Complexes of 2-hydroxynaphthylidene-2-aminothiazole with Titanium (III) and Vanadium (III)

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ABSTRACT:

The synthesis and characterization of a new series of metal complexes of Titanium (III) and Vanadium (III) as a metal ion and 2-hydroxynaphthylidene-2-aminothiazole as a ligand are studied. The complexes [C14H15N2SO4.TiCl2] and [C14H13N2SO3.VCl2] have been characterized by elemental, infrared, electronic, absorption spectral, and magnetic susceptibility measurements. An octahedral geometry is predicted for Ti(III) and V(III) complexes.

Keywords – Schiff base ligands, Titanium (III) complexes, Vanadium (III) complexes

Present State Knowledge:

Metal complexes of Schiff bases have played a central role in the development of coordination chemistry. Schiff base offers a versatile and flexible service of ligands capable of binding with various metal ions to give complexes with suitable properties of theoretical and practical application during the past two decades.

In recent years vanadium complexes have attracted much attention for their potential utility as a catalyst for various oxidation reactions viz. hydroxylation of phenols[1, 2], oxidation of sulfides to sulfoxides [3, 4], hydroxylation of benzene to mono

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and dihydroxy benzene [1, 5, 6] including reaction such as the coupling of 2-naphthols as well as Mannich type reaction [7, 8]. Most recently, the application of various oxovanadium complexes as catalysts in different oxidation reactions 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 3230-3117 cm\(^{-1}\) attributed to the stretching vibration of the intra-molecular hydrogen-bonded OH group(II). This band disappeared on complexation indicating the coordination of vanadium metal through the OH group after deprotonation.

IR spectra of NH stretching band at around 3329 cm\(^{-1}\) and carbonyl absorption band near 1647 cm\(^{-1}\) hence confirming the formation of Schiff base hydrazone. A strong band at 1648-1626 cm\(^{-1}\) of the spectra of the ligand was assigned to azomethane (C=\(\text{N}\)) stretching vibration.

**Experimental section:**

**Material:**

The chemical & reagents used were of A.R or equivalent grade. The ligand 2-hydroxy naphthalene aminothiazole has been prepared by 2-hydroxynaphthaldehyde and 2-aminothiazole, therefore that aldehyde & amine were used BDH.

The metal salts used were titanium (III) chloride (BDH, England) & Vanadium metal Salt (Fluka).

**Methods for preparation of 2-hydroxynaphthylodene-2-aminothiazole as a Schiff base ligand:**

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The schiff base was prepared by the condensation of a 1: a 1 mixture of 2-aminothiazole and 2-hydroxynaphthaldehyde in distilled ethyl alcohol for about 8 hr. After cooling yellow colour crystal was obtained. The purity of the sample was checked by TLC.

Characterization of Ligand:

The colour of the prepared ligand is yellow. The melting point of the ligand was determined by the open capillary method and is uncorrected. The ligand was subjected to elemental analysis for C, H, N & S [Table – 1] to show the presence of azomethine linkage.

Characterization of prepared Schiff base ligand [Table-1]

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Molecular Formula</th>
<th>Colour</th>
<th>M.P.</th>
<th>Elemental analysis</th>
<th>Imp. Peak in IR spectra</th>
</tr>
</thead>
</table>

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Method of preparation of complexes:

I. Triaquo-2-hydroxynaphthylidene-2-aminothiazole titanium(III) chloride-

The ethanolic solution of TiCl$_3$ was gradually added with stirring to a solution of the ligand in methanol. The solid complex Triaquo-2-hydroxynaphthylidene-2-aminothiazole titanium(III) chloride formed which was washed & dried over P$_4$O$_{10}$ in a vacuum desiccator.

II. Monochloro diaquo-2-hydroxynaphthylidene-2-aminothiazole vanadium (III) chloride-

The methanolic solution of vanadium chloride was gradually added with stirring of a solution of ligands in methanol the solid complex [monochlorodiaquo-2-hydroxynaphthylidene-2-amino thiazole vanadium (III) chloride] that separated was washed with aq. Methanol & dried over P$_4$O$_{10}$ in a vacuum desiccator.

Result and Discussion:

(i) Triaquo-2-hydroxynaphthylidene-2-aminothiazole titanium (III) chloride –

Based on elemental analysis for C, H, N and S, the molecular formula of the complex comes out to be [Ti(C$_{14}$N$_2$H$_9$SO).3H$_2$O]Cl$_2$ which indicates that the ligand has reacted with metal in a 1:1 molar ratio. The melting point of the ligand was 125°C and that of the complex was found to be 290°C. This vast difference in the melting points of the ligand and the complex indicates the formation of the complex.
The measurement of the molar conductance in methanol DMF and DMSO at 25°C and 10⁻³ M dilution indicates the 1:2 electrolytic nature of the complex.

The IR spectrum of the ligand exhibited strong bands at 1635 cm⁻¹ and 700 cm⁻¹ which may be assigned to \( \nu_{C=N} \) and \( \nu_{C=N} \) respectively.

The IR spectra of the complex showed a downward shift of 25 cm⁻¹ in the \( \nu_{C=N} \) and appeared at 1610 cm⁻¹. The shift indicated the involvement of the nitrogen atom of the azomethine group in coordination with the metal.

The \( \nu_{C=S} \) band has exhibited an upward shift of 10 cm⁻¹ indicating the coordination through the sulphur of the thitheole ring. The C-S stretching frequency was shifted to higher on account of an increased d\( \pi \)-d\( \pi \) contribution between the sulphur atom & ring system.

The IR spectrum of the ligand shows another band at 1344 cm⁻¹, which may be assigned to \( \nu_{C=O} \) phenolic mode. This band is absent in the spectrum of the complex. This suggested deprotonation and coordination of phenolic oxygen to the metal ion. The chelation of phenolic oxygen is supported by an upward shift of \( \nu_{C=O} \) (phenolic) in the spectrum of the complex.

The IR spectrum of the complex shows the new band at 3420 cm⁻¹ (\( \nu_{O-H} \)) which may be due to the presence of coordinated water molecules. The rocking and wagging modes of water molecules appear at 810 cm⁻¹ and 750 cm⁻¹, which further supports the coordinated nature of water molecules.

This is further supported by TGA. The thermogram shows a per cent loss corresponding to the loss of three water molecules at 160°C.

The electronic spectrum of the complex shows a band at 17250 cm⁻¹ which may be assigned to d-d transition. The value of the d-d transition corresponds to crystal field splitting energy. This is due to the \( ^2T_{2g} \rightarrow ^2E_g \) transition characteristic of octahedral geometry.

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Thus complex seems to have an octahedral geometry, three positions are occupied by monobasic tridentate Schiff base molecules and the remaining three positions are by water molecules. The complex may therefore be assigned the following structure.

### ii) Monochlorodiaquo-2-hydroxynaphthylidene-2-aminothiazole vanadium (III) chloride:

Based on elemental analysis for C, H, N and S, the molecular formula of the complex comes out to be [VC14N2H13SO3Cl2] which indicates that the ligand has reacted with metal 1:1 molar ratio. The melting point of the ligand and the complex were found to be 125° & 299°C respectively. This vast difference in the melting point of the ligand and the complex indicates the formation of the complex.

The measurement of the molar conductance at 25°C and 10⁻³ M dilution in DMF, DMSO & Methanol indicates 1: 1 electrolytic nature of the complex.

The IR spectrum of the ligand exhibited strong bands at 1635 cm⁻¹ and 700 cm⁻¹ which may be assigned to \( \nu_{C=N} \) and \( \nu_{C=S} \) respectively. The IR spectra of the complex
showed a downward shift of 35 cm\(^{-1}\) in the \(\nu_{\text{C=N}}\) and appeared at 1600 cm\(^{-1}\). This shift indicated the involvement of the nitrogen atom in azomethane group coordination and the \(\nu_{\text{C=S}}\) and has exhibited an upward shift of 15 cm\(^{-1}\) indicating the coordination through the sulphur atom of the Thiazole ring (13).

The IR spectrum of the complex shows strong bands at 3425 cm\(^{-1}\) and 327 cm\(^{-1}\) which may be due to the presence of coordinated water molecules and chlorine atoms respectively. This is also supported by the gravimetric estimation of chlorine.

The electronic spectrum of the complex exhibited weak and broad bands which were observed at 16250 cm\(^{-1}\) and 20800 cm\(^{-1}\). The band at the high wave number was considerably more intense and better resolved than the two bands mentioned above. The low energy band may be assigned to the \(3T_{1g}^F \rightarrow 3T_{2g}^{(F)}\) transition in octahedral symmetry and the high energy band to the \(3T_{1g}^{(F)} \rightarrow 3T_{2g}^{(P)}\) transition respectively.

Thus complex seems to have an octahedral geometry, three positions are occupied by one tridentate Schiff base ligand and the remaining three positions by two water molecules and one chlorine atom, therefore, the complex has the following structure.

**Conclusion**-

Based on studies performed octahedral geometry has been proposed for prepared metal complexes.

Elemental analysis & spectral data of the free ligand and metal complexes Titanium (III) and Vanadium(III) were found to be in good agreement with their structure.
References


