



## Synthesis, Characterization and Antimicrobial Properties of Titanium(III) complexes with Schiff Bases Derived From -Amino Acids

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### ABSTRACT

The complexes of Ti(III) with the ligands glycine indole-3-aldehyde(GIA),glycine 2,4-dihydroxy-benzaldehyde (GDHB),L-alanine indole-3-aldehyde (AIA), L-alanine 2,4-dihydroxybenzaldehyde (ADHB) and valine 2,4-dihydroxy benzaldehyde (VAIA) have been synthesised and characterised by analytical, conductivity,magnetic, infrared and electronic spectral data.Based on analytical data 1:2 (M:L) stoichiometry has been suggested. The electronic spectra and magnetic data suggested octahedral geometry for all complexes. The ligands and their respective Ti(III) complexes have been screened for their antimicrobial activities.

**Key words:** Ti(III),ligand,octahedral,antimicrobial activity.

### INTRODUCTION

Schiff bases are important class of ligands and have got-wide applications in various fields 1,2. The metal complexes derived from schiff bases have been found to have potential application in industry and biology<sup>3</sup>. The derivatives of such compounds as such and also after suitable structural modifications may become potential candidates for industry. In the absence of any complicating donor side chains, the naturally occurring amino acids have been found to coordinate solely through the amino and carboxylate groups forming stable chelate rings with the metal ions 4-6. First row transition metal complexes of virtually all the amino acids have been

studied in considerable detail but these are virtually few reports regarding Ti(III) complexes. Keeping this fact in view, we have studied Ti(III) complexes.

### EXPERIMENTAL

All the chemicals used in present work, various aldehydes and amino acids were of AR grade or equivalent purity. Ti(III)chloride was prepared in the lab by the standard method given in chemical literature. The ligands as well as metal complexes were analysed by standard methods. Melting points were determined by open capillary method and are uncorrected. Conductivity measurements were carried out on Philips

conductivity Bridge model PR 9500 using  $10^{-3}$  M (25°C) DMSO & DMF solutions at Deptt. of Chemistry, Bareilly College, Bareilly. The IR spectra were recorded using Perkin Elmer Pc-16f FTIR spectrophotometer by using KBr pellets. Magnetic susceptibility was determined by Gouy's balance using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as calibrant. Electronic spectra were recorded by Beckmann DU spectrophotometer.

### Preparation of ligands

NaOH(10m mol,0.4g) was dissolved in methanol (30ml) and the amino acid(10m mol) was added to it. The mixture was stirred magnetically at room temperature(20°C). When the mixture became homogeneous, a solution of the aldehyde(10m mol.) in ethanol (20 ml) was added. After 2 minutes the solution was evaporated to 20% of its's original volume and 1ml of  $\text{CH}_3\text{COOH}$  was added immediately. After 2 hours crystals appeared. Which were purified by recrystallisation. The purity of the samples was checked by TLC.

### Preparation of metal complexes

An ethanolic solution of the ligand (2.5m mol) was added to a solution of the titanium (III) chloride (1.25 m mol) in a similar solvent at 40°C. The mixture was stirred and boiled for 5 min. The precipitation was induced by the addition of acetonitrile. The micro crystalline complexes, so obtained, were filtered, washed successively with ethanol and ether and dried in vacuum. The entire procedure was carried out under the atmosphere dry nitrogen gas in a glove bag in order to avoid the possible oxidation of Ti (III).

### RESULTS AND DISCUSSION

The analytical data of the compounds are given in table-1.

The structural determination of synthesized Schiff bases was done on the basis of

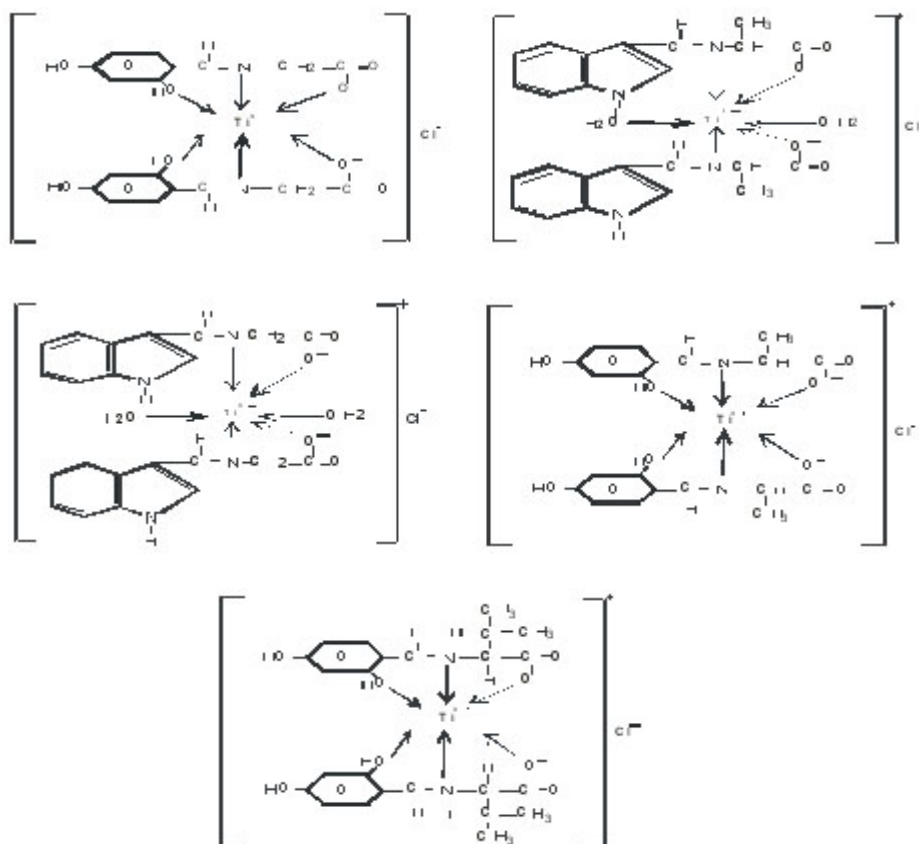


Table 1: Characterisation of complexes prepared

S. No.	Name of complex Formula	Molecular (In °C)	M.Pt.	Elemental analyses			Magnetic Moment (B.M.)	MOLAR Conductance Values ( $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )			
				%Metal	% C	% H		% N	%Cl	DMSO	DMF
1	L-Alanine 2,4 di hydroxy benzaldehyde titanium (III) chloride	$[\text{Ti}(\text{C}_{10}\text{H}_{10}\text{NO}_4)_2]\text{Cl}$	$310^\circ$	9.60 (9.51)	48.06 (48.04)	4.00 (3.90)	5.61 (5.50)	7.10 (7.40)	1.69	50	78
2	L-Alanine Indole -3- aldehyde titanium (III) chloride	$[\text{Ti}(\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}]\text{Cl}$	$290^\circ$	8.72 (8.65)	52.42 (52.35)	4.73 (3.86)	10.20 (10.00)	6.46 (6.41)	1.71	60	76
3	Glycine 2,4 di hydroxy benzaldehyde titanium (III) Chloride	$[\text{Ti}(\text{C}_9\text{H}_9\text{NO}_4)_2]\text{Cl}$	$270^\circ$	10.16 (10.12)	45.82 (45.75)	3.4 (3.35)	5.94 (5.90)	7.53 (7.45)	1.72	54	68
4	Glycine Indole -3- aldehyde titanium (III) chloride	$[\text{Ti}(\text{C}_{11}\text{H}_9\text{N}_2\text{O}_2)_2 \cdot 2\text{H}_2\text{O}]\text{Cl}$	$286^\circ$	9.18 (9.15)	50.63 (50.60)	4.22 (4.20)	10.74 (10.70)	6.81 (6.75)	1.75	59	75
5	Valine 2,4 di hydroxy benzaldehyde titanium (III) Chloride	$[\text{Ti}(\text{C}_{12}\text{H}_{14}\text{NO}_4)_2]\text{Cl}$	$297^\circ$	8.62 (8.58)	51.85 (51.80)	5.04 (5.01)	5.04 (5.00)	6.40 (6.00)	1.74	67	72

their I.R., <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and CHN analytical data.

The appearance of new bands in the range of 1620-1640 cm<sup>-1</sup> in the I.R. spectra of the ligands assignable to Schiff base azomethine linkage confirm the formation of the ligands. The <sup>1</sup>H- NMR and <sup>13</sup>C- NMR spectral data was assigned by comparing the chemical shifts of these molecules to those of known similar structures.

The comparison of IR spectra of the ligands (GIA),(GDHB),(AIA),(ADHB) and (VAIA) with their respective Ti(III) complexes revealed important information about various coordination sites. The comparison also revealed monobasic bidentate nature for (GIA) & (AIA) and monobasic tridentate nature for (GDHB), (ADHB) and (VAIA).

The band in the range of 1640-1620 cm<sup>-1</sup> due to  $\nu$ (C=N) in the IR spectra of all the ligands showed a downward shift in their corresponding Ti(III) complexes. These shifts suggested the coordination through nitrogen atom of azomethine group<sup>7</sup>. This was further supported by appearance of non ligand band in the IR spectra of Ti(III) complexes in the range of 520-550cm<sup>-1</sup>, assignable to  $\nu$ (Ti-N).

In the IR spectra of the ligands the (COO-) is greater than 200 cm<sup>-1</sup> which [(COO-) asym at 1600cm<sup>-1</sup> and (COO-)sym at 1400cm<sup>-1</sup>] indicates the unidenticity of the carboxylate group<sup>7</sup>. The asymmetric stretching  $\nu$  asym(COO-) has shifted to higher frequency and the symmetric carboxyl stretching sym(COO-) has shifted to lower frequency in the IR spectra of all the Ti(III) complexes. These shifts indicated coordination between metal ion and carboxylate oxygen atom<sup>8</sup>.

In the case of the ligands (GDHB),(ADHB) AND (VAIA) a band has appeared in the region 1535-1520 cm<sup>-1</sup> which has been assigned to  $\nu$ (C-O) (phenolic) stretching<sup>9</sup>. These bands have shifted to higher frequency in the IR spectra of the metal complexes, suggesting coordination of the phenolic oxygen with metal ion. It was further supported by the appearance of non-ligand band in the far IR spectra of the complexes in 440-400 cm<sup>-1</sup> region attributable to  $\nu$  (M-O) vibrations<sup>10</sup>.

Table 2: Antimicrobiol Activity MIC (mgL<sup>-1</sup>)

S. No.	Micro organism	Compound										
		GTA	GDHB	AIA	ADHB	VAIA	[Ti(GIA)]cl	[Ti(GDHB)]cl	[Ti(AIA)]cl	[Ti(ADHB)]cl	[Ti(VAIA)]cl	Sulphaguanidine
1	<i>S.aureus</i>	225	220	150	210	170	275	245	210	250	190	1200
2	<i>B.pumilis</i>	210	190	140	210	160	245	225	165	240	180	1400
3	<i>B.subtilis</i>	200	180	150	190	150	230	210	170	220	180	1200
4	<i>E.coli</i>	200	210	160	190	160	220	240	180	200	170	1500
5	<i>S.abony</i>	210	200	160	190	170	220	200	190	210	190	1500
6	<i>K.pneumoniae</i>	250	250	250	225	250	250	300	325	310	290	1700

In the complexes of Ti(III) derived from the ligands  $\nu(\text{GIA})$  and  $\nu(\text{AIA})$ , the coordinated nature of water molecules has been indicated by the appearance of new bands in their respective IR spectra in the region of  $3400\text{-}3200\text{ cm}^{-1}$  due to (OH) vibrations of coordinated water and OH rocking and wagging bands in the regions  $800\text{-}750\text{ cm}^{-1}$  and  $720\text{-}700\text{ cm}^{-1}$  respectively<sup>11</sup>.

The electronic spectra of the complexes exhibited only one band in the range of  $19607\text{-}20410\text{ cm}^{-1}$ , which has been assigned to  ${}^2T_{2g} \rightarrow {}^2E_g$  transition, characteristic of octahedral geometry<sup>12</sup>. The  $\mu_{\text{eff}}$  value of 1.69-1.74 B.M. for all the complexes indicated the paramagnetic nature with one unpaired electron, thereby suggesting octahedral geometry<sup>13</sup>. Conductivity of the complexes was measured in DMSO & DMF and all the complexes were found to be 1:1 electrolytic in nature of the type  $[\text{ML}]\text{Cl}$ . The aforesaid physico chemical evidences suggested octahedral geometry for all Ti(III) complexes.

All the ligands and their respective Ti(III) complexes were screened for their antibacterial activity. A series of glass tubes<sup>14,15</sup> containing different concentrations of the synthesized compounds in DMF, with Muller-Hinton broth was inoculated with the required amount of inoculum to obtain a suspension of microorganism which contained  $10^5$  colony forming units per millilitre. One growth control tube was prepared without the addition of compound and one blank tube was inoculated at  $37\text{ }^\circ\text{C}$  for 24 h. The turbidity produced was recorded by using a uv-visible spectrometer. The minimum inhibitory concentration (MIC- $\text{mg L}^{-1}$ ) was considered to be the lowest concentration which exhibited the same turbidity as the blank tube. The results are tabulated below.

These results revealed that the metal complexes are more potent antibacterial as compared to corresponding ligands.

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