

“COMPLEXES OF p-CHLOROBENZYLIDENE-o-AMINOPHENOL WITH TITANIUM (III) AND OXOVANADIUM (IV)”

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The preparation and characterization of a new research series of metal complex of Titanium (III) and Oxovanadium (IV). In which titanium (III) & Oxovanadium (IV) as a metal ion and p-chlorobenzylidene-o-aminophenolas a ligand are studied. The complexes $[\text{Ti}(\text{C}_{13}\text{H}_9\text{NCIO})_2 \cdot 2\text{H}_2\text{O}] \text{Cl}$, $[\text{V}(\text{C}_{13}\text{H}_9\text{ClO}) \cdot 4\text{H}_2\text{O}] \text{Cl}_2$ and $[\text{VO}(\text{C}_{13}\text{H}_9\text{NCIO})_2\text{H}_2\text{O}]$ have been characterized by elemental analysis, infrared, electronic absorptional spectral and magnetic susceptibility measurements. An octahedral geometry is predicted for Ti (III) & VO (IV) complexes.

KEYWORDS : Schiffbase ligand, oxovanadium (IV) complexes, Titanium (III) complex.

PRESENT STATE KNOWLEDGE

Metal complex of Schiff bases have played a central role in the development of coordination chemistry. Schiff bases offer a versatile & flexible serves of ligands capable to bind with various metal ion to give complexes with suitable properties of theoretical & practical applications during the past two decades.

In recent year Vanadium complexes have attracted much attention for their potential utility as catalyst for various oxidation reaction viz hydroxylation of phenols [1, 2], oxidation of sulfides to sulfoxides [3, 4], hydroxylation of benzene to mono and dihydroxy benzene [1, 5, 6] including reactions such as the coupling of 2-naphthols as well as Mannich type reaction [7, 8]. Most recently, the application of various oxovanadium complexes as catalyst in different oxidation reaction has been reviewed [9, 10].

The IR spectra of the ligands and their complexes were compared to determine any changes during complexation and to confirm their structure. The IR spectra of the ligands showed a broad absorption band at $3230\text{-}3117 \text{ cm}^{-1}$ attributed to the stretching vibration of intra molecular hydrogen bonded OH group (11). This band disappeared on complexation indicating the coordination of vanadium metal through OH group after deprotonation. A new medium intensity band near $3400\text{-}3500 \text{ cm}^{-1}$ is attributed to ν_{OH} stretching vibration of the coordinated water molecule to the central metal ion (12). A strong band at $1648\text{-}1626 \text{ cm}^{-1}$ of the spectra of the ligand was assigned to the azomethene (C=N) stretching vibration.

EXPERIMENTAL SECTION

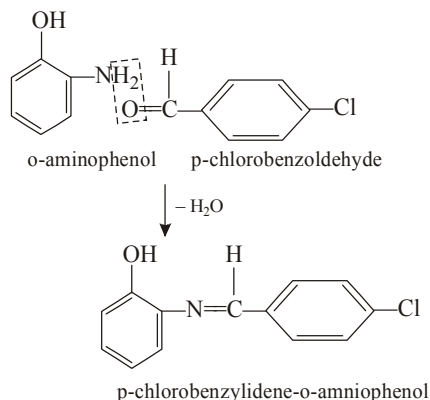
Material:

The chemicals & reagents used were of A.R. or equivalent grade. The aldehyde used were p-chloro benzaldehyde & o-amino phenol (BDH);

The Metal salt used were titanium (III) chloride (BDH, England) & oxovanadium (IV) sulphate (Fluka).

Method for preparation of p-chlorobenzylidene-o-aminophenol as a Schiff base ligand:

The pure crystal of o-aminophenol (1.09 gm) in 25ml of ethanol were mixed with p-chlorobenzaldehyde (1.40 gm) and the mixture was refluxed for about 6 hours. Dark brown shining crystals are separated out on cooling. The purity of the sample was checked by TLC.



Characterization of Ligand:

The colour of the prepared ligand (p-chlorobenzylidene-o-aminophenol) is dark brown. The melting point of the ligand were determined by open capillary method and are uncorrected. The ligand subjected to elemental analysis for C, H, N & Cl [Table-1]. The IR spectra of the ligand were regarded [Table-1] in order to show the presence of azomethine linkage.

Characterization of prepared Schiff base ligand [Table-1]

The Schiff base ligand were characterized by determination of melting point, elemental analysis and IR spectra. Solubility of this ligand was observed in various solvent.

Ligand	Molecular Formula	Colour	M.P.	Elemental Analysis			Imp. Peak in IR Sp.		Solubility
				%C	%H	%N	%Cl	$\nu_{C=N}$	
p-chlorobenzylidene-o-aminophenol	C ₁₃ H ₁₀ NCIO	Dark	102°C	67.30	4.31	6.04	15.30	1626cm ⁻¹	DMSO
o-aminophenol		Brown	(66.10)	(3.80)	(5.20)	(14.09)			Methanol

*Observed values are given in brackets.

Method of preparation of complexes.:

(i) Diaquobis (p-chlorobenzylidene-o-aminophenol) titanium (III) chloride:

Ethanol solution of TiCl₃ was gradually added with stirring to a solution of the ligand in molar ratio 1 : 2. The solid complex Diaquobis (p-chlorobenzylidene-o-aminophenol) titanium (III) Chloride formed which washed & dried over P₄O₁₀ in Vacuum desiccator.

(ii) Monoaquobis (p-chlorobenzylidene-o-aminophend), oxovanadium (IV):

The aqueous methanolic solution of vanadylsulphate & the ligand was reflux on water bath for about 5-6 hr. The pH of the solution was adjusted to 7 by dropwise addition of 10% methanolic sodium acetate solution. The metal chelates separated out on cooling. The product

was washed repeatedly with methanol & finally with petroleum ether (60-80°C) dried in vacuo.

Compare with complexes :

(i) Diaquobis (p-chlorobenzylidene-o-aminophenol) titanium (III) chloride-

The yellow coloured complex was subjected to elemental analysis which indicated that the ligand has reacted with metal in 2 : 1 molar ratio. On this basis, the molecular formula of the complex comes out to be $[\text{TiC}_{13}\text{H}_9\text{NClO}]_2\text{H}_2\text{O}]\text{Cl}$. The melting point of the ligand was found to be 102°C and that of the complex was 171°C. This vast difference between the melting points of the ligand & the complex indicate that the complex may have been formed.

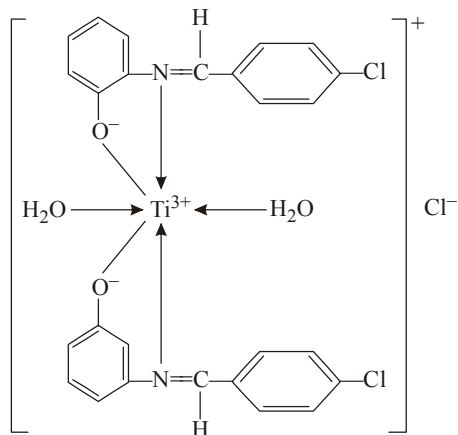
The IR spectrum of the ligand & the complex were recorded in KBr phase & compared. The IR spectrum of the ligand shows an important absorption band at 1626 cm^{-1} which may be assigned to the azomethine group (I). This band undergoes a negative shift of 25 cm^{-1} and appeared at 1601 cm^{-1} in the IR spectrum of the complex. [Table-2]. This shift indicated the involvement of nitrogen atom of azomethine group in coordination with the metal.

The thermogravimetric analysis also confirms the presence of two coordinated water molecules.

The percent weight loss at 180°C in the thermogram corresponds to the loss of two water molecule.

The electronic spectrum of the complex shows a band at 17850 cm^{-1} which may be assigned to d-d transition. The value of d-d transition corresponds to crystal field splitting energy. This is due to ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition and characteristic of octahedral geometry.

On the basis of above mentioned facts the complex appears to have octahedral geometry around Ti^{3+} ion. Thus the complex may therefore be assigned following structure.



(ii) Monoaquobis (p-chlorobenzylidene-o-aminophenol) oxovanadium (IV)

The analytical data of the complex suggested 1 : 2 metal ligand stoichiometry for the complex. On the basis the molecular formula comes out to be $[\text{VO}(\text{C}_{13}\text{H}_9\text{NClO})_2\cdot\text{H}_2\text{O}]$. The much higher melting point of the complex as compared to that of ligand indicated the formation of the adduct.

The measurement of magnetic susceptibility by GOUY's balance at room temperature a value of 1.69 BM for the magnetic moments of the complex. This value is very close to that expected for d¹ system ($\mu = 1.73$ BM) like VO(IV) metal ion.

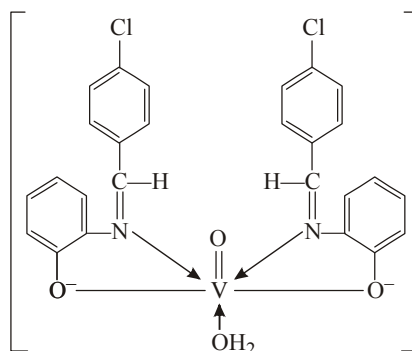
The IR spectrum of the ligand show the another important band at 1586 cm^{-1} , which may be assigned $\nu_{(c-o)}$ phenolic mode. This band undergoes a positive shift by 7 cm^{-1} suggesting the coordination of the deprotonated phenolic (c-o). [Table-2]

The TGA also onfirm the presence of one coordinated water molecule. The percent weight loss at 180° in the thermogram corresponds to the loss of one water molecule.

The IR spectrum of the complex show a non ligand band at 915 cm^{-1} assignable to $\nu_{v=0}$ moiety.

The electronic spectrum of the complex exhibit three bands of 10867 19424 and 26109 cm^{-1} assignable to $dxy (b_2) \rightarrow dxz, dyz (e^*)$, $dxy (b_2) \rightarrow d_{2-y_2} (b_1^*)$ and $dxy (b_2) \rightarrow dz_2 (a_1^*)$ transitions respectively, for octahedral stereochemistry.

On the basis of the studies performance, the complex may be assigned an octahedral geometry with possible distortion due to $V=O$ group.



CONCLUSION

On the basis of studies performed octahedral geometry has been proposed. Prepared metal complexes.

Elemental analysis & spectral data of the free ligand and metal complexes [Titanium (iii) oxovanadium (iv) were found to be in good agreement with their structure.

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