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COMPLEXES OF m-HYDROXYACETOPHENONE CARBOHYDRAZONE WITH TITANIUM(III) AND OXOVANADIUM(IV)

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Abstract

The synthesis and characterization of a new series of metal complex of Titanium (III) and Oxavanadium (IV) as a metal ion and m-hydroxy acetophenone Carbdrydrazone as a ligand are studied. The complexes $[Ti(C_{17}H_{16}N_4O_3).2H_2O]Cl$ and $[Vo(C_{17}H_{16}N_4O_3).H_2O]$ have been characterized by elemental, infrared, electronic, absorptional spectral and magnetic susceptibility measurement. An octahedral geometry is predicted for Ti(III) and VO(IV) complexes.

Keywords – Schiff base ligand, Titanium (III) complexes, oxovanadium (IV) complexes.

Present state knowledge –

Metal complex of schiff bases have played a central role in the development of coordination chemistry. Schiff bases offer a versatile and flexible serves of ligands capable to bind with various metal ion to give complexes with suitable properties of theoretical and practical application 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 bezene to mono 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 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 3230-3117 cm^{-1} attributed to the stretching vibration of intramolecular hydrogen bonded OH group (II). This band disappeared on complexation indicating the coordination of vanadium metal through OH group after deprotonation.

IR spectra of NH stretching band at around 3329 cm^{-1} and carbonyl absorption band near 1647 cm^{-1} (12) 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 azomethine (C=N) stretching vibration.

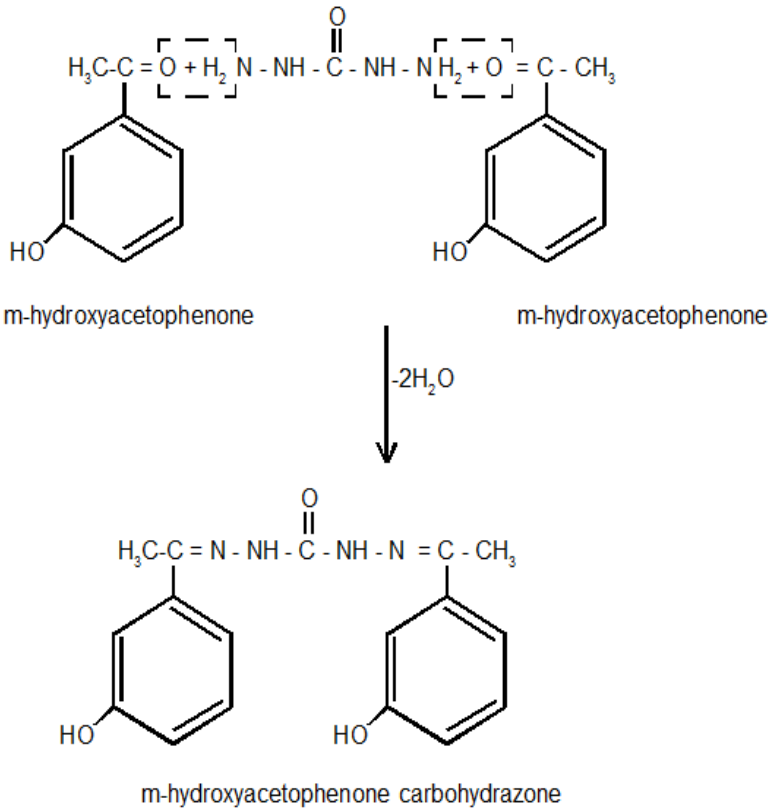
Experimental Section –

Material – The chemical & reagents used were of A.R. or equivalent grade. The ligand m-hydroxy acetophenone carbohydrazone has been prepared by m-hydroxy acetophenone (ketone) and carbohydrazide, therefore that ketone & amine were used BDH.

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

Method for preparation of m-hydroxy acetophenone carbohydrazone as a schiff base ligand –

Schiff base was prepared by condensation of 1 : 2 mixture of carbohydrazide (0.090 gm) and m-hydroxy acetophenone (0.272 gm) in distilled ethanol about 6-9 hr. Light brown crystal separated out on cooling. It was washed by ethanol, dried & recrystallised from hot ethanol.



Characterization of Ligand :

The colour of the prepared ligand is light brown. The melting point of the ligand was determined by open capillary method and are uncorrected. The ligand subjected to elemental analysis for C, H, N (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)

Ligand	Molecular Formula	Colour	M.P.	Elemental Analysis			Imp. Peak in IR Sp.			Sol-ubility
				%C	%H	%N	$\gamma_{C=O}$	$\gamma_{C=N}$	$\gamma_{C=O}$	
m-hydroxyacetophenone carbohydrazone	$C_{17}H_{18}N_4O_3$	Light Brown	140^0C	62.50 (62.40)	5.50 (5.20)	17.70 (17.60)	1693 cm^{-1}	1639 cm^{-1}	1499 cm^{-1}	DMSO Methanol

* Observed values are given in brackets

Method of Preparation of complexes :

(i) Diaquo-m-hydroxy acetophenone carbohydrazone titanium (III) chloride

Ethanolic solution of $TiCl_3$ was gradually added with stirring to a solution of the ligand in methanol. The solid complex. Diaquo-m-hydroxy acetophenone carbohydrazonetitanium (III) chloride formed which washed and dried over P_4O_{10} in vacuum desiccator.

(ii) Monoaquo m-hydroxy acetophenone carbohydrazone oxovanadium (IV)-

The aqueous methanolic solution of vanadyl sulphate of the ligand was reflux on water bath for about 5-6 hour. 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 and finally wash wtih petroleum ether (60-80^{0}C) dried in vacuum.

Results and Discussion :

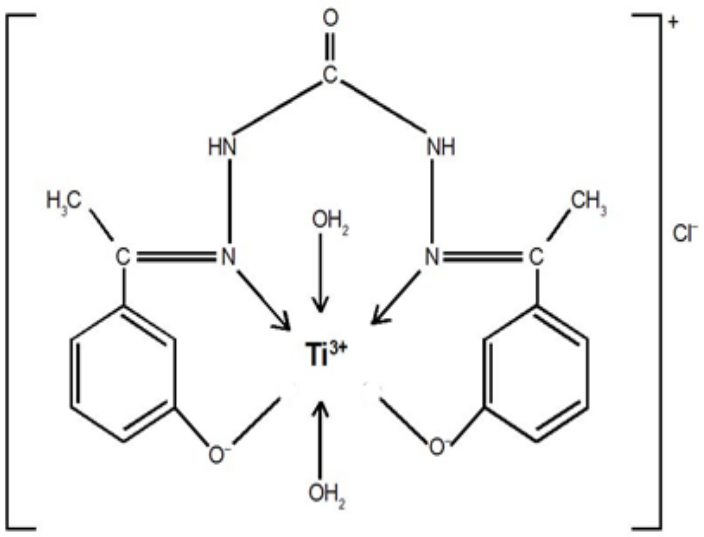
(i) Diaquo-m-hydroxy acetophenone carbohydrazone titanium (III) chloride -

On the basis of elemental analysis for C, H and N and gravimetric estimation of metal, the molecular formula of the complex comes out to be [Ti ($C_{17}H_{16}N_4O_3$).$2H_2O$]Cl which indicated that the ligand has reacted with metal 1: 1 molar ratio. The melting points of the ligand was 140^{0}C and that of the complex was found to be 295^{0}C. This vast difference in the melting points of the ligand and the complex indicates the formation of the complex.

The IR spectrum of the ligand shows a broad band at 3400cm^{-1} which may be attributed to intramolecular hydrogen bonding ν_{OH} vibration. The medium intensity bands observed at 1693cm^{-1},1639 cm^{-1}, and 1499 cm^{-1} have been assigned to ν_{OH}(azide), $\nu_{C=N}$ (azomethine) and ν_{C-O}(phenolic) respectively (4). In the spectrum of the complex the vibrational mode at 3400 cm^{-1} disappears, and in its place a broad band appears at 3500 cm^{-1} which is characteristic of ν_{OH} of coordinated water (5). The appearance of a non-ligand band at 830cm^{-1} may be assigned to rocking mode of water (3). The presence of coordinated water molecules is also supported by TGA data.

The electronic spectra of the complex shows a band at 18025 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 $^2T_{2g} \rightarrow {}^2E_g$ transition characteristic of octahedral geometry.

On the basis of above mentioned facts the complex may be assigned an octahedral geometry. Four positions are occupied teradentate ligands molecule and two by water molecules, the complex may therefore be assigned the following structure –



(ii) Monoaquo –m-hydroxy acetophenone carbohydrazone oxovanadium (IV)

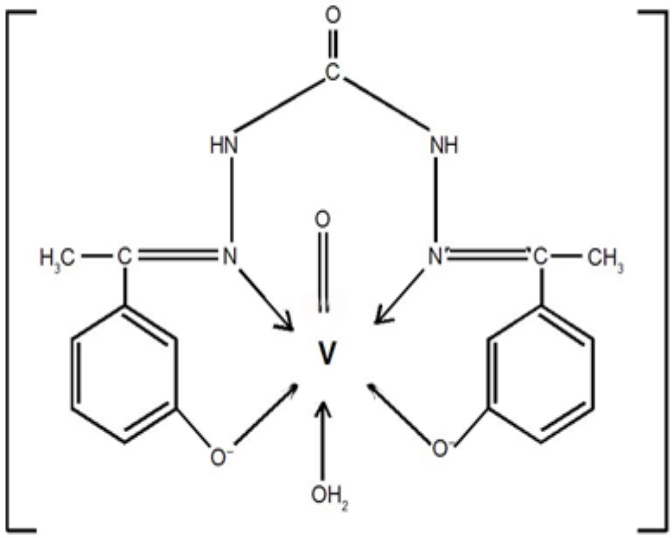
The elemental analysis for carbon, hydrogen & nitrogen and metal indicate that the schiff base ligand reacts with metal in 1 : 1 stoichiometric ratio. Thus the composition of dark pink colour adduct may be written as [($C_{17}H_{16}N_4O_3$) H_2O.VO]. The melting point of the ligand was 140^0C and that of the complex was found to be 285^0C. The vast diffference in the melting points of the ligand and the complex indicates the formation of the complex.

The molar conductance of the complex in two solvents methanol & DMF at 10^{-3} M dilution at room temperature indicates its non-electrolyte nature of the complex.

The IR spectrum of the ligand shows a broad band at 3400 cm^{-1} which may be attributed to intra-molecular hydrogen bonding ν_{O-H} vibration. The medium intensity bonds observed 1693cm^{-1}, 1639cm^{-1} and 1499cm^{-1} have been assigned to $\nu_{C=O}$ (azide), $\nu_{C=N}$ (azomethene) and ν_{C-O}(Phenolic) respectively(4). In the spectrum of the complex the vibrational mode at 3400cm^{-1} disappears, and its place a broad band appears 3515 cm^{-1} which is characteristic of ν_{OH} of coordinated. The appearance of a non-ligand band at 830 cm^{-1} may be assigned to rocking mode of water. The presence of coordinated water molecule is also supported by TGA data. Another non-ligand band at 915 cm^{-1} assignable to $\nu_{V=O}$ moiety in complex has been observed.

The electronic spectrum of the complex exhibit three bands at 10869, 19428 and 26112 cm^{-1} assignable to dxy(b_2) $\rightarrow$ dxz – dyz (e*), dxy (b_2) $\rightarrow$ dx^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 performed, the complex may be assigned on octahedral geometry with possible distortion due to V=O moiety.



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) and oxovanadium (IV) were found to be in good agreement with their structure.

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