

## The qualitative analysis of Bis (p'-methoxybenzaldehyde) Sulphonamide Titanium (III) Chloride

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### Abstract

Titanium was discovered by William Gregor and Klaproth in 1791 later found this element in the form titanium dioxide. Titanium is the second member of first transition series of metals. It has four valency electrons and its oxidation states varies from (IV) to -(I). The most common co-ordination number of titanium is six for all the oxidation states of metal. However, only few complex compounds are known in which its coordination number is four, five, seven or eight. This chapter comprises of titanium (III) complexes (consisting d<sup>1</sup> system) with some schiff base ligands like bis (p'-methoxy benzaldehyde) sulphonamide, p'-methoxy benzaldehyde sulphafurazole, p'-methoxy benzaldehyde sulphisomedine, bis (N,N'-Di methyl-4-amino benzaldehyde) Sulphonamide, N,N'-Dimethyl-4-aminobenzaldehyde Sulphafurazole, N,N'-Dimethyl-4-amino benzaldehyde Sulphisomedine, bis (N,N'-Di methyl-4-amino cinnamaldehyde) Sulphonamide, N,N'-Dimethyl-4-amino cinnamaldehyde sulphafurazole and N, N'-Di methyl-4-amino cinnamaldehyde Sulphisomedine.

**Keywords:** titanium, Schiff base, co-ordinate compounds.

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### I. Introduction

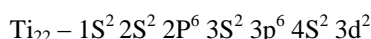
Titanium is reasonably common element which has been known for over 170 years. The average titanium content of the earth's crust is 0.63% by weight, which makes it the ninth most abundant element in the earth's crust. It is only really in this country that elemental titanium has developed any industrial potential, partly because of difficulties associated with its refinement.

Titanium was discovered in 1791 by William Gregor, an English clergyman and amateur chemist. He identified it in the black sand (now known to be ilmenite) sent to him for analysis from the Menacchan Valley in Cornwall. Four years later, the favour German chemist Klaproth rediscovered the element in the ore rutile, a form of titanium dioxide. He christened the element as titanium.

The element was first obtained pure in 1910 by Hunter (1) via reduction of its tetrachloride with sodium. In 1925, Van Arkel and de Boer (2) obtained a very pure form of the metal by dissociation of the tetraiodine. Nonetheless, the titanium metal industry really dates from the publication of the Kroll Process (3) in 1940, which involves reduction of the tetrachloride with magnesium.

The most important use titanium is in the form of the dioxide (rutile or anatase) as a white pigment in the paint industry. Its outstanding property is its capacity or covering power; this, with its relative chemical inertness, has resulted in its almost complete replacement of all over white pigment. Related uses arise in the paper, plastic, rubber, textile and vitreous enamel industry.

Titanium is a transition or d block element of the first transition series and belongs to the IV B group, having electronic configuration -



Titanium is a silvery, ductile metal with important industrial uses because it is less dense than iron, much stronger than aluminum and almost as corrosion resistant as platinum. Moreover, titanium dust is explosive in air. The kinetic of oxidation of metal in the range 850-1050°C have been studied (4).

Titanium is the first member of 3d-transition series and has four valence electrons. The most common oxidation state, +4 involves the loss of all these electrons. However, the element may also exist in a range of lower oxidation states, most importantly as Ti (III), which is much less stable and has 4f<sup>0</sup>3d<sup>1</sup> configuration. Tripositive titanium is more ionic and exists in aqueous solution as a blue violet [Ti (H<sub>2</sub>O)<sub>6</sub>]<sup>+3</sup> ion. Due to change in Ti<sup>+4</sup> it has strong reducing property. Few titanium (III) complexes have been studied till now. Compound of many stoichiometric ratio are known e.g. [TiCl<sub>6</sub>]<sup>+3</sup>, [ML<sub>4</sub>X<sub>3</sub>] & [ML<sub>2</sub>X<sub>4</sub>]

A survey of the range of those compounds and their electronic spectral and magnetic properties is given in Clark's review (5). Fowles *et al.* have isolated a range of titanium (III) iodine species. TiI<sub>3</sub>L<sub>2</sub> (L = NMe<sub>3</sub>, ∞ - Picoline), TiI<sub>3</sub>L<sub>3</sub> (L = Py, ∞ - Picoline) and TiI<sub>3</sub> (MeCN)<sub>4</sub>, the last being assigned the formula [TiI<sub>2</sub>(MeCN)<sub>4</sub>].

The magnetic properties of  $\text{TiBr}_3(\text{NMe})_2$  (6) and its single crystal X-Ray structure have been studied (7), the later showing it to be monomeric and basically trigonal bipyramidal.

The relative Ti (III)-N complexes of the dialkylamides are useful synthetic reagents, readily reacting with protic solvents like alcohols, unsaturated compounds such as isocyanates to yield ureido derivatives, or metal hydrides to give Ti-M bonded compounds (8). Rare three co-ordination occurs in  $[\text{Ti}\{\text{N}(\text{SiMe}_3)_3\}]_3$  (9). It is possible to use electronic spectroscopy to distinguish the penta-co-ordinate  $\text{MX}_3\text{L}_2$  ( $\text{L} = \text{NMe}_3$   $\infty$ -picoline) species from the hexa co-ordinate  $\text{MX}_3\text{L}_3$  species, since the former have characteristic absorption band in the near Infra Red region (10), whereas ESR spectroscopy has been used to show that the  $\text{TiCl}_3(\text{Py})_2$  complex is determined and hexa co-ordinate via. Chlorobridge in pyridine at 77K (11).

The blue en. and pn. complexes have the formula  $[\text{Ti}(\text{ligand})_3]^{+3}$ , where as for bipy. and phen  $[\text{TiCl}_2(\text{ligand})_2][\text{TiCl}_4(\text{lig.})]$  salts are obtained (4), the salts  $[\text{TiI}_2(\text{Phen})_2]\text{I}$  and  $(\text{TiI}_2(\text{bipy})_2)[\text{TiI}_4(\text{bipy})]$  are also known (12). Whereas most transition metal complexes of tris (2-dimethylamino ethyl) amine (Me tren) normally involve all four nitrogen co-ordinated, in  $\text{TiCl}_3(\text{Meg tren})$  only three amines are bounded. With terpy all three nitrogen are bounded in the detahedral monomeric  $\text{TiCl}_3$ , (terpy)(13).

Nearly all titanium complexes exhibit room temperature magnetic moment close to 1.73 BM, and at low temperature the fall in value is related not only to the temperature but also to the asymmetry of ligand field (4,13, 14). Most complexes contain a ground term  ${}^2\text{T}_{2g}$ , split by  $500\text{ cm}^{-1}$ ; the orbital angular moment is reduced by a factor K which is usually 0.65-0.95.

Early workers assumed that alcohol ligands formed  $[\text{TiL}_6\text{Cl}_3]$  complexes, analogous to the hexa aqua species. However, electronic spectra have pointed to these complexes as being of the type  $[\text{TiCl}_2\text{L}_4]$ . For THF, dioxane, DMF, MECN and some other nitrogen ligands the  $[\text{TiL}_3\text{Cl}_3]$  complexes are known, but all of these are very susceptible to oxidation.

## **TITANIUM (III) COMPLEXES WITH SCHIFF BASES**

### **EXPERIMENTAL PROCEDURE**

#### **1. PREPARATION OF TITANIUM (III) CHLORIDE**

The titanium (III) chloride was prepared from 12.5% titanium trichloride (aqueous) and concerned procedure is described in materials and methods (15).

#### **2. PREPARATION OF SCHIFF BASE LIGANDS**

Schiff bases were synthesised from various aldehydes like p-methoxybenzaldehyde,  $\text{N}_1, \text{N}^1$ -Dimethyl-4-amino benzaldehyde and  $\text{N}, \text{N}^1$ -Dimethyl-4-amino cinnamaldehyde, while sulphadiazole and sulphisomedine were used as amines. The methods of preparation of the schiff bases are described in chapter of materials and methods.

#### **3. PREPARATION OF COMPLEXES**

The complexes of titanium (III) were prepared by addition of  $\text{TiCl}_3$  solution in THF to the ethanolic solution of ligands in an inert atmosphere of nitrogen; the precipitate thus obtained was immediately filtered and washed with the solvent to remove any excess of ligands. The precipitate was dried in vacuum desiccators over anhydrous calcium chloride.

#### **4. CHARACTERIZATION OF COMPLEXES**

The complexes so obtained were subjected to various physico-chemical studies such as-

- Elemental analysis were also performed for chlorine, sulphur and nitrogen. Chloride and sulphur were estimated gravimetrically as  $\text{AgCl}$  and  $\text{BaSO}_4$  respectively. Nitrogen was estimated by micro kjeldahl method.
- The IR spectra of the complexes were recorded.
- Conductivity measurements were carried out at  $10^{-3}\text{M}$  concentration in three solvents methanol, DMF and DMSO.
- MP./decomposition temperature of these adducts were determined.
- The magnetic moments were also measured at room temperature by Gouy method. The sample was calibrated with  $\text{CoHg}(\text{SCN})_4$ .
- Some complexes were subjected to thermo-gravimetric studies.

## **II. RESULTS AND DISCUSSION**

### **Bis (p--methoxybenzaldehyde) Sulphonamide Titanium (III)Chloride**

The analytical data of this complex reveals that two moles of the ligand have reacted with a titanium (III) ion. The composition of complex has been found to be  $[(\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4)_2, 2\text{H}_2\text{O} \cdot \text{TiCl}_3]$ . The complex obtained was of cream colour.

The melting point of the schiff base ligand has been found to be  $180^\circ\text{C}$ . However, the melting point of complex was found to be  $207^\circ\text{C}$ . It indicates that a new complex compound has been formed.

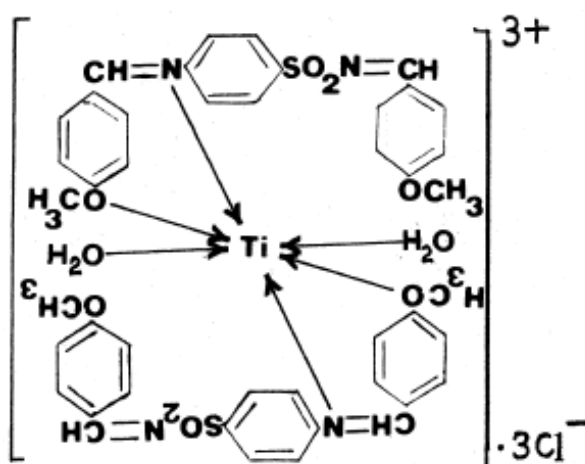
The molar conductance of the complex in the three solvents i.e. methanol, DMF and DMSO at 0.001 molar concentration comes to be 324.0, 298.6 and 301.4  $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , respectively. Which are indicative of the 1:3 electrolytic nature of the complex,

The magnetic moment of the complex at room temperature was found to be 1.64 B.M., which is quite close to expected value of 1.73 B.M. as calculated for  $d^1$  system.

The IR spectra of the schiff base ligand shows some important peaks at 2800 (m)  $\text{cm}^{-1}$  1670 (w)  $\text{cm}^{-1}$  1610 (s)  $\text{cm}^{-1}$ , 1340 (w)  $\text{cm}^{-1}$  and 1175 (s)  $\text{cm}^{-1}$ , which assigned to  $\gamma$ C-H vibration in aromatic ring, C=O stretching, C=N stretching vibration,  $\gamma$ N C<sub>aromatic</sub> vibration, and  $\gamma$  C<sub>aromatic</sub>O<sub>aromatic</sub> C vibrations, aromatic aromatic aliphatic respectively. The spectra of the complex exhibits the shifts in the peaks at azomethine group and methoxy group. It indicates that co-ordination must have occurred through nitrogen of azomethine and oxygen of the methoxy groups (10 & 11).

A new peak appears in the spectra of the complex at 925 (m)  $\text{cm}^{-1}$ . This may be due to co-ordinated water molecules. Thus the schiff base seems to be acting as a bidentate ligand. The metal ion is hexa co-ordinated and, therefore, should have octahedral geometry. The presence of co-ordinated water is also supporting by TGA.

The probable structure of the complex is



#### *p*-methoxy benzaldehyde Sulphafurazole Titanium (III) Chloride

The analytical data of this complex shows that two molecules of schiff base ligands are co-ordinated with one titanium (III) ion. The composition of pale yellow coloured adducts may be written as  $[(C_{19}H_{19}N_3O_4S)_2 \cdot 2H_2O TiCl_3]$ . The melting point of the schiff base ligand is 108°C and that of the complex is 198°C. It indicates that a new complex compound has been formed.

The molar conductance of the complex in the three solvents viz., methanol, DMF and DMSO at 0.001 molar concentration were found to be 301.0, 320.6 and 299.6  $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , respectively, which are indicative of 1:3 electrolytic nature for complex.

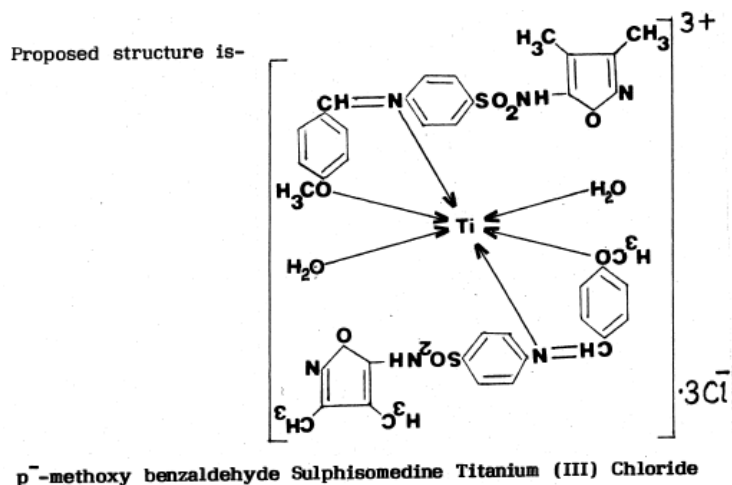
The values of magnetic moment for the complex has been found to be 1.68 B.M., indicating its paramagnetic behaviour due to presence of an unpaired electron. It has slightly lower magnetic moment as expected for one unpaired electron i.e. 1.73 B.M.

The IR spectra of the ligand shows a number of important absorption bands at 2920(w)  $\text{cm}^{-1}$  2805(w)  $\text{cm}^{-1}$ , 1660(m)  $\text{cm}^{-1}$ , 1600 (S)  $\text{cm}^{-1}$  1350(w)  $\text{cm}^{-1}$  and 1135(S)  $\text{cm}^{-1}$  which may be attributed to  $\gamma$  C-N,  $\gamma$ C-H vibration in aromatic ring, C=O stretching, C=N stretching vibration,  $\gamma$ C<sub>aromatic</sub>N vibration and  $\gamma$  C<sub>aromatic</sub>O<sub>aliphatic</sub> C vibrations, respectively.

The spectra of the complex also exhibits a number of significant peaks, a few of them showing shifts. The spectra of the complex show shifts in the peak of azomethine group (1630(vs)  $\text{cm}^{-1}$ ) and methoxy group (1130(vs)  $\text{cm}^{-1}$ ), which suggested that nitrogen of azomethine group and oxygen of methoxy group participated in co-ordination.

A new peak appears in the spectrum of complex at 925(m)  $\text{cm}^{-1}$ . It may be due to involvement of water molecules in co-ordination. Thus the schiff base ligand seems to be acting as bidentate ligand.

It, therefore, appears that out of the six co-ordinated sites four are occupied by two ligand molecules and two by water molecules. On the basis of above finding complex seems to have possess octahedral geometry.



The composition of dark yellow coloured titanium complex on the basis of analysis for various elements was established as [(C<sub>20</sub>H<sub>20</sub>N<sub>4</sub>O<sub>3</sub>S)<sub>2</sub>·2H<sub>2</sub>O TiCl<sub>3</sub>], which indicates 1:2 metal-ligand ratio. The melting point of the schiff base ligand is 155°C and that of the complex is 190°C. It indicates a new complex compound has been formed.

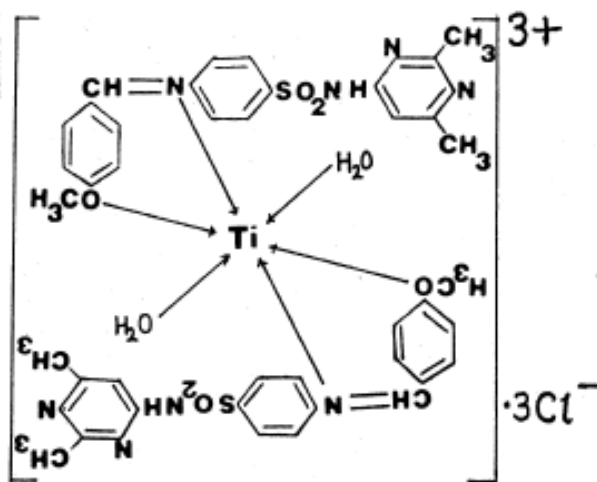
The molar conductance of the complex at 0.001 molar concentration in three solvents i.e. methanol, DMF and DMSO corresponds to the value that of 1:3 electrolytic nature.

The magnetic moment of the complex at room temperature was found to be 1.67 B.M., which indicate that the complex containing titanium (III) ion. Since the value of  $\mu_{\text{eff}}$  corresponds to the presence of one unpaired electron ( $\mu_{\text{eff}}$  1.73 B.M.).

The IR spectra of the schiff base ligand shows some important absorption peaks at 2890(w), cm<sup>-1</sup>, 2800(w) cm<sup>-1</sup>, 1665 (m) cm<sup>-1</sup>, 1620(s) cm<sup>-1</sup>, 1355(w) cm<sup>-1</sup> and 1130(m) cm<sup>-1</sup> which may be assigned to  $\gamma_{\text{C-N}}$ ,  $\gamma_{\text{C-H}}$  vibration in aromatic ring, C=O stretching, C=N stretching vibration,  $\gamma_{\text{C-aromatic-N}}$  vibration and  $\gamma_{\text{C-aromatic-O}}$  C vibration respectively.

In the spectra of the complex a weak and broad band appears at 3440 cm<sup>-1</sup> which is due to O-H and  $\gamma_{\text{C=N}}$  vibration is shifted to a lower frequency on complexation (in complex  $\gamma_{\text{C=N}}$  at 1610(vs) cm<sup>-1</sup>) suggested the participation of azomethine nitrogen take place in the Co-ordination (5 & 8). It also shows a lowering in frequency observed for  $\gamma_{\text{C-aromatic-O-aliphatic-C}}$  vibrations, which appears at 1125(s) cm<sup>-1</sup> suggesting the involvement of methoxy oxygen in co-ordination. Beside it so many other absorption peaks appeared with-out or with slight deviations. A new peak appears in the spectra of the complex at 735 (m) cm<sup>-1</sup>. This may be attributed to the participation of the water molecules in co-ordination. Thus the schiff base acts as a bidentate ligand.

In this way out of six co-ordination sites four are occupied by two bidentate ligand molecules and two sites by two water molecules. Thus complex appears to have octahedral geometry around the central metal ion. Proposed structure is



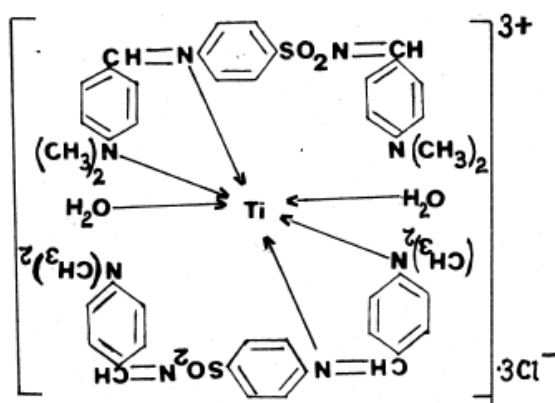
### Bis (N, N'-Dimethyl-4-amino benzaldehyde) Sulphonamide Titanium (III) Chloride

The elemental analysis shows that titanium metal reacts with bis (N,N-Dimethyl-4-amino benzaldehyde) sulphonamide in the 1:2 molar ratio and helped in ascertaining the molecular composition of complex to be  $[(C_{24} H_{26} N_4 O_2 S)_2 \cdot 2H_2O TiCl_3]$ . It is a cream coloured crystalline solid adduct.

The melting point of the ligand was found to be 198°C and that of the complex was 216°C. This indicates that a new complex compound has been formed. The molar conductance of the complex at room temperature in methanol, DMF and DMSO at 0.001 molar concentration exhibit its 1:3 electrolytic nature, the values being 336.0, 306.4 and 330.0  $Ohm^{-1} cm^2 mol^{-1}$ , respectively. The infra red spectra of the ligand exhibits some significant absorption bands at 1620(s)  $cm^{-1}$ , 1640(s)  $cm^{-1}$  and 1140(m)  $cm^{-1}$ . These have been shifted to 1630(vs)  $cm^{-1}$ , 1655(vs)  $cm^{-1}$  and 1145(s)  $cm^{-1}$ , respectively in the spectrum of the complex. It indicates the co-ordination has occurred through azomethine nitrogen.

The complex containing two molecules each of water and the schiff base. This suggests that the ligand is acting as bidentate. The other co-ordination site in the ligand must be the nitrogen atom of the amino group [-N(CH<sub>3</sub>)<sub>2</sub>] because it has shifted at 1145(S)  $cm$  in the spectra of the complex. In this way, the six co-ordination sites in the complex are occupied by two schiff base ligand molecules and two by two water molecules. It is confirmed by a sharp peak at 760(s)  $cm^{-1}$  in the spectra of the complex which is not present in the spectra of the ligand. In this way, the complex is six co-ordinated and to have octahedral geometry around the central metal ion. The value of magnetic moment for the complex has been found to be 1.66 B.M. It indicates the presence of an unpaired electron.

Proposed structure is



### N, N'-Dimethyl-4-amino benzaldehyde Sulphafurazole Titanium (III) Chloride

The molecular formula of this complex is  $[(C_{20} H_2 N_4 O_3 S)_2 \cdot 2H_2O TiCl_3]$  as deduced from its elemental analysis and estimation of metal and chloride. The melting point of the ligand is 200°C and that of complex is 285°C this shows the complex is quite stable.

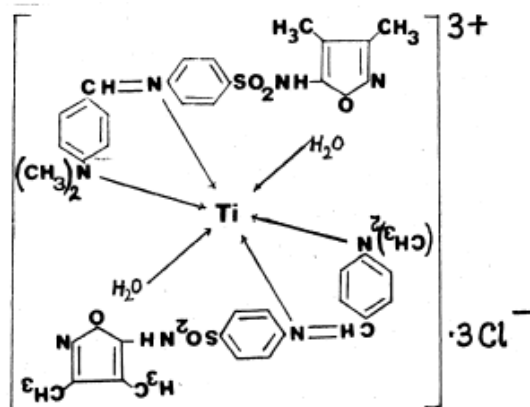
The molar conductance in the three solvents, i.e. methanol, DMF and DMSO indicates 1:3 electrolytic nature of the complex. The magnetic moment of the complex has been found to be 1.68 B.M. It indicates that the complex containing titanium (III) ion. Since the value corresponds to the presence of an unpaired electron (i.e. 1.73 B.M.).

The IR spectra of the schiff base ligand shows some important bands at 1615(vs) $cm^{-1}$ , 1640(vs)  $cm^{-1}$  and 1125(m)  $cm$  these may be attributed by HC=N and  $\nu$  C-N vibrations, respectively. These have been found in the spectra of the complex at 1625(8)  $cm$ , 1650(s)  $cm$  and 1140(s)  $cm$ , respectively. This suggested that the co-ordination is occurring through the nitrogen of azomethine as well as terminal nitrogen of aldehyde (-N(CH<sub>2</sub>),]. Similar observations has also been made by other workers in this field (12).

A sharp band in the free schiff base ligand at 1485  $cm$  remains unaltered in the complex. This is due to ring vibrations. A band at 730(s)  $cm^{-1}$  of the complex reveals the presence of co-ordinated water molecules. It appears, therefore, that the complex has octahedral geometry, in which schiff base molecules are acting as a bidentate ligand and the two sites are occupied by water molecules. In this way the complex is six co-ordinated and must have octahedral shape.



Proposed structure of the complex is



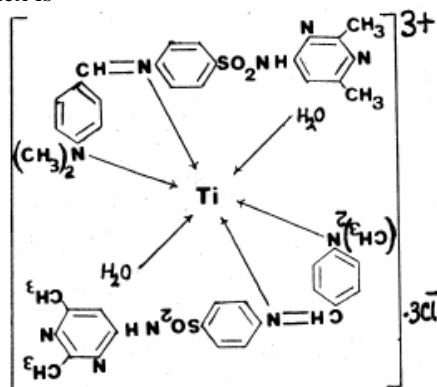
### N, N'-Di methyl-4-amino benzaldehyde Sulphisomine Titanium (III) Chloride

On the basis of elemental analysis for carbon, hydrogen, nitrogen, chlorine and metal, the composition of complex is  $[(C_{21} H_{23} N_5 O_2 S)_2 2H_2O TiCl_3]$  establishing 1:2 metal-ligand stoichiometry. It is milky coloured adduct, which shows the sharp melting point of 204°C. However, the melting point of the schiff base ligand is (150°C). The fact indicates that a new complex compound has been found,

The molar conductance of the complex in the three solvents such as methanol, DMF and DMSO at 0.001 molar concentration were found to be 345, 6, 296.0 and 316.2  $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , respectively, which are indicative of 1:3 electrolytic nature of the complex.

The IR spectra of the schiff base ligand shows some important absorption bands at 1620(s)  $\text{cm}^{-1}$  1600(s)  $\text{cm}^{-1}$  and 1135(m)  $\text{cm}^{-1}$  which are assigned to  $\gamma \text{C}=\text{N}$ ,  $\gamma \text{C}-\text{N}$  vibrations, respectively. These peaks have shifted in the spectra of the complex to 1630(vs)  $\text{cm}^{-1}$ , 1610(vs)  $\text{cm}^{-1}$  and 1140(s)  $\text{cm}^{-1}$ , respectively. It appears that the complexation has occurred through the nitrogen of azomethine and nitrogen of substituted amino groups. As the metal ligand ratio is 1:2, it appear that the nitrogen atom of dimethyl amino group is also taking part in coordination. A new peak appears in the spectra of the complex at 730(s)  $\text{cm}^{-1}$ , this may be due to co-ordinated water molecules.

A sharp peak at 1495(s)  $\text{cm}^{-1}$  in the ligand, also appears in the complex is probably due to ring vibrations. In this way, out of six co-ordination sites, four are occupied by two schiff base ligand molecules and two sites by two water molecules. Thus, possible geometry of the complex is octahedral. The magnetic moment of the complex at room temperature was found to be 1.62 B.M., which is quite close to the expected value of 1.73 B.M. for one unpaired electron. This indicates that the  $Ti^{3+}$  ion has not be oxidised during complexation. The probable structure of the complex is



### Bis (N, N'-D1 methyl-4-amino cinnamaldehyde) Sulphonamide Titanium (III) Chloride

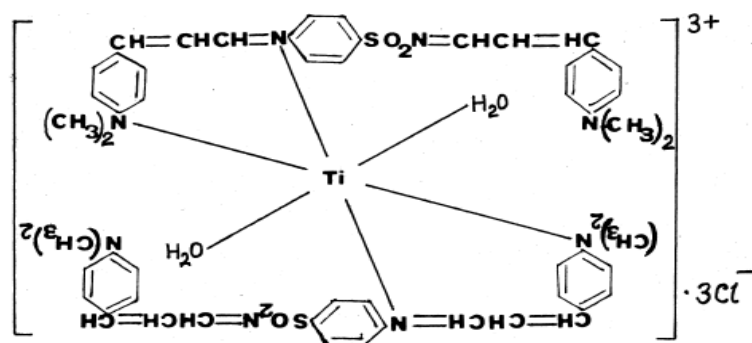
The elemental analysis indicates that schiff base ligand bis (N,N'-Di methyl-4-amino cinnamaldehyde) sulphonamide reacts with titanium (III) chloride in 1:2 stoichiometric ratio. It is brick red coloured solid complex and shows the melting point of 270°C, whereas, the melting point of the schiff base ligand is 230°C. The composition of complex is  $[(C_{28} H_{30} N_4 O_2 S)_2 \cdot 2H_2O TiCl_3]$ .

The molar conductance of the complex at room temperature in three solvents i.e. methanol, DMF and DMSO were found to be 354.6, 373.6 and 301.0  $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  at 0.001 molar concentration, respectively. These values indicate its 1:3 electrolytic nature,

The IR spectra of schiff base ligand shows a number of absorption bands. Some of these are at 1610(s)  $\text{cm}^{-1}$ , 1625(8)  $\text{cm}^{-1}$  and 1130(s)  $\text{cm}^{-1}$  which may be attributed to  $\gamma\text{HC}=\text{N}$  and C-N vibrations, respectively. However, the same peaks have been found at 1625 (vs)  $\text{cm}^{-1}$ , 1640 (vs)  $\text{cm}^{-1}$  and 1140(vs)  $\text{cm}^{-1}$  in the spectra of the complex (179). These shifts indicate that azomethine group (H-C=N) and the terminal nitrogen atom of the schiff base ligand have taken part in co-ordination (151).

A sharp peak at 1500 (8)  $\text{cm}^{-1}$  in the schiff base ligand also appears in the complex which is probably due to ring vibrations. A new sharp peak appears in the spectra of the complex at 740 (s)  $\text{cm}^{-1}$ . It may be due to co-ordinated water molecules. It, therefore, appears that schiff base ligand is acting as bidentate ligand. In this way, out of six co-ordinated sites four are occupied by two bidentate ligand molecules and two by water molecules. Thus, the possible geometry of the complex is octahedral.

The magnetic moments of the complex at room temperature were found to be 1.58 BM, which is lower than expected spin only value for an unpaired electron. The lowering in the value of magnetic moment may ascribed to lesser orbital contribution. Proposed structure of the complex is



#### N.N -Dimethyl-4- amino cinnamaldehyde Sulphafurazole Titanium (III) Chloride.

The analytical data of the complex indicates that two molecules of schiff base ligand have reacted with titanium (III) ion. The metal-ligand ratio is established as 1:2. Therefore, the composition of the complex is  $[\text{C}_{22}\text{H}_{24}\text{N}_4\text{O}_3\text{S}]_2\text{H}_2\text{O TiCl}_3$ . The complex thus obtained is of bluish brown colour.

The melting point of the schiff base ligand is 145°C. However, the melting point of the complex was observed as 189°C. It indicates that a new complex compound has been found.

The molar conductance of the complex in three solvents i.e. methanol, DMF and DMSO at 0.001 molar concentration indicates its 1:3 electrolytic nature. The values being 334.0, 294.6 and 312.4  $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ , respectively.

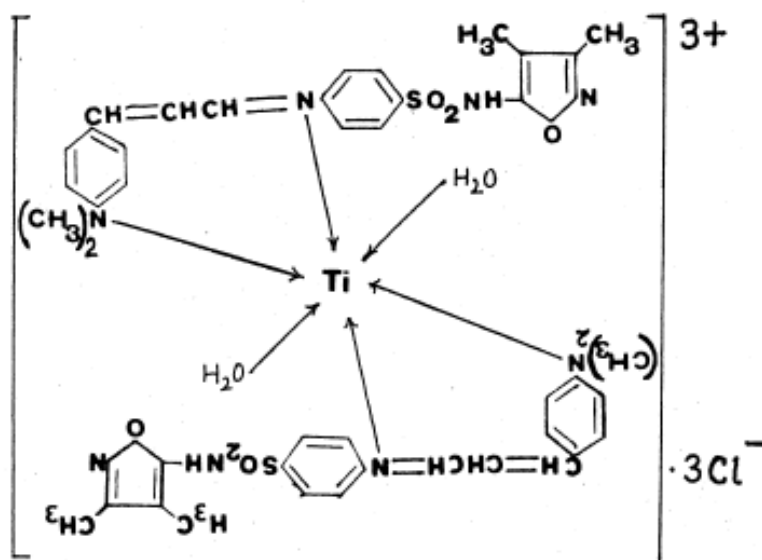
The magnetic moment of the complex has been found to be 1.49 B.M., which is subnormal to the expected  $\mu_{\text{eff}}$  for  $d^1$  system. The lowering in the value of  $\mu_{\text{eff}}$  is probably due to spin-spin coupling between the electrons of two metal ions.

The IR spectra of schiff base ligand shows some significant peaks at 1605(s)  $\text{cm}^{-1}$ , 1625(s)  $\text{cm}^{-1}$  and 1160{M}  $\text{cm}^{-1}$ , respectively. These may attributed to  $\gamma\text{H-C}=\text{N}$  and  $\gamma\text{C-N}$  vibrations (151). These peaks have shifted in the spectra of the complex at 1625 (VS)  $\text{cm}^{-1}$ , 1640 (VS)  $\text{cm}^{-1}$  and 1140 (S)  $\text{cm}^{-1}$ , respectively. The ligand seems to be acting as bidentate.

A sharp band in the schiff base ligand at 1490(s)  $\text{cm}^{-1}$  appears in the complex which is due to ring vibrations. A sharp band in the spectrum of the complex appears at 745(S)  $\text{cm}^{-1}$ . This may be due to participation of water molecules (180) in co-ordination.

It, therefore, appears that the out of six co-ordinated sites four are occupied by two bidentate ligand molecules and two sites by two water molecules. In this way, the complex is six coordinated and must have octahedral geometry.

Proposed structure of the complex is-



#### N, N<sup>1</sup>-Di Methyl-4-amino cimanaldehyde sulphisomedine Titanium (III) chloride

The analytical data of the complex indicates that two molecules of schiff base ligand have reacted with titanium (III) chloride, the composition of the complex, therefore, is [(C<sub>23</sub> H<sub>24</sub> N<sub>5</sub> O<sub>2</sub> S)<sub>2</sub> 2H<sub>2</sub> TiCl<sub>3</sub>]. The melting point of the schiff base ligand is 110°C, while that of the complex was found to be 169°C. It indicates a new complex compound has been formed.

The molar conductance of the complex in three solvents viz., methanol, DMF and DMSO at 10<sup>-3</sup> M dilution indicates its 1:3 electrolytic nature.

The magnetic moment of the complex has found to be 1.70 B.M. This indicates that complex containing titanium (III) ion, since the value corresponds to the presence of an unpaired electron,

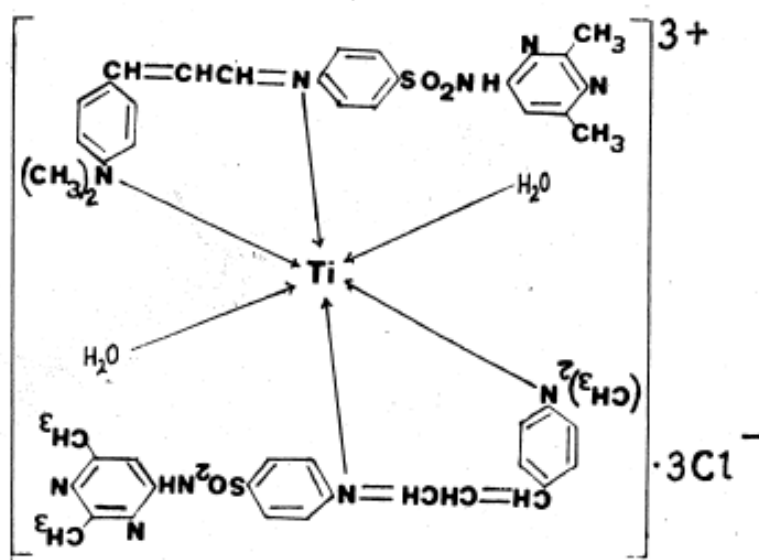
The IR spectra of the schiff base ligand indicates a number of absorption peaks. Some important absorption peaks appears at 1605 (VS) cm<sup>-1</sup>, 1630 (vs) cm<sup>-1</sup> and 1130(s) cm<sup>-1</sup> attributed to γ H-C=N and γ C-N vibration, respectively. These have been found in the spectra of the complex at 1620(s) cm<sup>-1</sup>, 1660(s) cm<sup>-1</sup> and 1140(m) cm<sup>-1</sup>. The absorption peaks attributed that azomethine group (C=N) and substituted amino group (C-N) have been positively shifted after complexation, thus both groups are participating in co-ordination with the metal ion. The similar observations have also been made by other workers in this field (180).

A sharp band in the spectra of schiff base ligand at 1500(s) cm<sup>-1</sup> appears in the complex spectra as well. This may be due to ring vibrations. A new sharp band in the spectra of the complex appears at 735(s) cm<sup>-1</sup>, it may be due to participation of water molecules in co-ordination. Thus, the schiff base ligand is acting as bidentate ligand.

On the basis of all above findings the complex appears to have octahedral geometry around the titanium (III) ion.



Proposed structure for the complex is-



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