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# Application of transition metal complexes put togather N, O, S donor 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 (III) chloride and vanadylsulphate with bidentate Schiff base such as p$^{-}$-chlorobenzylidene–o$^{-}$-amino-phenol, p$^{-}$-chlorobenzylidene-2-aminobenzothiazole and m$^{—}$hydroxyacetophenone carbohydras one 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 their metal complexes were screened for antimicrobial activities. All the complexes were found to be six coordinated with presumably distorted octahedral geometry with 1:1 electrolytic nature.

**Keywords:** Titanium, vanadium, vanadylsulphate, IR, UV

## 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 background 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-amino-benzothiozole and m$^{—}$hydroxyacetophenone carbohydras one 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-hydroxynaphthaldehyde (Fluka), 4-methoxy benzaldehyde (Fluka) & m$^{-}$-hydroxyacetophenone (Otto) and amine compounds are 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 and Brown crystalline Schiff bases were obtained.

## Preparation of Ti (III) chloride

250 ml. of Titanium trichloride 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 a water bath afterward and kept inside a freezing mixture for about 10 hrs., when the dark blue crystals of $TiCl_3.6H_2O$ were obtained at the bottom of the flask [4].

## Preparation of complexes

Obtained Schiff bases in methanol were added with ethanolic solution of $TiCl_3.6H_2O$ and methanolic solution of $VCl_3$ and $VOSO_4$ added with stirring for about 2 hrs., adducts were obtained. The solid complexes that separated out were washed with absolute methanol and dried over $P_4O_{10}$ 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 [4].

IR spectra of the ligands & their complexes were recorded in FT/IR-4100 type A in KBr/nujol mull phase 4000-200 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 $HgCo(SCN)_4$ as standard. The diamagnetic correlation was calculated by using Pascal's constant.Mass spectra of ligands and their complexes were recorded at ToF magnetic sector and Quardrupole- SIMS instrument at New Delhi.The molecular weight of the compounds were carried out by rast's method using camphor as solvent [5]. Antimicrobial and antifungal activity of the ligands and their complexes were tested *in vitro* against bacteria and fungal species by disk diffusion methods.

## 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 ratio. On the basis of the general molecular formula of the complexes came out to be $ML_2nH_2OX$ (n=2, 1). There are significant difference in the melting point of all complexes with ligands. These vast differences of melting point indicated that the complexes may have been formed.

**Table 1:** Physico-chemical analysis of the complexes

| Complexes/Mol. Wt. | | Mol. Formula | Colour | m.p. | Elemental Analysis | | | | | | (ohm$^{-1}$ cm$^{2}$ mol$^{-1}$) | | | μeff |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | %C | %H | %N | %S | %Cl | %M | MeOH | DMF | DMSO | (B.M.) |
| 1. | P$^{--}$-chlorobenzylidene-o-aminophenol Ti(III) Chloride (551.24) | $C_{26}H_{22}N_2O_4Cl_2TiCl_3$ | Yellow | 171 °C | 53.9 | 3.61 | 4.82 | | 18.10 | 8.0 | 88.3 | 54 | 27.1 | 1.71 |
| 2. | P$^{-}$-chlorobenzylidene-2-aminobenzothiazoleTi(III)chloride (709.57) | $C_{26}H_{22}N_4S_2Cl_2O_2TiCl_3$ | Yellow | 160 °C | 44.0 | 3.10 | 7.92 | 9.0 | 24.71 | 6.21 | 92.4 | 62 | 28.4 | 1.71 |
| 3. | m$^{-}$-hydroxyacetophenone carbohydrazone Ti(III)chloride (511.14) | $C_{17}H_{20}N_4O_5TiCl_3$ | Cream | 295 °C | 46.10 | 4.52 | 12.61 | | 7.90 | 9.14 | 82.2 | 61 | 30.0 | 1.71 |
| 4. | P$^{-}$-chlorobenzylidene-o- aminophenol vanadium (III) chloride (429.35) | $C_{26}H_{22}N_2O_4Cl_2VCl_3$ | Pink | 195 °C | 36.92 | 4.02 | 3.31 | | 24.88 | 10.94 | 89.2 | 57 | 26.2 | 2.90 |
| 5. | P$^{-}$-chlorobenzylidene-2-aminobenzothiazoleV(III)chloride (712.22) | $C_{26}H_{22}N_4S_2O_2Cl_2VCl_3$ | Red Brown | 190 °C | 43.88 | 3.09 | 7.87 | 9.0 | 24.61 | 6.83 | 94.3 | 60 | 29.10 | 2.89 |
| 6. | m$^{-}$-hydroxyacetophenone carbohydrazone V(III) chloride (513.11) | $C_{17}H_{20}N_4O_5VCl_3$ | Orange | 290 °C | 45.80 | 4.49 | 12.58 | | 7.86 | 9.28 | 95.0 | 57 | 27.5 | 2.90 |
| 7. | P$^{-}$-chlorobenzylidene-o-aminophenol $VOSO_4$ (638.54) | $C_{26}H_{20}N_2O_3Cl_2VOSO_4$ | Black Brown | 197 °C | 47.41 | 3.34 | 4.25 | 4.86 | 10.63 | 7.20 | 90.1 | 54 | 26.9 | 1.69 |
| 8. | P$^{-}$-chlorobenzylidene-2-aminobenzothiazole $VOSO_4$ (509.85) | $C_{26}H_{20}N_4S_2Cl_2OVOSO_4$ | Dirty green | 175 °C | 29.54 | 2.46 | 5.30 | 6.01 | 14.91 | 9.18 | 87.0 | 63 | 28.8 | 1.78 |
| 9. | m$^{-}$-hydroxy acetophenone carbohydrazone $VOSO_4$ (501.69) | $C_{17}H_{18}N_4O_4VOSO_4$ | Dark Pink | 285 °C | 39.08 | 3.83 | 10.72 | 6.13 | - | 10.03 | 94.0 | 60 | 29.0 | 1.69 |

The magnetic moment values ranges 1.69-1.71 BM or 2.89-2.90 BM for these complexes are close to that expected for $d^1$ as well as $d^2$ systems like metals $Ti^{+3}$, $V^{+3}$, $VO^{++}$. All complexes were found to be insoluble in common organic solvents but soluble in DMF & DMSO. The molar conductance values 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 1625-1630 cm$^{-1}$ which may be assigned to the azomethine group. These bands undergo a negative shift of 20-25 cm$^{-1}$ in their IR spectrum of the complexes. These are indicative of nitrogen atoms of azomethine group in coordination with the metals [7, 8]. The IR spectrum of the ligand shows another important band at ranges 1586-1590 cm$^{-1}$ which may be assigned $\nu_{(C\text{-}O)}$ phenolic mode. This band undergoes a positive shift range 8-10 cm$^{-1}$ suggesting the co-ordination of the deprotonated phenolic (C-O) group. The IR spectrum of the ligands shows broad bands at ranges 3400-3450 cm$^{-1}$ which may be attributed to intramolecular H-bonding $\nu_{OH}$ vibrates. The medium intensity bonds observed 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 $\nu_{C\text{-}O}$ (Phenolic), respectively. The IR spectrum of the complexes showed vibrational mode at ranges 3400-3410 cm$^{-1}$ disappears and in its place a broad band appears at ranges 3500-3510 cm$^{-1}$ which is characteristic of $\nu_{OH}$ of coordinated water [8].

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 assigned to C=S. The deprotonation of thiol-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. Metal sulphur bond formation is further confirmed by a band at ranges 380-340 cm$^{-1}$ in the far IR region. A new bond appears in the region ranges 760-770 cm$^{-1}$ which may be assigned to C-S supporting the coordination through S-atom. A strong bond in the region ranges 1620-1625 cm$^{-1}$ in the free ligands assigned to-(N=CH) is lowered by ranges 20-30 cm$^{-1}$ in the spectrum of the complexes [8] (II, V, VIII) suggesting coordination through azomethine nitrogen atom of schiff base. This is further supported by metal-nitrogen bonds in the region ranging 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 $^2T_{2g} \rightarrow {}^2Eg$ 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 show paramagnetic character of the complexes [9]. It also shows that $Ti^{+3}$ has not been oxidized to $Ti^{+4}$ during or after complexation although it is very 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 exhibits 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 [9].

Oxovanadium complexes usually exhibit magnetic moments corresponding to the spin only value of 1.73BM, at room temperature. The observed values of the μeff for the present complexes are in range 1.69-1.78 BM, suggesting that the mixed ligand complexes prepared in this investigation are mono nuclear [9, 10]. The electronic spectra of the oxovanadium complex were recorded in solid state. The complexes exhibit three spin allowed transitions in the range 12500-13500 $cm^{-1}$, 15500-17000 $cm^{-1}$, and 23500-24500 $cm^{-1}$ region and have been assigned to $^2B2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B2 \rightarrow {}^2A1$ transitions respectively [9, 10]. Which indicate the presence of oxovanadium (iv) acceptor centre in a distorted octahedral coordination environment with the unpaired electron located in the $d_{xy}$ level in the ground state. Presence of metal hyperfine lines in the powder spectrum indicates that the separation between the nearest $VO^{+2}$ acceptor centres is quite large and as result the hyperfine interaction is greater than the exchange interaction. Absence of any nitrogen hyperfine splitting signifies that the unpaired $e^{-1}$ is predominantly localised on vanadium and that in plane $\pi$ bonding is very slight. So the probable structure of complexes of formula may be $VOL_2 * H_2O$ by replacing the coordinated water molecule by V=O. the structure of $[VOL_2 * H_2O]SO_4$ follows from that of the enolic compound by the appropriate modification of the ligand skeleton. The present work describes a general strategy for fabrication a penta coordinated complex core around a monooxocation like $VO^{++}$ with the position the coordinated octahedron trans to the $v\text{-}o_{(1)}$ multiple bond capable of harbouring a bidentate donors influences of this sixth donor on the $V\text{-}O_{(1)}$ mode is clearly reflected in the observed shift of the relevent frequency. On the bases of above facts and discussion the geometry of these complexes is suggested to be octahedral.

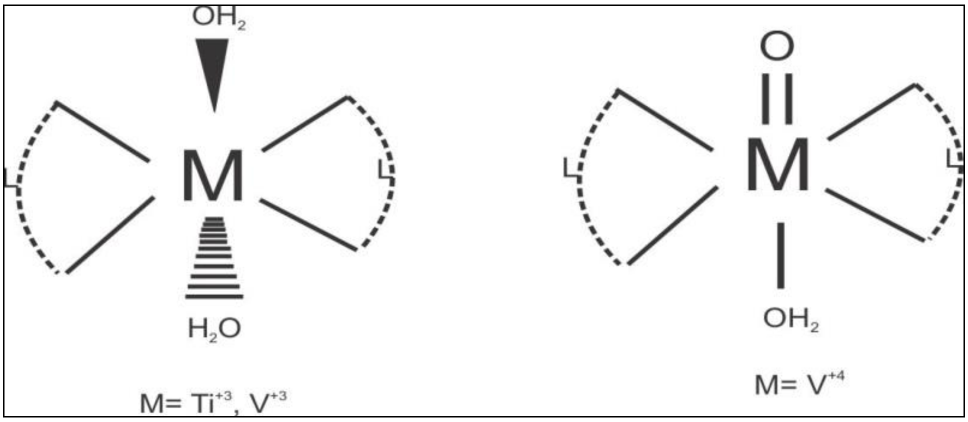

**Table 2:** Mass spectra data of Schiff base ligands and their metal complexes.

| Compounds | Calculated Mass | Observed Mass | Peak |
|---|---|---|---|
| $p^-$-chlorobenzylidene-$o^-$- amino phenol ($L_1$) | 231.5 | 231.5 | M |
| $P^-$-chlorobenzylidene-2-aminobenzothiozole ($L_2$) | 260.5 | 260.5 | M |
| $m^-$-hydroxyacetophenone carbohydrazone ($L_3$) | 326.0 | 326.0 | M |
| Ti $L_1$ $2H_2O.Cl_3$ | 580.36 | 581.10 | M+1 |
| Ti $L_2$ $2H_2O.Cl_3$ | 719.36 | 720.40 | M+1 |
| Ti $L_3 2H_2O.Cl_3$ | 443.36 | 445.42 | M+2 |
| V $L_1$ $2H_2O.Cl_3$ | 424.44 | 425.51 | M+1 |
| V $L_2$ $2H_2O.Cl_3$ | 714.44 | 714.40 | M+1 |
| V $L_3$ $2H_2O.Cl_3$ | 446.44 | 447.52 | M+1 |
| VO $L_1$ $H_2O.SO_4$ | 601.94 | 602.89 | M+1 |
| VO $L_2$ $H_2O.SO_4$ | 512.44 | 514.19 | M+2 |
| VO $L_3$ $H_2O.SO_4$ | 504.94 | 506.78 | M+2 |

The mass spectra data of schiff base ligands and their complexes are given in table (2), showed molecular peaks, which were in good agreement for expected values [10]. The mass spectra of the ligands give some peaks at 231.5 m/z, 260.5 m/z and 326 m/z, respectively, which are assigned for H/Peaks. Titanium (III) and Vanadium(IV) give some peaks at 581.10 m/z, 720.40 m/z, 425.51 m/z, 714.40 m/z and 447.52 m/z, respectively which assigned as M+1 peak in all the cases but in the spectra of only one titanium (III) complex, this peak was at 445.42m/z which assign to M+2 peak. Whereas mass spectra of Vanadium (IV) complexes showed peak at 602.89 m/z,514.19 m/z, and 506.78 m/z as compared to ligands values assigned for M+1, M+2, M+2 peaks, respectively [10].

**Table 3:** Antimicrobial effect of the ligands and their complexes (Microorganism Inhibition Zone)

| Compounds | *S. cerevisiae* | *B. subtilis* | *E. coli* | *S. pneumoniae* | *M. luteus* | Control |
|---|---|---|---|---|---|---|
| p$^-$-Chlorobenzylidene-o$^-$- amino phenol ($L_1$) | 20 | 36 | 26 | 31 | 24 | - |
| $[Ti A_2 2H_2O]Cl_3$ | - | 14 | - | 10 | 23 | - |
| $[V A_2 2H_2O]Cl_3$ | - | 12 | 6 | 9 | 12 | - |
| $[VO A_2 H_2O]SO_4$ | - | 18 | 16 | 12 | 10 | - |
| p$^-$-chlorobenzylidene-2-aminobenzothiozole ($L_2$) | - | 17 | 13 | 10 | 9 | - |
| $[Ti B_2 2H_2O]Cl_3$ | 12 | 14 | 10 | 12 | - | - |
| $[V B_2 2H_2O]Cl_3$ | - | - | - | 11 | 10 | - |
| $[VO B_2 H_2O]SO_4$ | - | - | - | 10 | - | - |
| m$^-$-hydroxyacetophenone carbohydrazone ($L_3$) | 10 | 12 | 11 | 12 | 11 | - |
| $[Ti C_2 2H_2O]Cl_3$ | - | - | 6 | 10 | 9 | - |
| $[V C_2$ 2H2O$]Cl_3$ | - | - | 6 | 10 | 7 | - |
| $[VO C_2 H_2O]SO_4$ | - | - | 5 | 9 | 7 | - |

$^a$Concen= 100µg/disc$^b$ including disc diameter(6mm) (A=$L_1$, B=$L_2$, C=$L_3$ Ligands)

Antimicrobial activities of the L1, L2, and L3 ligands and their metal complexes against bacteria and yeast are recorded in the table (3) and in fig. (1) as well. In this study one of the striking features is that while ligands L1 & L2 and the Ti (III) complexes with ligand L3 have actively against saccharomyces cerevisiae. The ligand L1 and other compounds have not much activity against the same organism. It is apparent that the ligands L1 & L3 centring two free hydroxyl groups are more active than the L2 ligand containing free –SH group.

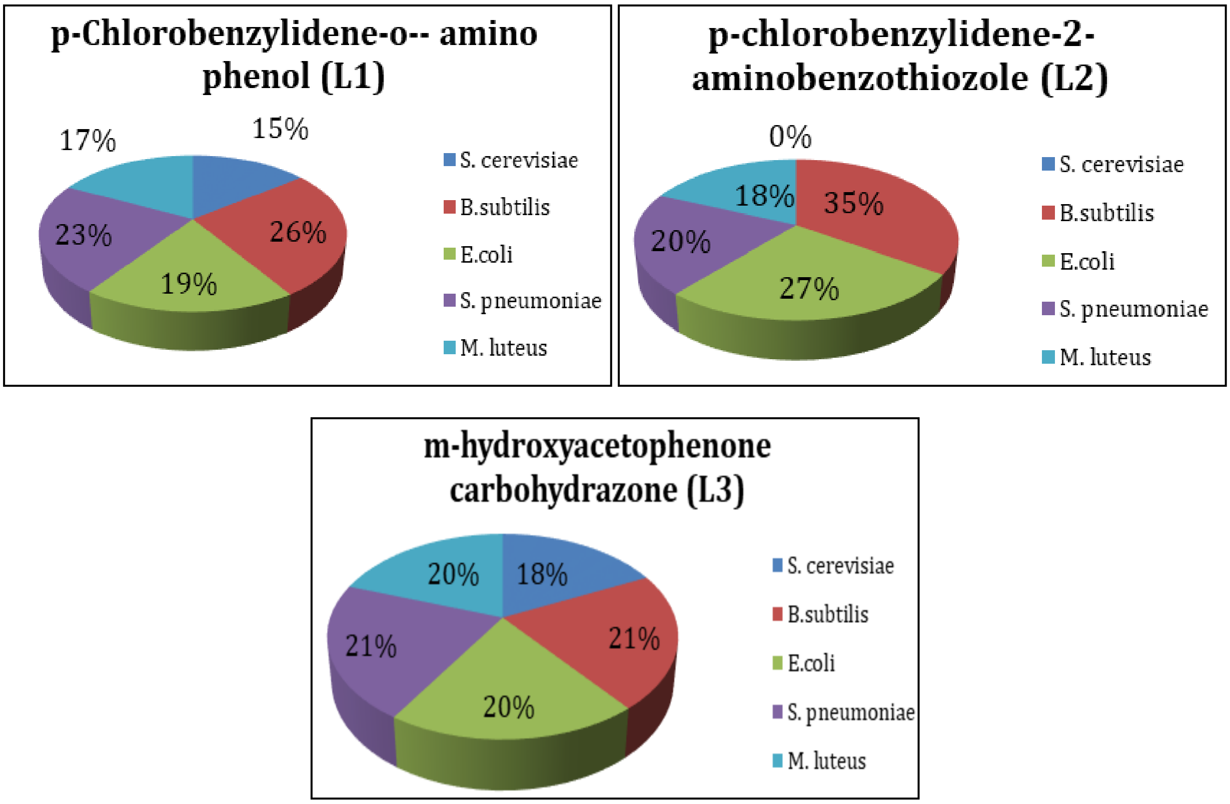

**Fig 1:** Showing Microoganism inhibition activities of the ligands and their complexes

Since the hydroxyl group substituent is known to increase the activity of the compound [11, 12] we have shown that the activity decreased on undergoing complex action. Since chelation reduces 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(-).

## Conclusion

In this manuscript Ti (III) and V(III) &(IV) complexes have been synthesized using schiff base ligands, and are suggested to be distorted octahedral complexes through N,O,S type donor atoms present in the ligands. The synthesized free ligands are found to be biologically active and their metal complexes showed significantly enhanced antibacterial and antifungal activities against microbial strains in comparison to the free ligands.

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