The chemicals used were all reagent grade products. The compound manganese(III) acetate dihydrate,  $\text{Mn}(\text{CH}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$  was prepared by method reported<sup>20</sup> in the literature.

### **SYNTHESIS OF LIGANDS**

#### **(i) Synthesis of ( $\text{H}_2\text{L}^1$ ) [ $\text{H}_2\text{L}^1 = \text{C}_6\text{H}_4(\text{OH})\text{CH}=\text{NC}_6\text{H}_4(\text{COOH})$ ]**

Schiff base ligand ( $\text{H}_2\text{L}^1$ ) was synthesized by the addition of a methanolic solution of  $1.52 \text{ cm}^3$  (14.5mmol) of salicylaldehyde to a methanolic solution ( $20 \text{ cm}^3$ ) of 2.0g (14.5mmol) para-aminobenzoic acid with continuous stirring when yellow microcrystalline solid started to separate out. The resultant mixture was heated over a water bath for ca.30min. The yellow microcrystalline product thus formed was separated out by filtration, washed with cooled ethanol and dried in vacuo over anhydrous  $\text{CaCl}_2$ . The product was further recrystallized from ethanol.

Yield: 2.16g (90%)

#### **(ii) Synthesis of ( $\text{H}_2\text{L}^2$ ) [ $\text{H}_2\text{L}^2 = \text{CH}_3(\text{CH}_2\text{COCH}_2)\text{C}=\text{NC}_6\text{H}_4(\text{COOH})$ ]**

Ligand ( $\text{H}_2\text{L}^2$ ) was synthesized by the addition of a methanolic solution  $1.5 \text{ cm}^3$  (14.60mmol) of acetylacetone to a methanolic solution 2.0g (14.60mmol) of para amino benzoic acid with continuous stirring. The resulting mixture was heated over a water bath for ca. 30 min. and kept undisturbed overnight when brownish microcrystalline product separated. The product was collected by filtration in suction, washed with small portion of ethanol and finally dried in vacuo over anhydrous calcium chloride. The crude product was recrystallized from aqueous methanol.

Yield: 1.83g (84%)

### **SYNTHESIS OF SCHIFF BASE COMPLEXES**

#### **(i) Synthesis of [ $\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2$ ], **1**, [ $\text{H}_2\text{L}^1 = \text{C}_6\text{H}_4(\text{OH})\text{CH}=\text{NC}_6\text{H}_4(\text{COOH})$ ]**

0.482g (2.0mmol) of Schiff base ligand ( $\text{H}_2\text{L}^1$ ) and 0.224g (4.0mmol) of KOH was dissolved in  $20 \text{ cm}^3$  of methanol by warming over a water bath for 10 min. To the clear solution, 0.268g (1.0mmol) of manganese(III) acetate was added slowly with continuous stirring, keeping the metal:ligand ratio as 1:2. The resultant reaction mixture was refluxed for a period ca.40-45min., when reddish brown solid product separated. The product was collected by filtration in suction, washed 3-4 times with a small volume of ethanol and finally dried in vacuo over anhydrous  $\text{CaCl}_2$ .

Yield: 2.95g (76%)

**(ii) Synthesis of  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ , 2,  $[\text{H}_2\text{L}^2=\text{CH}_3(\text{CH}_3\text{COCH}_2)\text{C}=\text{NC}_6\text{H}_4(\text{COOH})]$**

To a methanolic solution (20cm<sup>3</sup>) Schiff base ligand  $\text{H}_2\text{L}^2$  (0.490g, 2.24mmol) was added manganese(III)acetate (0.3g, 1.12mmol) dissolved in 10cm<sup>3</sup> methanol with continuous stirring. The metal-to-ligand ratio was maintained at 1:2. The reaction mixture was further stirred for a period of ca.15min. The resultant mixture was then refluxed for a period of ca.45min, when reddish brown microcrystalline product separated. The product was filtered, washed with a small portion of ethanol and finally dried in vacuo over anhydrous  $\text{CaCl}_2$ .

Yield: 3.02g (71%)

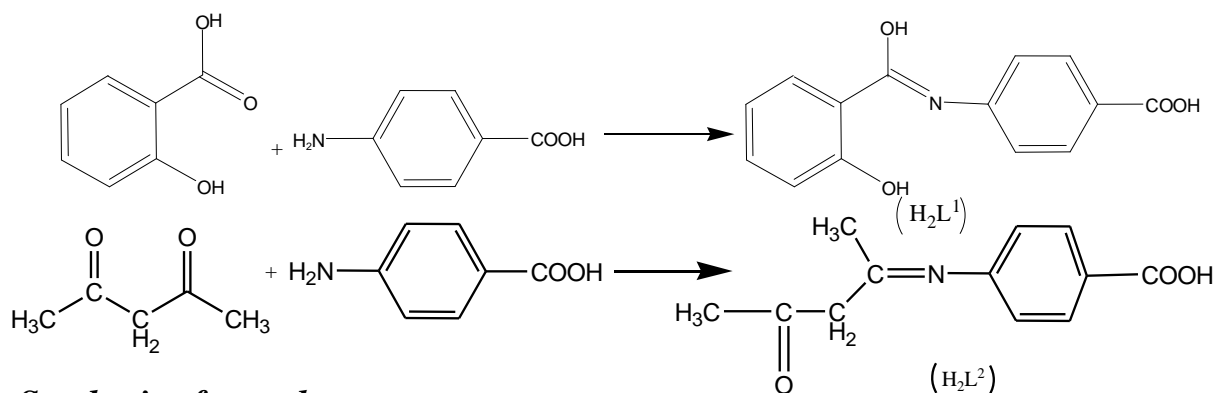
***CATALYTIC OXIDATION OF CYCLOHEXENE WITH  $\text{H}_2\text{O}_2$  AS OXIDANT***

A 250 ml round bottom flask equipped with a mechanical stirrer, and thermometer was placed 30 cm<sup>3</sup> (60.00 mmol) of 85% formic acid and to it 7.0 cm<sup>3</sup> (6.2 mmol) of 30%  $\text{H}_2\text{O}_2$  was added slowly in small portions. To the resultant colourless solution, 30 mg of  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ , 1, was added, the colour of the reaction mixture gradually changed to reddish brown. Cyclohexene 5.1 cm<sup>3</sup> (5.0 mmol) was added slowly over a period of 20-30 mins. to the reaction mixture keeping the temperature of the reaction at ca.45°C. The reaction mixture was kept at ~40°C for an hour after addition of cyclohexene was complete and then the mixture was allowed to stand overnight at room temperature. The unreacted formic acid and water were removed from the reaction mixture by distillation under reduced pressure. An ice-cold solution of sodium hydroxide (10 cm<sup>3</sup>) was added in small portions to the residual mixture. The resultant mixture was warmed to 45°C and added an equal volume (30 cm<sup>3</sup>) of ethyl acetate. The mixture was extracted with ethylacetate, washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Solvent was removed by distillation under reduced pressure when a white solid crystallized out. The product was separated by filtration, washed with small portions of alcohol and dried in vacuo over anhydrous  $\text{CaCl}_2$ . A Similar reaction was also performed with the substrate without using the catalyst.

Yield of the oxidation product ~0.359 g (oxidation in the presence of catalyst), ~0.116 g (blank reaction)  
m.p. of the product: 104°C

## REACTION SCHEMES

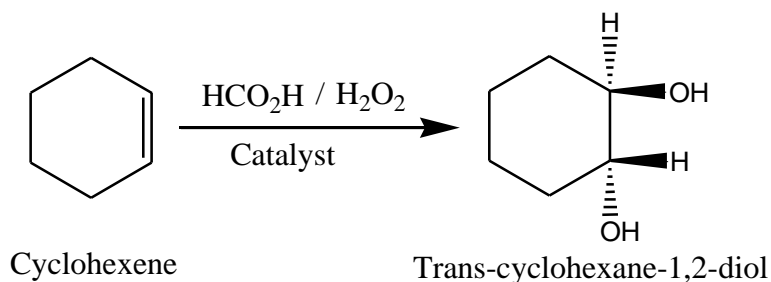
### Synthesis of ligand



### Synthesis of complex



### Catalytic study



## RESULTS AND DISCUSSION

Tridentate phenyl-salicylalidenimine type of Schiff base ligand (H<sub>2</sub>L<sup>1</sup>) with (N, O, O) donor sites was readily obtained by condensation of para-aminobenzoic acid and salicylaldehyde in methanolic solution. Schiff base ligand (H<sub>2</sub>L<sup>1</sup>) on reacting with a methanolic solution of Mn(CH<sub>3</sub>COO)<sub>3</sub>·2H<sub>2</sub>O in the presence of KOH (~1N) maintaining the metal:ligand:base ratio as 1:1:2, led to the successful synthesis of mononuclear manganese(III) Schiff base complex, [Mn(L<sup>1</sup>)(CH<sub>3</sub>COO)(H<sub>2</sub>O)<sub>2</sub>] in reasonably good yield. Tridentate Schiff base (H<sub>2</sub>L<sup>2</sup>) was synthesized by condensation of a carbonyl function of β-diketone, 2, 4 pentanedione with para- aminobenzoic acid in methanol solution. The reaction of manganese(III)acetate with H<sub>2</sub>L<sup>2</sup> in methanol containing KOH resulted in an easy access to

the mononuclear manganese(III) complex of composition  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ . The newly synthesized Schiff base ligands are yellow and light-brown coloured microcrystalline solids. They are poorly soluble in most of the common organic solvent but soluble in DMSO. The ligands were characterized based on elemental analyses, IR,  $^1\text{H}$  NMR and molar conductance measurements. The synthesized complexes are reddish-brown microcrystalline solids and are stable for prolong periods. They are poorly soluble in common organic solvents but appreciably soluble in dimethyl sulphoxide. Molar conductance measurement of the synthesized ligands and complexes in DMSO solution ( $10^{-3}\text{M}$ ) exhibit quite low values ranging from 8-12  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$  and reveal their non-electrolytic nature. The complexes were characterized based on elemental analyses, infrared spectroscopy, magnetic moment measurements and electronic spectral studies. The results of elemental analyses of the ligands and the complexes agree very well with the formulation of the complexes. The room temperature magnetic susceptibility measurements showed that the compounds are paramagnetic with the magnetic moments of  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ , 1, and  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ , 2, being 5.3, 5.48 B.M. respectively, which are normal as expected for the existence of high spin  $d^4$  system of manganese(III) <sup>21</sup>.

**TABLE 1 Analytical data of ligands,  $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$  and manganese(III) schiff base complexes,  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ , 1, and  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ , 2.**

Compound	Yield (%)	Molar conductance ( $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ )	$\mu_{\text{eff}}$ (B.M.)	Found (Calcd.) (%)			
				Mn	C	H	N
$\text{H}_2\text{L}^1$	90	8.01	-	-	69.89 (69.70)	4.43 (4.56)	5.98 (5.80)
$\text{H}_2\text{L}^2$	84	8.77	-	-	64.62 (65.75)	5.91 (5.93)	6.0 (6.39)
$[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$	76	11.65	5.3	14.15 (14.13)	50.47 (49.35)	3.96 (4.11)	3.61 (3.59)
$[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$	71	12.03	5.48	12.87 (12.91)	45.49 (45.07)	4.78 (4.92)	3.43 (3.28)

$^1\text{H}$  NMR spectra provided useful data for characterization of the ligands. In the NMR spectrum of the ligand,  $\text{H}_2\text{L}^1$  a singlet due to proton attached to the azomethine group ( $\text{HC}=\text{N}$ ) was observed at  $\delta 8.9$  ppm (1H, s). The multiplets due to aromatic protons (8H, m) were observed in the range  $\delta 6.8$ -8.0 ppm. In the case of  $\text{H}_2\text{L}^2$ , multiplets due to aromatic protons were observed between  $\delta 6.6$ -8.0 ppm (8H, m). A singlet

(1H, s) at  $\delta$ 1.29 ppm was assigned to methyl proton attached to azomethine moiety; whereas signal of methyl proton attached to carbonyl function was observed at  $\delta$ 2.0-2.1 ppm. The signal for the methylene proton of the acetylacetone moiety was noticed at  $\delta$ 3.3 ppm. Thus the  $^1\text{H}$  NMR spectral data gave useful information for ascertaining the composition and structure of synthesized ligands. Electrochemical behaviour of the complexes was studied by cyclic voltametry.

### ***Infrared spectra***

Infrared spectra of ligands and their complexes were recorded as KBr discs from 4000 to  $400\text{cm}^{-1}$ . The IR spectra of the ligand,  $\text{H}_2\text{L}^1$  and its corresponding complex with manganese(III) ion displayed well resolved spectral pattern, the significant features of which are summarized in Table 2. The IR spectrum of  $\text{H}_2\text{L}^1$  was characterized by the appearance of bands at  $3430\text{cm}^{-1}$  due to  $\nu(\text{OH})$  and at  $1700\text{cm}^{-1}$  arising from  $\nu(\text{COOH})$ . The characteristic C=N stretching vibration,  $\nu(\text{C}=\text{N})$ , was observed at  $1678\text{cm}^{-1}$  and the appearance of a sharp band at  $1287\text{cm}^{-1}$  was assigned as phenolic  $\nu(\text{CO})$ . The IR spectra showed characteristic differences between the spectral pattern originating from the complex and the spectra of the free ligand,  $\text{H}_2\text{L}^1$ . The notable features of the IR spectra of the complex,  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ , 1, involve absorptions due to coordinated azomethine nitrogen, phenolic and carboxylate oxygen atoms of the Schiff base ligand and the acetato group. The stretching vibration of the azomethine group,  $\nu(\text{C}=\text{N})$ , for the complex was observed at  $1624\text{cm}^{-1}$ . The strong  $\nu(\text{C}=\text{N})$  band in the complex shifted considerably towards lower frequency compared to that observed in the case of free ligand,  $\text{H}_2\text{L}^1$ , indicating coordination of the imine nitrogen atom of azomethine moiety to the metal centre<sup>22</sup>. Absorption due to phenolic CO stretching was observed at  $1284\text{cm}^{-1}$ . This band is also shifted slightly to lower frequency suggesting the participation of phenolic oxygen in coordination with the manganese(III) centre<sup>23</sup>. The deprotonation of phenolic  $-\text{OH}$  and subsequent coordination of oxygen atom with the metal ion was further confirmed by the reduction in the intensity of peak in the region  $2934\text{-}2969\text{cm}^{-1}$  compared to the corresponding bands in the free Schiff base ligand,  $\text{H}_2\text{L}^1$ . The absence of any band at  $1700\text{cm}^{-1}$  suggests deprotonation of the carboxylic group of the Schiff base ligand. Bands at  $\text{ca.}1603\text{cm}^{-1}$  and  $1415\text{cm}^{-1}$  were assigned as  $\nu_{\text{asy}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$  modes of vibration of coordinated carboxylate group of the Schiff base ligand,  $\text{H}_2\text{L}^1$ . The appearance of additional bands at  $\text{ca.}1568\text{cm}^{-1}$  and  $1367\text{cm}^{-1}$  were attributable to asymmetric and symmetric carboxylate stretchings of the acetato group respectively. The frequency difference between symmetric and asymmetric stretching of the carboxylate group,  $\Delta\nu [\nu_{\text{asy}}(\text{COO}) - \nu_{\text{sym}}(\text{COO})]$ , of nearly  $200\text{cm}^{-1}$  for both Schiff base ligand and

acetato group is typical of monodentate coordination of the carboxylate groups<sup>24</sup>. A broad band at  $3422\text{cm}^{-1}$  was assigned as  $\nu(\text{OH})$  mode of vibration of water molecules. Although from the appearance and the observed position for  $\nu(\text{OH})$ , no clear inference could be made regarding the nature of the water molecule, however, the observance of distinct band at  $790\text{cm}^{-1}$  was assigned to rocking mode ( $\rho_r$ ) of water<sup>25</sup> and provide evidence for the existence of coordinated water molecule. Medium intensity bands in the low frequency region at  $533\text{cm}^{-1}$ ,  $441\text{cm}^{-1}$  were assigned as  $\nu(\text{Mn-N})$ ,  $\nu(\text{Mn-O})$  mode of vibrations respectively<sup>26</sup>. Observance of these bands further manifests the idea of coordination of azomethine nitrogen, phenolic and carboxylate oxygen atoms to the manganese(III) centre. Thus the infrared spectral data suggest an overall tridentate coordination of the Schiff base ligand,  $\text{H}_2\text{L}^1$  and monodentate coordination of the acetato group respectively.

The notable features of the infrared spectra of the ligand,  $\text{H}_2\text{L}^2$ , were strong bands observed at  $1698\text{cm}^{-1}$  and  $1608\text{cm}^{-1}$  assigned as  $\nu(\text{COOH})$  and  $\nu(\text{C=N})$  modes of vibration respectively. The absence of any prominent band in the region  $1570\text{-}1580\text{cm}^{-1}$  due to  $\nu(\text{C=O})$  indicates condensation has taken place between the  $-\text{NH}_2$  and  $-\text{CO}$  moieties of p-aminobenzoic acid and acetylacetone. A medium intensity band observed at  $ca.1516\text{cm}^{-1}$  is assignable to  $\text{C=C}$  stretching and suggested that the other carbonyl group of the acetylacetone molecule probably exists in enol form<sup>27</sup>. The absorption at  $3382\text{cm}^{-1}$  is assignable to  $\nu(\text{OH})$  of the enol form of acetylacetone moiety. The strong band occurring at  $ca.1574\text{cm}^{-1}$  due to  $\nu(\text{C=N})$  for complex,  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ , 2, shifted considerably towards lower frequency compared to that of free Schiff base,  $\text{H}_2\text{L}^2$  ( $1608\text{cm}^{-1}$ ) suggesting an imino nitrogen coordination<sup>22</sup>. The absence of any absorption band at  $1700\text{cm}^{-1}$  indicates deprotonation of the carboxylate group. The appearance of strong bands at  $1644\text{-}1664\text{cm}^{-1}$  and  $1442\text{cm}^{-1}$  were assigned as  $\nu_{\text{asy}}(\text{COO}^-)$  and  $\nu_{\text{sym}}(\text{COO}^-)$  modes of vibrations of carboxylate group of the Schiff base,  $\text{H}_2\text{L}^2$ , and suggest the involvement of carboxylate oxygen atom in coordination to the manganese(III) centre. Additional bands at  $1601\text{cm}^{-1}$  and  $1422\text{cm}^{-1}$  were attributed to asymmetric and symmetric stretchings modes of vibration of  $(\text{COO}^-)$  moiety of acetato ligand respectively. The observed frequency differences  $\Delta\nu$ ,  $[\nu_{\text{asy}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)]$ , of nearly  $200\text{cm}^{-1}$  suggests monodentate coordination of acetato group<sup>24</sup>. The occurrence of coordinated water molecules was evidenced by the typical band observed at  $ca.3461\text{cm}^{-1}$  and at  $771\text{cm}^{-1}$  due to  $\nu(\text{OH})$  and rocking mode of vibration ( $\rho_r$ ) of coordinated water. The coordination of ligands to the metal centre was substantiated by two more bands appearing for  $\nu(\text{Mn-N})$  at  $552\text{cm}^{-1}$  and for  $\nu(\text{Mn-O})$  at  $499\text{cm}^{-1}$  in the complex<sup>26</sup>.



TABLE 2 Significant IR Spectral Bands of ligands,  $H_2L^1$ ,  $H_2L^2$  and manganese(III) Schiffbase complexes,  $[Mn(L^1)(CH_3COO)(H_2O)_2]$ , 1 and  $[Mn(L^2)(CH_3COO)_2(H_2O)_2]$ ,

Compounds	$\nu$ (OH)	$\nu$ (COOH)	$\nu$ (C=N)	$\nu$ (C=C)	$\nu$ (C-O)	$\nu_{sym}(CO$ O)					
$H_2L^1$	3430	1700	1678	1287							
$H_2L^2$	3382	1698	1608	-	1516						
$[Mn(L^1)(CH_3COO)(H_2O)_2]$ , 1	3422		1624			1603 1568	1415 1367	790	533	441	
$[Mn(L^2)(CH_3COO)_2(H_2O)_2]$ , 2	3364- 3461		1574			1644- 1664 1601	1442 1422	771	552	499	

An additional band at  $\text{ca.}3364\text{cm}^{-1}$ , probably due to the stretching mode of vibration of enolic O-H group. The nearly unaltered position of this band in the complex suggests that the enolic oxygen atom is not involved in coordination with the metal centre. Thus spectral data suggest that the Schiff base ( $\text{H}_2\text{L}^2$ ) is coordinated to manganese(III) centre in a bidentate fashion involving its azomethine nitrogen and carboxylate oxygen atom respectively.

The electronic spectra of ligands and the complexes were recorded in DMSO solution. General shape and intensity of the spectral display of the complexes are similar to those for other manganese(III) Schiff base complexes<sup>28</sup>. The spectra show several bands and poorly resolved shoulders and therefore are difficult to analyze accurately. In complex,  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ , 1, the band at  $\text{ca.}29,069\text{ cm}^{-1}$  was assigned as intra ligand  $\pi\text{-}\pi^*$  transition<sup>29</sup>. The spectrum also showed two medium intensity absorption bands associated with the d-d transition in the range 523-640nm. The electronic spectrum of  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ , 2, displayed a strong absorption band in region  $28,735\text{cm}^{-1}$  arose due to intra ligand  $\pi\text{-}\pi^*$  transition as observed in case of complex 1. Additional bands observed at  $\text{ca.}23,255\text{ cm}^{-1}$  and  $\text{ca.}17,482\text{cm}^{-1}$  arise from d-d transitions as usually observed in case of similar manganese(III) complexes<sup>30</sup>.

The electrochemical behaviour of the synthesized complexes was ascertained from cyclic voltametric studies in DMSO solution. Complexes display cyclic response with anodic ( $\text{Ep}_a$ ) and cathodic ( $\text{Ep}_c$ ) peak potentials and  $\text{E}_{1/2}$  values in the range -2.0 to +2.0V VS SCE. Complex  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ , 1, shows quasi reversible behaviour for Mn(III)/Mn(II) couple with  $\text{Ep}_c$  at -1.7V,  $\text{Ep}_a$  at -0.75V and  $\Delta\text{Ep}=0.95\text{V}$  respectively. Whereas for complex  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ , 2, the cathodic process is not well defined but shows an irreversible oxidative response at 1.1V. The irreversibility of the redox processes of the complexes under discussion may be attributed to changes in the coordination geometry or coordination number upon the change in oxidation state. However, this does not completely rule out the applicability of the complexes as oxidation catalysts.

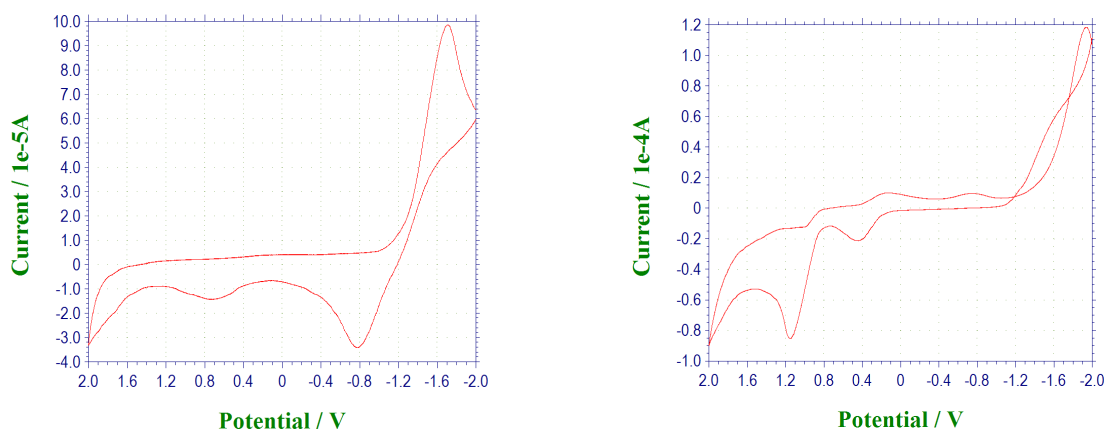


Figure Cyclic voltammogram of (a)  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$  and (b)  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$

To assess the catalytic potential of the synthesized manganese(III) Schiff base complexes towards oxidation of the selective organic substrate, an oxidation reaction was carried out involving cyclohexene as substrate,  $\text{H}_2\text{O}_2$  as oxidizing agent and compound, 1, as the catalyst. Oxidation of cyclohexene in the presence of formic acid (85% solution) by  $\text{H}_2\text{O}_2$  in the presence of complex, 1 followed by workup of the reaction solution afforded a white crystalline product. Melting point of the crystalline product as obtained was  $104^\circ\text{C}$ . The  $^1\text{H}$  NMR spectrum of the compound in  $\text{DMSO-d}_6$  showed signal at  $\delta 1.05\text{-}2.08$  and  $\delta 3.5\text{-}3.6$  and  $\delta 8.2$ . The IR spectrum of the product shows absorption at  $3442\text{ cm}^{-1}$  assignable to  $\nu(\text{OH})$ . The other significant absorptions were observed at ca  $2837\text{ cm}^{-1}$  and in between  $700\text{-}1600\text{ cm}^{-1}$ . Based on these results as well as a comparison with those given in the literature<sup>31</sup>, the identity of the compound has been ascertained to be trans-1, 2 cyclohexenediol.

## CONCLUSION

Thus to summarize, it may be inferred that, two new mononuclear Schiff base complexes of manganese(III) viz.  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ , 1, and  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ , 2, have been synthesized with tridentate Schiff base ligands by proper choice of the reaction conditions. Schiff base ligand  $\text{H}_2\text{L}^1$  was obtained by condensation of salicylaldehyde with para-aminobenzoic acid, while  $\text{H}_2\text{L}^2$  was derived from condensation of a carbonyl function  $\beta$ -diketone viz. acetylacetone with para-aminobenzoic acid. Spectral data revealed that in  $[\text{Mn}(\text{L}^1)(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2]$ , 1, Schiff base ligand  $\text{H}_2\text{L}^1$  is coordinated to the metal center in tridentate fashion through azomethine nitrogen, phenolic and carboxylate oxygen atoms, whereas in  $[\text{Mn}(\text{L}^2)(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2]$ , 2, Schiff base ligand  $\text{H}_2\text{L}^2$  is ligated

to manganese(III) center in bidentate manner involving its azomethine nitrogen and carboxylate oxygen atoms respectively. Coordination polyhedra in complexes 1 and 2 are completed by the presence of acetato group/s and molecule/s of water. Schiff base complexes have demonstrated their catalytic potentials in oxidizing selective organic substrate viz. cyclohexene by hydrogen peroxide as the oxidizing agent. The oxidized products have been ascertained as trans-cyclohexane-1, 2- diol. In addition to the synthetic and structural investigations, the present work also helped to evaluate the potentiality and effectiveness of the synthesized binuclear manganese(III) Schiff base complexes to use as catalytic agents.

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