

## Physico-chemical studies on titanium (III) complexes of polydentate Schiff bases

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(Received: October 04, 2008; Accepted: December 09, 2008)

### ABSTRACT

The present investigation describes the synthesis and complexation of Schiff base derivatives with Ti(III). The complexes were characterized by physico-chemical methods and spectroscopy.

**Key words:** Titanium (III), Polydentate schiff bases.

### INTRODUCTION

The co-ordination chemistry has developed into almost a full fledged branch of chemistry during 19th century. A co-ordination compound results from the interaction of the metal ion with the ligand. During the last 30 years schiff bases have occupied an important position among the ligands. A schiff base results by the condensation of the compound containing carbonyl group and a compound containing amino group. Titanium has been called "the wonder metal" because of its unique and useful properties. Keeping in view the importance of titanium complexes, we synthesised and characterised the complexes of titanium and results of study are reported here.

The complexes of titanium (III) with Schiff bases viz salicylaldehyde-2-furoic acid hydrazide (SFH), Dihydro acetic acid carbodihydrazone (DHACH) and N-Benzoyl N'-2-furan thio carbonylhydrazide (BFTCH). The schiff base SFH was formed by the condensation of salicylaldehyde and 2-furoic acid hydrazide, DHACH was formed by carbonylhydrazide and 3-acetyl-6-methyl 2H pyran-2,4 (3H) dione and BFTCH was formed by N-Benzoyl-N-2-furan thio carbonylhydrazide and benzoic acid hydrazide and carboxy methyl 2-furan dithioate. These complexes were characterized by elemental analyses, molar conductance, magnetic measurements, electron spin resonance NMR, IR and UV spectroscopic studies.

### MATERIAL AND METHODS

All chemical used were of analytical grade. The ligands were prepared by different carbonyl and amino compounds. The carbonyl compound used were salicylaldehyde, dihydroacetic acid and furan-2-di-thioic acid and the amino compound used were 2-furoic acid hydrazide, carbonylhydrazide and benzoic acid hydrazide.

The elemental analysis were carried out of RSIC CDRI, Lucknow. Conductivity measurements were carried out at Philips Conductivity Bridge model PR 9500 with a dip type conductivity cell at Deptt. of Chemistry, Bareilly College, Bareilly. The conductance of the complex were measured in methanol, DMF and DMSO at 25°C. Magnetic susceptibility of the complexes were determined by Gouy method at the Deptt. of Chemistry in Bareilly College, Bareilly. The sample tube was calibrated with  $\text{CuSO}_4$ . The IR spectra of complexes were recorded with Perkin Elemer Spectrometer model 651 in KBr or in nujol phase at RSIC, CDRI, Lucknow. The visible spectra were recorded with Beckmann DU-2. Spectro-photometer in the range of  $750\text{ cm}^{-1}$  to  $300\text{ cm}^{-1}$  at Chemistry Department in Bareilly College, Bareilly.

### Preparation of ligands

The schiff base were prepared by the condensation of carbonyl and amino compound. The amino compound was dissolved in ethanol and

refluxed for about half an hour. Now the requisite amount of carbonyl compound was added to the flask and this mixture was refluxed for about six hours and kept for 24 hours. The crystals of ligand were obtained and purified by recrystallisation. The purity of ligands were checked by elemental analysis and M.P.

#### Preparation of Titanium (III) complex

Approximately 250 ml of Titanium (III) chloride aqueous solution (containing 15% of  $TiCl_3$ ) was taken and 4-5 gm titanium metal sponge added to it. This mixture was cooled over a freezing mixture and dry HCl gas was passed through the solution at a low temperature. Now the Ti (III) chloride solution was covered by a thick layer of toluene which protected it against oxidation. After saturation with HCl gas the solution was warmed over a water bath.

The titanium metal reacted with HCl gas to form  $TiCl_4$  which was subsequently reduced to  $TiCl_3$  by hydrogen gas produced during the reaction. The deep blue coloured solution was obtained the titanium (III) chloride in the solution with high concentration was kept inside a freezing mixture for 10 hours when the dark blue coloured crystals of  $TiCl_3 \cdot 6H_2O$  were obtained at the bottom of the flask.

### RESULTS AND DISCUSSION

Elemental analysis reveals that the titanium complexes have the compositions with SFH has  $C_{12}H_8N_2O_3$ ,  $TiCl_3 \cdot H_2O$ , DHACH has  $C_{17}H_{16}N_4TiCl_2 \cdot 2H_2O$  and with BFTCH has  $C_{12}H_8N_2O_2S$   $TiCl_2 \cdot H_2O$ . The electrolytic nature of titanium (III) complexes measured in DMF, DMSO and methanol at  $10^{-3}$  dilution indicate 1:1 electrolytic nature of the complexes.

The measurement of the magnetic property by Gouy's method gives a value varies from 1.69 to 1.78 BM for the magnetic moment of the complexes. These values are close to the expected value for  $d^1$  system. The electronic spectral bands of the present titanium (III) complex shows a band at  $17900\text{ cm}^{-1}$ . Which may be assign to d-d transition. The value of d-d transition corresponds to crystal field spitting energy. The spectrum of the complex also show a weak band at  $22525\text{ cm}^{-1}$  with a

Table 1: Physical and Analytical data of Titanium (III) Complexes

S. No.	Name & molecular formula of complexes	Colour	M.P.	C	G	N	S	Cl	Solubility	Magnetic molar moment conduc in B.M. tance $Ohm^{-1} mol^{-1} cm^{-1}$
1.	Salicylaldehyde-2-furoic acid hydrazide $C_{12}H_8N_2O_3 \cdot TiCl_3 \cdot 3H_2O$	Yellow	360	39.41 (39.39)	3.83 (3.68)	7.66 (7.32)	-	9.71 (9.58)	DMF	1.71 3.76
2.	Dihydro acetic acid carbohydrazone $C_{17}H_{16}N_4 \cdot TiCl_2 \cdot 2H_2O$	Light Yellow	280	40.2 (39.98)	3.94 (3.62)	11.03 (11.00)	-	6.99 (6.74)	DMSO	1.78 4.08
3.	N-Benzoyl N-2-furan thiocarbohydrazide $C_{12}H_8N_2O_2 \cdot STiCl_2 \cdot 2H_2O$	Brown	350	39.62 (39.18)	3.30 (3.08)	7.70 (7.20)	8.80 (8.28)	9.76 (9.24)	DMSO	1.69 3.90

shoulder in the region of 17350  $\text{cm}^{-1}$ . These bands have been assigned to  ${}^2B_{1g} \leftarrow {}^2B_{2g}$  and  ${}^2D_{1g} \leftarrow {}^2B_{2g}$  transition respectively. The transition is characteristic to have octahedral geometry.

The ir spectra of the SFH shows an important absorption band at 1640  $\text{cm}^{-1}$  which may be assigned  $\nu(\text{C}=\text{O})$  vibration this band is absent in the spectra of the complex indicating the destruction of carbonyl group due to enolisation. The enolisation is enhanced due to stabilization of anion by conjugation with  $>\text{C}=\text{N}-\text{N}=\text{C}<$  group.

A strong band in the spectra of the schiff base at 1620  $\text{cm}^{-1}$  may be assigned to  $\nu\text{C}=\text{N}$  which under goes a negative shift by 10  $\text{cm}^{-1}$  in the spectra of the complex this indicate the co-ordination is occurring through azomethine nitrogen<sup>1</sup>.

The ir spectrum of the ligand shows another important absorption band at 1550  $\text{cm}^{-1}$ , which may be assigned  $\nu\text{C}=\text{O}$  phenolic mode. This band undergoes a positive shift by 8  $\text{cm}^{-1}$  suggesting the co-ordination of the phenolic C-O group<sup>2</sup>.

The ir spectrum of the complex shows a new band at 3400  $\text{cm}^{-1}$  which may be due to co-ordinated water molecules. The appearance of a band at 810  $\text{cm}^{-1}$  may be assigned to wagging and rocking modes of co-ordinated water molecules.

The  $\nu\text{C}-\text{O}-\text{C}$  mode of furan moiety occurs in the free ligand at 1080  $\text{cm}^{-1}$ . This band remains

unaffected in the complex indicating the non involvement of the oxygen atom of furan moiety in coordination. Thus the ir data indicate that the schiff base behaves as tridentate ligand co-ordinated through ONO donor system<sup>5</sup>.

The ir spectra of DHACH titanium (III) complex a new band at 3500  $\text{cm}^{-1}$  appears which is characteristic of co-ordinated water molecule<sup>4</sup>. The appearance of a non ligand band at 830  $\text{cm}^{-1}$  may be assigned to rocking mode of water<sup>5</sup>. The absence of  $\nu\text{OH}$  phenolic band at 3400  $\text{cm}^{-1}$  of the ligand in the spectrum of the complex suggests the cleavage of intramolecularly hydrogen bonded OH and subsequent deprotonation of phenolic group and coordination of phenolic oxygen to the metal ion<sup>6</sup>.

The  $\nu\text{C}=\text{N}$  azomethine observed at 1640  $\text{cm}^{-1}$  in the free ligand undergoes a downward shift at 25  $\text{cm}^{-1}$  in the spectrum of the complex this indicate the participation of azomethine nitrogen in complexation<sup>5</sup>. The medium intensity band at 1510  $\text{cm}^{-1}$  of carbodihydrazone shows a upward shift and appears at 1530  $\text{cm}^{-1}$  in the spectrum of complex. This shows that phenolic oxygen in exhibiting in monodentate behaviour. A new band appears to 325  $\text{cm}^{-1}$  which may be attributed to metal chlorine band.

From the above ir spectra data it has been concluded that the ligand behaves as a dibasic tetradentate ligand co-ordinating through deprotonated phenolic oxygen and azomethine nitrogen in O:N:N:O donor sequence.

**Table 2 : Spectroscopic data of Titanium (III) Complexes**

S. no.	Name & Molecular Formula of complexes	Important peaks in ir spectra		
		$\nu\text{C}=\text{N}$	$\nu\text{-Co-ordinated water molecule}$	$\nu\text{C}-\text{O}$ phenolic mode
1.	Salicylaldehyde-2-furoic acid hydrazide $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_3\text{TiCl}_3\cdot 3\text{H}_2\text{O}$	1620 $\text{cm}^{-1}$	3400 $\text{cm}^{-1}$	1500 $\text{cm}^{-1}$
2.	Dihydro acetic acid carbohydrazone $\text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_7\text{TiCl}_2\cdot 2\text{H}_2\text{O}$	1640 $\text{cm}^{-1}$	3500 $\text{cm}^{-1}$	1510 $\text{cm}^{-1}$
3.	N-Benzoyl N-2-furan thiocarbohydrazone $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2\text{STiCl}_2\cdot 2\text{H}_2\text{O}$	-	3420 $\text{cm}^{-1}$	-

The ir spectral data of BFTCH titanium (III) complex show one peak at  $3125\text{ cm}^{-1}$  due to a  $\nu\text{N-H}$  suggesting the loss of one hydrazine proton via enolisation a strong band in the spectrum of the ligand at  $1640\text{ cm}^{-1}$  due to  $\nu\text{C=O}$  is found to be absent in the spectrum of the complex and a new band appears due to  $\nu\text{N=C}$  of NCO suggesting that enolic oxygen is involved in bonding. The spectrum of the complex shows a negative shift of  $20\text{ cm}^{-1}$  in  $\nu\text{C=S}$  suggesting an additional bonding through thio sulphur.

The spectrum of the complex shows a positive shift of  $20\text{ cm}^{-1}$  in  $\nu\text{N=N}$  indicates the involvement of hydrazine nitrogen in bonding. Further the band at  $1460$ ,  $1325$  and  $1000\text{ cm}^{-1}$  due to thioamide I, II and  $\nu\text{N-N}$  undergo positive shift of  $25$ ,  $15$  and  $20\text{ cm}^{-1}$  respectively showing the involvement of thiolato sulphur (8). This shows that

the ligand is acting in bidentate tetradentate manner co-ordinating through thiolato sulphur, both the hydrazinic nitrogen and enolic oxygen.

A new band appears at  $3420\text{ cm}^{-1}$  which may be due to presence of co-ordinated water molecule. The rocking wagging modes of water molecules appears at  $810\text{ cm}^{-1}$  which confirmed its co-ordinated nature.

#### ACKNOWLEDGEMENTS

The authors are highly thankful to Dr. R.P.Singh Principal, Bareilly College Bareilly for providing Lab facilities to carry out this work. The author are highly thankful to Dr. A.K. Garg, Principal Scientist, Animal Nutrition, IVRI for encouragement and guidelines. We are also thankful to CDRI, Lucknow and RSIC to provide analytical facilities.

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