

The Quantitative Analysis of Ti (III) & V (III) & (IV) Transition Metal complexes with biologically Active Schiff Base Ligands

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Abstract- In the present manuscript complexes of Titanium (III), Vanadium III & IV were isolated by reacting Titanium III chloride, vanadium trichloride and vanadyl sulphate with bidentate Schiff base such as p-chlorobenzylidene -O-amino-phenol, p-chlorobenzylidene-2-aminobenzothiazole and m-hydroxyacetophenone carbohydra-zone in stoichiometric ratio (1:2). The obtained complexes were characterized on the basis of their analysis viz. m.p., molar conductance, magnetic susceptibility, IR, UV, mass spectral data and molecular weight measurement. The free ligands and thin metal complexes were screened for their antimicrobial activities. All the complexes were found to be coordinated with presumably distorted octahedral geometry with 1:1 electrolytic nature.

INTRODUCTION

The survey of chemical literature has revealed that various types of Schiff base have been prepared and their complexes have been reported ⁽¹⁻³⁾. Metal complexes of Schiff base have played a central role in development of coordination and medicinal chemistry. With this back ground the preference of coordination number and nature of coordination complexes of transition metals (Titanium and Vanadium) with bidentate ligands such as p-chlorobenzylidene-o-aminophenol, p-chlorobenzylidene-2-aminobenzothiazole and m-hydroxy acetophenone carbohydrazone are reported in the present communication.

Material and Method

The chemicals and reagents used were of AR or equivalent grade. The aldehydes and ketones used were p-chlorobenzyldehyde (Otto), 2-hydroxynaphthal-dehyde(Fluka), 4-methoxy benzaldehyde (Fluka) & m-hydroxyacetophenone (otto) and amine compounds one otto, BDH and Aldrich, Schiff bases were prepared by condensation of 1:2 molar mixture of aldehyde and amine in distilled EtOH reflex for about 6 hrs, light brown, dark brown, Brown crystalline Schiff bases were obtained.

Preparation of Ti(III) chloride

250 ml. of Titanium tri chloride aqueous solution (containing 15% of $TiCl_3$) was taken and 4-5 gm titanium metal sponge was 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 titanium(III) chloride was covered by a thick layer of toluene which protect it against oxidation. After saturation with HCl gas the solution was warmed over waterbath afterward keep it inside a freezing mixture for about 10 hrs, when the dark blue crystals of $TiCl_3 \cdot 6H_2O$ were obtained at the bottom of the flask⁽⁴⁾.

Preparation of complexes

Obtained Schiff base in methanol were added with ethanol solution of $TiCl_3 \cdot 6H_2O$ and methonic solution of VCl_3 and $VOSO_4$ add with stIRring for about 2 hrs, adduct were obtain. The solid complexes that separated out were washed with absolute methanol and dried over P_2O_5 in vacuum desiccators.

Ligands and their complexes were subjected to elemental analysis for C, H, N, S, whereas metals were estimated gravimetrically in the lab⁽⁵⁾. Molecular conductance at 25°C indicated 1:1 electrolytic nature of the metal chelates.⁽⁶⁾

The IR spectra of the ligands showed an important absorption band at range 1625-1630 cm^{-1} , which may be assigned to the azomethine group. These bands undergo a negative shift of 20-25 cm^{-1} in the IR spectrum of the complexes. These are indicative of nitrogen atom of azomethine group in coordination with the metals⁽⁷⁾. IR spectrum of the ligand shows another important band at ranges 1586-1590 cm^{-1} , which may be assigned to $\nu_{(C-O)}$ phenolic mode. This band undergoes a positive shift of 8-10 cm^{-1} suggested the coordination of the deprotonated phenolic (C-O) group. The IR spectrum of the ligands shows a broad band at ranges 3400-3450 cm^{-1} , which may be attributed to intramolecular H-bonding ν_{OH} vibration.

The medium intensity bands observed at ranges 1693-1697 cm^{-1} , 1639-1644 cm^{-1} and 1499-1508 cm^{-1} have been assigned to $\nu_{C=O}$ (azide), $\nu_{C=N}$ (azomethine) and $\nu_{(C=O)}$ phenolic, respectively. IR spectrum of the complexes shows vibrational mode at ranges 3400-3410 cm^{-1} disappears and its place a broad band appears at ranges 3500-3510 cm^{-1} ⁽⁸⁾.

The IR spectrum of the ligands shows characteristic -NH and -SH bands at 3160 and 2000 cm^{-1} , respectively. Another band at 1090 cm^{-1} is assigned to C=S. The deprotonation of thio group and complexation through sulphur is indicated by the absence of a band at 2600 cm^{-1} due to the SH in the spectra of the complexes. M-S band formation is further confirmed by a band at ranges 380-340 cm^{-1} in the far IR region.

Complexes	Mole. Formula	Colour	m.p.	Elemental Analysis					\uparrow	$(\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1})$	
				C	H	N	S	Cl		μ_{eff} (B.M.)	DMF
1. p-chlorobenzylidene-o-aminophenol Ti(III) Chloride	$\text{C}_{26}\text{H}_{22}\text{O}_4\text{TiCl}_3$	Yellow	171°C	53.9	3.61	4.82		18.10	1.71	54	27
2. p-chlorodenzylidene-2-aminobenzothiazoeTi(III) chloride	$\text{C}_{26}\text{H}_{22}\text{N}_4\text{S}_2\text{Cl}_2\text{O}_2\text{TiCl}_3$	Yellow	160°C	44.0	3.10	7.92	9.0	24.71	1.71	62	28.4
3. m-hydroxyacetophenone carbohydrazone Ti(III)chloride	$\text{C}_{17}\text{H}_{20}\text{N}_4\text{O}_5\text{TiCl}_3$	Cream	295°C	46.10	4.52	12.61	7.90		1.71	61	30.0
4. p-chlorobenzylidene-o-aminophenol vanadium (III) chloride	$\text{C}_{13}\text{H}_{17}\text{NO}_5\text{VCl}_3$	Pink	195°C	36.92	4.02	3.31		2488	2.90	57	26.2
5. p-chlorobenzylidene-2-aminobenzothiazole V(III) chloride	$\text{C}_{26}\text{H}_{22}\text{N}_4\text{S}_2\text{O}_2\text{Cl}_2\text{VCl}_3$	Red Brown	190°C	43.88	3.09	7.87	9.0	24.61	2.89	60	29.10
6. m-hydroxyacetophenone carbohydrazone V(III) chloride	$\text{C}_{17}\text{H}_{20}\text{N}_4\text{O}_5\text{VCl}_3$	Orange	290°C	45.80	4.49	12.58		7.86	2.90	57	27.5
7. P-chlorobenzylidene-o-aminophenol oxo VO_4	$\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_3\text{Cl}_2\text{VOSO}_4$	Black Brown	197°C	47.41	3.34	4.25	4.86	10.63	1.69	54	26.9
8. p-chlorobenzylidene-2-aminobenzothiazole VO_4	$\text{C}_{13}\text{H}_{11}\text{N}_2\text{SCl}_3\text{OVO}_4$	DIRty green	175°C	29.54	2.46	5.30			1.78	63	28.8
9. m-hydroxy acetophenone oxo vanadium (IV) sulphate	$\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_4\text{VOSO}_4$	Dark Pink	285°C	39.08	3.83	10.72	6.13	-	1.69	60	29.0

IR spectra of the ligands & their complexes were recorded in FT/IR-4100 type A in KBr/myol mull phase $4000\text{-}200 \text{ cm}^{-1}$, ITL labs Pvt. Ltd. Delhi. Electronic spectra of the complexes recorded with the help of UV-backman Du-2-spectrophotometer at Bareilly College, Bareilly. Molar conductance of the complexes in different solvents viz. MeOH, DMF & DMSO in 10^{-3} M dilution were observed at 25°C by Philips conductivity Bridge PR 9500 with a dip type conductivity cell in Department of Chemistry, Bareilly College, Bareilly. Magnetic susceptibility measurement were carried out by Gouy balance using $\text{HgCo}(\text{SCN})_4$ as standard. The diamagnetic correlation were calculated by using Paskel's constant⁽⁴⁾. Man spectra of ligands and their complexes were recorded at ToF magnetic sector and Quadrupole-SIMS instrument at New Delhi. The molecular weight of the compounds were carried out by rast method using camphor as solvent.

Result and Discussion

Complexes were subjected to elemental analysis given in Table-1, which revealed that the ligands have reacted with metals in 2:1 or 1 : 1 ratio. On the basis of the general molecular formula of the complexes came out to be $\text{ML}_2\text{nH}_2\text{OX}$ ($n= 2, 1$). There are significant difference in the melting point of all complexes formed with ligands. These vast difference of melting point indicated that the complexes may have been formed.

The magnetic moment values ranges 1.69-1.71 BM or 2.89-2.90 BM for these complexes are closed to that expected for d^1 as well as d^2 system like metals Ti^{+3} , V^{+3} , VO^{++} .

All complexes were found to be insoluble in common organic solvents but soluble in DMF & DMSO.

The IR spectra of the ligands showed an important absorption band at $1625\text{-}1630 \text{ cm}^{-1}$ which may be assign to the azomethine group. These bands under goes a negative shift of $20\text{-}25 \text{ cm}^{-1}$ in their IR spectrum of the complexes. These are indicative of nitrogen atom of azomethine group in coordination with the metals⁷⁻⁸. IR spectrum of the ligand shows the another important band at ranges $1586\text{-}1590 \text{ cm}^{-1}$ which may be assigned $\square_{(\text{C-O})}$ phenolic mode. These band undergoes a positive shift ranges $8\text{-}10 \text{ cm}^{-1}$ suggested the co-ordination of the deprotonated phenolic (C-O) group. The IR spectrum of the ligands shows broad band at ranges $3400\text{-}3450 \text{ cm}^{-1}$ which may be attributed to intramolecular H-bonding \square_{OH} vibrates. The medium intensity bonds observed ranges $1693\text{-}1697 \text{ cm}^{-1}$ $1639\text{-}1644 \text{ cm}^{-1}$ and $1499\text{-}1508 \text{ cm}^{-1}$ have been assigned to $\square_{\text{C=O}}$ (azide), $\square_{\text{C=N}}$ (azomethine) and $\square_{\text{C-O}}$ (Phenolic), respectively. In the spectrum of the complexes short vibrational mode at ranges $3400\text{-}3410 \text{ cm}^{-1}$ disappears and its place a broad band appears at ranges $3500\text{-}3510 \text{ cm}^{-1}$ which is characteristics of \square_{OH} of coordinated water⁸.

The IR spectrum of the ligands show characteristics NH and S-H band at 3160 and 2000 cm^{-1} , respectively. Another band at 1090 cm^{-1} is assign to C=S . The deprotonation of thio-group and complexation through sulphur is indicated by the absence of band at 2600cm^{-1} due to the SH in the spectra of the complexes. Metal sulphur bond formation is further confirmed by a band at ranges $380\text{-}340 \text{ cm}^{-1}$ in the far IR region. A new band appears in the region of 760 cm^{-1} which may be assign to C-S, supported the coordination through S atom. A strong band in the region 1620 cm^{-1} in the free ligand assigned to (-N=CH) is lowered by $20\text{-}30 \text{ cm}^{-1}$ in the spectrum of the complexes⁸ (2.58), suggesting coordination through azomethine nitrogen.

A new bond appears in the region ranges $760 - 770 \text{ cm}^{-1}$ which may be assign to C-S supported the coordination through S-atom. A strong bond in the region ranges $1620\text{-}1625 \text{ cm}^{-1}$ in the free ligands assigned to (-N=CH) is lowered by ranges $20\text{-}30 \text{ cm}^{-1}$ in the

spectrum of the complexes⁸ (II, V, VIII) suggesting coordination through azomethine nitrogen atom of schiff base. This is further supported by metal-nitrogen bond in the region ranges 540-480 cm^{-1} .

The presence of coordinated water molecules are suggested by a broad band in the region ranges 3400-3450 cm^{-1} and supported by wagging and rocking modes in the region of range 840-850 and 740-755 cm^{-1} , respectively. It is also supported by T.G.A.

The electronic spectra of Titanium (III) complexes show a single broad band at 19560-19666 cm^{-1} due to ${}^2T_{2g} \rightarrow {}^2E_g$ transition for OH symmetry. The values of magnetic moment of these complexes are ranges 1.71 cm^{-1} BM, which are in the expected range for d^1 system (Ti^{+3}) and shows paramagnetic character of the complexes. It is also shows that Ti^{+3} has not been oxidized to Ti^{+4} during or after complexation although it is vary sensitive to oxidation.

The observed values of magnetic moment of the complexes are in the range 2.89 – 2.90 BM as expected for d^2 -System (V^{+3}). The electronic spectrum of the complex exhibit a band at ranges 16110-16120 cm^{-1} with a shoulder at 20530-20620 cm^{-1} . The low energy band may be assigned to ${}^2A_{1g} \rightarrow {}^2T_{2g}$ and the high energy band at ${}^2A_{1g} \rightarrow {}^3T_{2g}$ (P) transition. These are characteristic of octahedral geometry.

Oxovanadium complexes usually exhibit magnetic moment corresponding to the spin only value of 1.73BM, at room temperature. The observed value of the μ_{eff} for the present complex are in range 1.69-1.78 BM, suggested that the mixed ligand complexes prepared in this investigation are mononuclear⁽¹⁰⁾. The electronic spectra of the oxovanadium complex were recorded in solid state. The complexes exhibit there spin allowed transition in the range 12500-13500 cm^{-1} , 15500-17000 cm^{-1} , and 23500-24500 cm^{-1} region and have been assigned to ${}^2B_2 \rightarrow {}^2E$, 2B_1 and ${}^2B_2 \rightarrow {}^2A_1$ transitions respectively²⁷.

On the bases of above facts and discussion the geometry of these complexes is suggested to be octahedral.

Table- Mass spectra data of Schiff base ligands and its metal complex.

Compounds	Calculated Mass	Observed Mass	Peak
P-chlorobenzylidene-o-amino phenol (L1)	231.5	231.5	M
P-chlorobenzylidene-2-aminobenzothiazol (L2)	260.5	260.5	M
m-hydroxyacetophenone carbohydrazone (L3)	326.0	326.0	M
Ti L1 2H ₂ O.Cl ₃	580.36	581.10	M+1
Ti L2 2H ₂ O.Cl ₃	719.36	720.40	M+1
Ti L3 2H ₂ O.Cl ₃	443.36	445.42	M+2
V L1 2H ₂ O.Cl ₃	424.44	425.51	M+1
V L2 2H ₂ O.Cl ₃	714.44	7114.40	M+1
V L3 2H ₂ O.Cl ₃	446.44	447.52	M+1
VO L1 H ₂ O.SO ₄	601.94	602.89	M+1
VO L2 H ₂ O.SO ₄	512.44	514.19	M+2
VO L3 H ₂ O.SO ₄	504.94	506.78	M+2

Table- Antimicrobial effect of the ligand and their complexes (Microorganisms Inhibition)

Compounds	S Crevial	B.Subtitle	E.Coli	X Pneremonia	M.Lulerus	Control
P-Chlorobenzylidene-O-amino phenol (L1)	20	36	26	31	24	-
[Ti A2 2H ₂ O]Cl ₃	-	14	-	10	23	-
[V A2 2H ₂ O]Cl ₃	-	12	6	9	12	-
[VO A2 H ₂ O]SO ₄	-	18	16	12	10	-
P-chlorobenzylidene-2-aminobenzothiazol (L2)	-	17	13	10	9	-
[Ti B2 2H ₂ O]Cl ₃	12	14	10	12	-	-
[V B2 2H ₂ O]Cl ₃	-	-	-	11	10	-
[VO B2 H ₂ O]SO ₄	-	-	-	10	-	-

m-hydroxyaceto-phenone carbohydrazone (L3)	10	12	11	12	11	-
[Ti C2 2H2O]Cl3	-	-	6	10	9	-
[V C2 2H2O]Cl3	-	-	6	10	7	-
[VO C2 H2O]SO4	-	-	5	9	7	-

Concen= 100µg/disc^b including disc diameter(6mm)

Antimicrobial activities of the L1, L2, and L3 ligands and their metal complexes against bacteria and yeast are recorded in the table () in this study on of the striking feature in that while ligands L1 & L2 and the Ti(III) complexes with ligand L3 have actively against *saccharomyces chevisiae*. The ligand L1 and other compounds have no much activity against same organism. It is apparent that the ligands L1 & L3 centring two free hydroxyl groups are more active that the L2 ligand containing free -SH group. The hydroxyl substituent is known to increase the activity of the compound^{11,16} we have shown that the activity decreased on undergoing complex action. Since chelation reduce that partial sharing of its position charges with the oxygen atom of the free hydroxyl group and nitrogen atom of C=N group, some complexes are not showing activity against bacteria and yeast, are not mentioned in the table and denoted by sign(-).

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