

# Synthetic, spectral, electrical and antibacterial studies on titanium (III), manganese(III) and iron (III) complexes containing diabolic tetradentate Schiff bases

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## ABSTRACT

Several M(III) Complexes of the type  $[M(LL')_2 \cdot 2H_2O]Cl$  (where  $LL'$ =tetradentate Schiff bases &  $M=Ti(III)$ ,  $Mn(III)$  or  $Fe(III)$ ) have been synthesised by the reaction of respective Schiff bases having the donor groups (O,N) viz., O-hydroxyacetophenone tetramethylene diamine (OHAOTMDA), O-hydroxyacetophenone O-phenylenediamine (OHAOPDA) and  $\beta$ -hydroxynaphthaldehyde tetramethylene diamine (*b*-HNATMDA) in 1:1 molar ratio. All the complexes have been characterised on the basis of elemental analyses, spectral (IR, Electronic), electrochemical and magnetic data. The complexes have also been screened for antibacterial properties.

**Key words:** Antibacterial activities, octahedral, Schiff bases, tetradentate.

## INTRODUCTION

Schiff bases possess strong ability to form metal complexes<sup>1</sup> and they deserve and are receiving attention proper attention because of their potential as antimicrobial agents<sup>2</sup>. The chelation of schiff bases with metals enhance their antimicrobial properties<sup>3</sup>. It has been found that the drugs when administered as metal chelates get their activity enhanced. Metal schiff base complexes, particularly those containing oxygen and nitrogen donor atoms have been found to be very efficient catalysts in oxidation of alcohols and alkenes<sup>6</sup>. Electron transfer reactions are fundamental and they play an important role in Chemical and biological processes<sup>7</sup>. Chelates of Ti(III), Mn(III) & Fe(iii) are suitable for such studies as little work has been done on these metal chelates.

In view of the aforesaid facts, the present communication deals with the synthesis, characterisation and antibacterial studies of title compounds.

## EXPERIMENTAL

All the reagents used were of highest purity, AR grade or equivalent. Solvents were purified and dried before use according to standard procedure. The compounds used for the preparation of schiff bases were procured from reputed firms like Ranbaxy and Sigma. Titanium (III) chloride was prepared in the lab while Iron(III) and Manganese(III) were procured from reputed companies and used as such.

### Preparation of the ligands

The schiff bases were prepared by literature methods<sup>8,9</sup>. The Ketone/aldehyde and the amino compound were mixed in the molar ratio of 2:1 in benzene and the mixture was refluxed for about 4-5h. The resulting solid was filtered & washed repeatedly with pet. ether. The purity of the sample was checked by TLC. The melting points of the synthesised ligands were determined and ir spectra were recorded.

### Preparation of metals complexes

The ethanolic solution of metal of metal salt (0.01 mmol) was added to the solution of the respective ligand ( 0.01mmol) and stirred magnetically for about one hour, when a solid was separated. It was filtered and washed with pet. ether. The purity was checked by TLC. The complexes were finally dried in vacuo.

### RESULTS AND DISCUSSION

The analytical data of the metal chelates are given in Table-1. The comparison of the ir spectra of metal chelates with their corresponding free ligands gave useful information regarding the Coordination sites.

The ir spectra of the Schiff base ligands were compared with those of their respective Ti(iii), Mn(iii) & Fe(iii) complexes. A strong band was observed at 1630 - 1610  $\text{cm}^{-1}$  in the spectra of the free schiff bases, which is characteristic of azomethine (- HC = N - ) group<sup>10</sup>. It is expected that coordination of nitrogen to the metal atom would reduce the electron density in the azomethine link and thus lower the - HC=N- absorption. In the ir spectra of the complexes this band has shifted to the region around 1610-1590 $\text{cm}^{-1}$  indicating coordination through nitrogen atom of azomethine group<sup>11</sup>.

A strong band has appeared in the range of 1270-1260 $\text{cm}^{-1}$  in the free schiff bases. It has been assigned to phenolic C-O absorption. On Complexation this band has shifted to a higher frequency range of 1320-1280 $\text{cm}^{-1}$  indicating the coordination of schiff bases through phenolic oxygen atom<sup>12</sup>. This inference is further supported by the disappearance of the broad band assignable to  $\nu_{(\text{OH})}$  in the range of 2950-2930  $\text{cm}^{-1}$  in the ir spectra of the complexes, suggesting that deprotonation of phenolic group occurs prior to coordination<sup>13</sup>. All other bands present in the ir spectra of the ligands appeared unaltered in the ir spectra of the corresponding metal complexes. This indicated dibasic tetradentate nature of the ligands.

The presence of coordinated water molecules in all the complexes has also been revealed by the ir spectra of the complexes.

Presence of water molecules is confirmed by the appearance of broad band of 3370-3395  $\text{cm}^{-1}$  due to  $\nu_{(\text{OH})}$  and a sharp shoulder at 1652-1656  $\text{cm}^{-1}$  due to  $\nu_{(\text{H}_2\text{O})}$ . The coordinated nature of water molecules, is indicated by a strong sharp band at 830-835  $\text{cm}^{-1}$   $\delta_{(\text{OH})}$  14, 15.

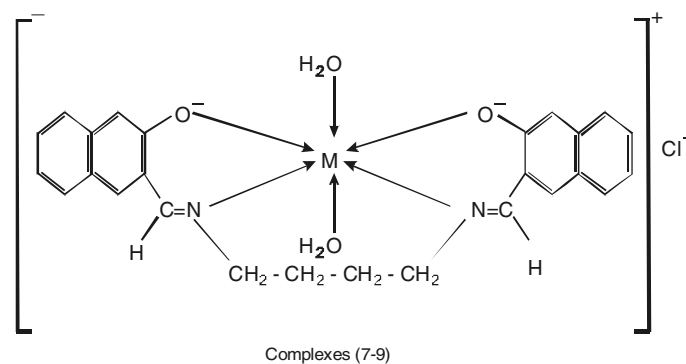
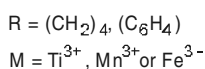
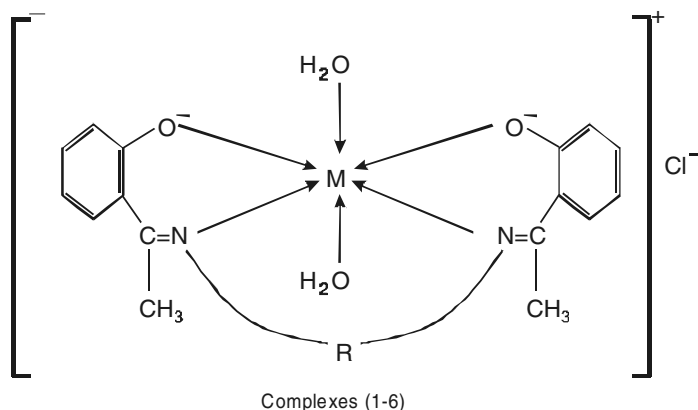
The electronic spectra of Ti(III) complexes in DMF exhibited one band at 19500-20950  $\text{cm}^{-1}$  with a shoulder at 18520-19000  $\text{cm}^{-1}$ . This band has been assigned to  ${}^2T_{2g} \rightarrow {}^2T_{Eg}$  transition for Oh symmetry<sup>16</sup>. The observed values of effective magnetic moment of titanium (III) complexes lie in the range of 1.65-1.87 B.M. at room temperature, which indicated their paramagnetic nature and that Ti(III) has not been oxidised to Ti(IV) during or after complexation as the values correspond to the presence of one unpaired electron.

Usually MnIII has a 5D electronic ground state and in a pure octahedral symmetry, a single absorption band is expected due to spin-allowed transitions  ${}^5E_g \rightarrow {}^5T_{2g}$ . However, even for symmetrical ligand fields, they are subjected to John-Teller distortions<sup>17</sup> (high spin d4 configuration) and three absorption bands are expected due to  ${}^5B_{1g} \rightarrow {}^5A_{1g}$ ,  ${}^5B_{1g} \rightarrow {}^5A_{2g}$  and  ${}^5B_{1g} \rightarrow {}^5E_g$  transitions as the distortion is an elongation of the Z-axis of D4th symmetry. All the Mn111 complexes under present study show two bands in the region of 19000-19500 and 13000-13200  $\text{cm}^{-1}$  assignable to  ${}^5B_{1g} \rightarrow {}^5B_{2g}$  and  ${}^5B_{1g} \rightarrow {}^5E_g$  transitions<sup>18</sup>. The band observed in the vicinity of 27000  $\text{cm}^{-1}$  may be assigned to charge transfer transitions, probably due to  $\text{Mn}_{(d\pi \rightarrow \pi^*)}$  (azomethine)<sup>19</sup>. All the complexes have  $\mu_{\text{eff}}$  values in the range of 4.80 to 5.10 B.M. which are in good agreement with reported octahedral manganese (III) complexes.

The magnetic moment of Fe(III) complexes were in the range of 5.89-5.97 B.M. corresponding to five unpaired electrons and high spin state of Fe(III) ion. Three bands in the regions of 11235-11300, 21560-21730 and 27780-27790  $\text{cm}^{-1}$  were observed in the electronic spectra of Fe(III) complexes. These bands have been assigned to  ${}^6A_{1g} \rightarrow {}^4T_{1g}$ ,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  and  ${}^6A_{1g} \rightarrow {}^4E_g$  transitions respectively and suggested an octahedral geometry for these complexes<sup>21</sup>.

Table 1: Analytical, physical data and ir spectral bands of the complexes characterisation of metal complex (obs. values)

S. No.	Complexes	Colour	M.P. °C	Elemental analysis						% of M	Magnetic moment (B.M.)	Molar conductance	
				% of C	% of H	% of N	% of S	% of Cl	DMSO			DMF	
1.	[Ti (OHATMDA).2H <sub>2</sub> O]Cl mol.wt = 441.5	Yellow	180	54.36 (54.12)	5.88 (5.79)	6.34 (6.28)	-	7.92 (7.79)	10.87 (10.68)	1.74	45	60	
2.	[Mn (OHATMDA).2H <sub>2</sub> O]Cl mol.wt = 448.5	Brown	195	53.51 (53.42)	5.79 (5.71)	6.24 (6.10)	-	7.80 (7.71)	12.26 (11.99)	4.80	55	70	
3.	[Fe (OHATMDA).2H <sub>2</sub> O]Cl mol.wt = 449.5	Reddish Yellow	210	53.39 (53.12)	5.78 (5.69)	6.22 (6.11)	-	7.78 (7.71)	12.45 (12.34)	5.89	45	65	
4.	[Ti (OHATMDA).2H <sub>2</sub> O]Cl mol.wt = 461.5	Yellow	175	57.20 (56.98)	4.76 (4.72)	6.06 (5.93)	-	7.58 (7.18)	10.40 (10.31)	1.65	50	75	
5.	[Mn (OHATMDA).2H <sub>2</sub> O]Cl mol.wt = 469.5	Brown	185	56.35 (56.28)	4.69 (4.58)	5.97 (5.91)	-	7.41 (7.32)	11.75 (11.61)	4.92	55	70	
6.	[Fe (OHATMDA).2H <sub>2</sub> O]Cl mol.wt = 513.5	Reddish Yellow	195	56.23 (56.10)	4.68 (4.59)	5.96 (5.82)	-	7.45 (7.39)	11.92 (11.72)	5.92	45	65	
7.	[Ti(β-NATMDA).2H <sub>2</sub> O]Cl mol.wt = 513.5	Light Yellow	185	60.75 (60.71)	5.06 (4.97)	5.45 (5.38)	-	6.87 (6.71)	9.34 (9.31)	1.87	56	75	
8.	[Mn(β-NATMDA).2H <sub>2</sub> O]Cl mol.wt = 520.5	Yellow	190	59.94 (59.78)	4.99 (4.93)	5.37 (5.32)	-	6.72 (6.71)	10.56 (10.34)	5.10	56	70	
9.	[Fe(β-NATMDA).2H <sub>2</sub> O]Cl mol.wt = 521.5	Yellow	205	59.82 (59.78)	4.98 (4.92)	5.36 (5.29)	-	6.71 (6.69)	10.73 (10.61)	5.10	45	60	



Room Temperature molar conductance of the complexes was determined at 10<sup>-3</sup>M dilution in DMF and DMSO (Table 1). All the complexes were found to be 1:1 electrolytic in nature [ML<sub>2</sub>.2H<sub>2</sub>O]<sub>n</sub>.Cl<sup>-</sup>, Where M=Ti<sup>III</sup>, Mn<sup>III</sup> or Fe<sup>III</sup>.

The aforesaid physio-chemical and spectral evidences suggested octahedral geometry for all the reported complexes.

All the ligands and their corresponding Ti(III), Mn(III) and Fe(III) complexes were screened for their antibacterial activities by Agar Well diffusion method<sup>22</sup>. Seven days old cultures of *E. feacale*'s and *S. typhi* were used as test organism which were grown on nutrient agar (NA) medium. 1% of solutions of the complexes in DMSO were used for the studies. The results showed that all metal complexes were more toxic than their corresponding free ligands. This can be attributed to Tweedy's

chelation theory<sup>23</sup>, according to which the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor group and possible p electron delocalisation over the whole ring. This increases the lipophilic character of the metal chelate which favours its permeation through lipid layers of the bacterial membranes. Further more, the mode of action of the compounds may involve the hydrogen bond through >C=N group with active centres of cell constituents resulting in the interference with normal cell process<sup>24</sup>.

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