

Synthesis and Biological activity studies of some Vanadyl (IV) Complexes with Schiff base

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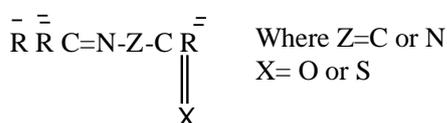
Abstract

In this communication were report the synthesis and characterization of the vanadyl(IV) complexes of Schiff base (L) used vanadium salts chloride, iodide, isothio cyanate and nitrate have been prepared and characterized by spectral data and conductance studies, nitrogen determined by Kjeldahl's method and other physiochemical measurement were done for prepared complexes revealed that the complexes have general formula $[V(OH)_2(NO_3)(L)]$, $[V(OH)X(L)_2]$ X= Cl⁻, I⁻ or NCS⁻ L=(P-nitro benzalidene)amino phenol. The Schiff base ligand acts as a bidentate N,O donor ligand Vanadium atom appear six coordinate in these complexes. Antifungal studies on the representative have been done successfully.

Key words: Schiff base complexes, Vanadyl(IV), Synthesis, Biological activity.

Introduction

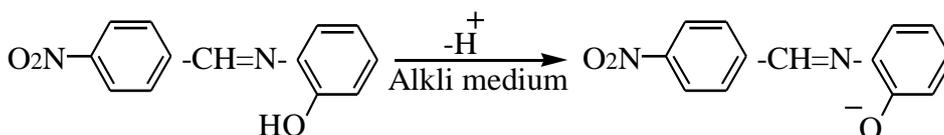
Schiff bases have recently received much attention because of their power of chelation with traces of metal ions. The active grouping is shown below, structure (1).



Structure (1). Active groups in schiff base compounds .

Schiff bases have been studied extensively as reagent for different metal ions, as bivalent-metal complexes

(semicarbazone)[1], and as a biologically active system (semicarbazone)[2,3]. In the recent past a number of workers [4-7], have reported a series of complex compounds formed by dioxouranium(VI), Zirconyl(IV), and Vanadyl(IV) metal ion with donor ligands including Schiff bases. This paper reports anew method to obtain V(IV) complexes at high yield (more than 70%). In this present communication we wish to report the investigation compounds of vanadyl(IV) metal ion with Schiff base ligand derived from 2-amino phenol and P-nitro benzaldehyde is shown below neutral and anion form, see structure(2):



Structure(2): The neutral and anion form of schiff base

The ligand was found to be anion bidentate (N,O coordinating) and lead to formation of compounds having the general composition $[V(OH)X(L)_2]$ X = Cl⁻, I⁻ or NCS⁻ and $[V(OH)_2(NO_3)(L)]$. These complexes are generally soluble in common organic solvents such as chloroform, benzene and carbon tetrachloride etc. They are quite stable.

Experimental

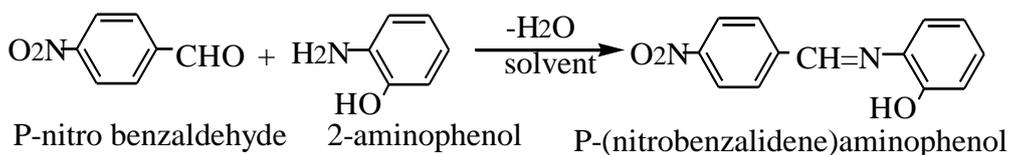
All the chemicals used in this study were of the best analytical grade supplied by B.D.H and S. Merck including metal salts Vanadyl chloride, isothiocyanate, iodide and nitrate, solvents used were ethanol, chloroform, benzene, nitrobenzene and Double distilled water, CuSO₄, K₂SO₄, H₂SO₄, NaOH, H₃BO₃ was used.

They were prepared by reported methods [8]. IR Spectra were recorded with a Bio-Rad melin Excalibue-Series Spectrophotometer class II Laser product (4000-400) cm⁻¹ range. The samples were prepared as KBr pellets. Nitrogen was estimated in the laboratory by Kjeldahl's method. The analyses of the metal ions were carried out gravimetrically by standard oxalate method[8]. The conductivity of the complexes were measured in nitrobenzene using Pw9526 Digital conductivity meter(Siemens). Melting points were determined using

Electro thermal 9100(U.K). The PH value measurements were made using a (901-Orion Research Microprocessor (Ion analyzer) PH meter. The ratio L:M of the ligand (Schiff base)and metal ions were determined by Job's method. Solution of (P-nitrobenzalidene)amino phenol (Schiff base) 0.01M was prepared in 50% ethanol and diluted to 100ml with same solvent. The results were plotted in form of graph. Wich shows the ligand metal ratio L:M for $[V(OH)_2(NO_3)(L)]$ complex(1:1) and $[V(OH)X(L)_2]$ Formation 2:1 complex, using UV-Visible Spectrophoto meter.

Synthesis of ligand

Schiff base were synthesized by the following procedure. Reaction(1) represent the processes employed for the synthesis, (0.151g; 0.001mol) of P-nitro benzaldehyde dissolved in 5ml absolute alcohol ethanol mixed with corresponding 2-amino phenol (0.105g ;0.001mol) in the same solvent and the mixture was stirred for 2hrs. The solution gave bright yellow shining crystalline precipitate. Which was then filtered using whatman42 filter paper, washed, dried in Vaccum desiccators for 24hrs. and the weight which was obtained (0.2g) the yield of the Schiff base so obtained in this modified procedure was (81%).



Reaction(1):ligand synthesis reaction

Synthesis of complexes

On slowly mixing the respective metal salt solutions were treated with ligand soln. in ethanol (20ml) and adjusting its PH between 7.5-8.5 by drop wise addition of NaOH solution 0.1M for deprotonation of hydroxide group substituted on phenol ring refluxing the resulting mixture for 2-3hrs. at 70-90C⁰. In some cases complexes were isolated immediately in cold while in some cases in hot solutions after refluxing. The complexes were collected washed with solvent and finally with anhydrous ether and dried in Vacuum desiccator's for about 24hrs..

Results and Discussion

The interaction of Schiff base ligand with Vanadyl(IV) metal ion results in formation of [V(OH)X(L)₂], [V(OH)₂(NO₃)(L)] complexes. All the complexes were characterized on the basis of their elemental analysis, conductance and infrared data. The elemental analysis of

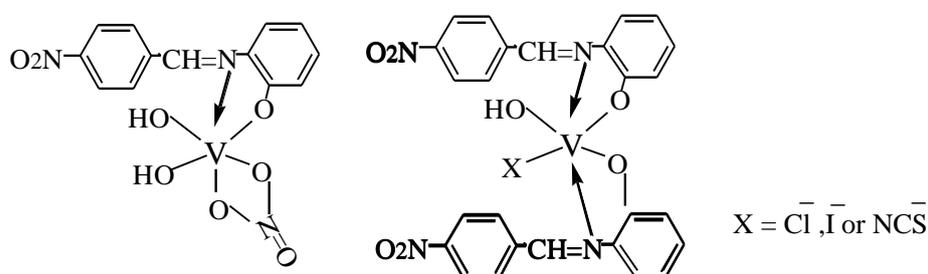
these complexes are given in Table 1. These complexes are quite stable and can be stored at room temperature 25C⁰ except the iodide which decomposes to sticky mass after a few weeks. All are sufficiently soluble in common organic solvents such as benzene, chloroform, ethanol. Electrical conductance values for these complexes were recorded in nitrobenzene (C₆H₅NO₂) medium and it was inferred that the complexes are essentially non-electro type which is in general agreement with previous observations[9].

It is realed from the electrical conductance and molecular weight studies that in halo and isothiocyniato complexes V-atom is six coordinate as these anions are covalently bonded as it is clear form i.r data these complexes have general formula [V(OH)X(L)₂] (X=Cl⁻,I⁻or NCS⁻). In case of [V(OH)₂(NO₃)(L)] V-atom is again six coordinate see structure(3).

Table 1: Analytical studies of Vanadyl(IV)Complexes of [P-Nitro benzalidene]amino phenol.

Metal Complexes	Yield %	Colour	m.p C ⁰	Analytis form(Calcd.)%			Molar conductance ohm ⁻¹ cm ⁻¹ mol ⁻¹
				M	N	Anion	
V(OH) ₂ (NO ₃)(L)	73	Brown	220	12.9 (13.1)	11.0 (10.8)	15.6 (15.9)	3.5
V(OH)Cl(L) ₂	70	Black	200	8.3 (8.7)	10.0 (9.6)	5.7 (6.0)	3.8
V(OH)I(L) ₂	74	Black	230	7.2 (7.5)	8.5 (8.3)	17.7 (18.7)	3.6
V(OH)(NCS)(L) ₂	76	Brown	250	8.1 (8.4)	10.8 (11.5)	9.0 (9.5)	4.1

Found (Calcd.)



Structure(3):The suggested chemical formula of [V(OH)X(L)₂]and[V(OH)₂(NO₃)(L)]coplexes

Infrared spectra

The infrared data shown in Table.2, the IR spectra of the complexes when compared with these of the ligands shows considerable shift. Indicates that the band at 1624 cm^{-1} present in the spectrum of the ligand due to $\nu(\text{C}=\text{N})$ azomethine absorption replaced by a lower frequency (1563-1610) cm^{-1} as a consequence of the coordination through azo methane nitrogen. And at 1239 cm^{-1} present in the spectrum of the ligand was absent from the spectra of all the chelates due to in-plane bending mode of C-O-H group [10]. It is possible that the band at 1239 cm^{-1} may arise due to the in-plane bending mode of C-O-H and the fact that the corresponding band is missing in the spectra of metal chelates suggests the deprotonation of the C-O-H group for the bond formation. This is essential in order to keep a charge balance between the metal ion and the ligand molecules. The infrared spectra of the Schiff base also show a weak and broad absorption band in the region

(3326-3329 cm^{-1}) this may be assigned to hydrogen bonded. However, upon complex formation the bands appeared in the region (3553-3540 cm^{-1}), may be assigned to the coordination (νOH) group. Two new bands appeared in the spectra of all the chelates between (500-470) cm^{-1} due to $\nu(\text{M}-\text{N})$ coordination and (440-420) cm^{-1} due to $\nu(\text{M}-\text{O})$ coordination may be coupled bands vibrations supports the involvement of nitrogen and oxygen atoms in complexation with metal ions [11,12]. Two strong bands observed in the (1530-1345 cm^{-1}) in the ligand spectra assigned to the symmetrical and asymmetrical bending of the N-O bonds for NO_2 group. The two additional bands which are present in the spectra of vanadyl nitrate complex appear at (1484-1520 cm^{-1}) are assigned respectively to (symmetrical stretching of the third oxygen atom) and (asymmetrical stretching of two N-O bonds close to the metal atom). Figure(1) and (2) shows IR spectra for the ligand and $[\text{V}(\text{OH})\text{Cl}(\text{L})_2]$ complex.

Table 2: IR frequencies in cm^{-1} for the Schiff base and complexes.

Complexes	C=N _{str.} Azomethane	C-O-H _{str.}	C=C _{str.}	M-N	M-O	OH _{str.}
Ligand	1624	1239	1587	-----	-----	3326
$[\text{V}(\text{OH})\text{Cl}(\text{L})_2]$	1563	-----	1550	500-470	440-420	3553
$[\text{V}(\text{OH})\text{I}(\text{L})_2]$	1572	-----	1570	500-465	442-422	3540
$[\text{V}(\text{OH})(\text{NCS})(\text{L})_2]$	1575	-----	1568	495-460	443-425	3545
$[\text{V}(\text{OH})_2(\text{NO}_3)(\text{L})]$	1570	-----	1565	498-463	440-415	3548

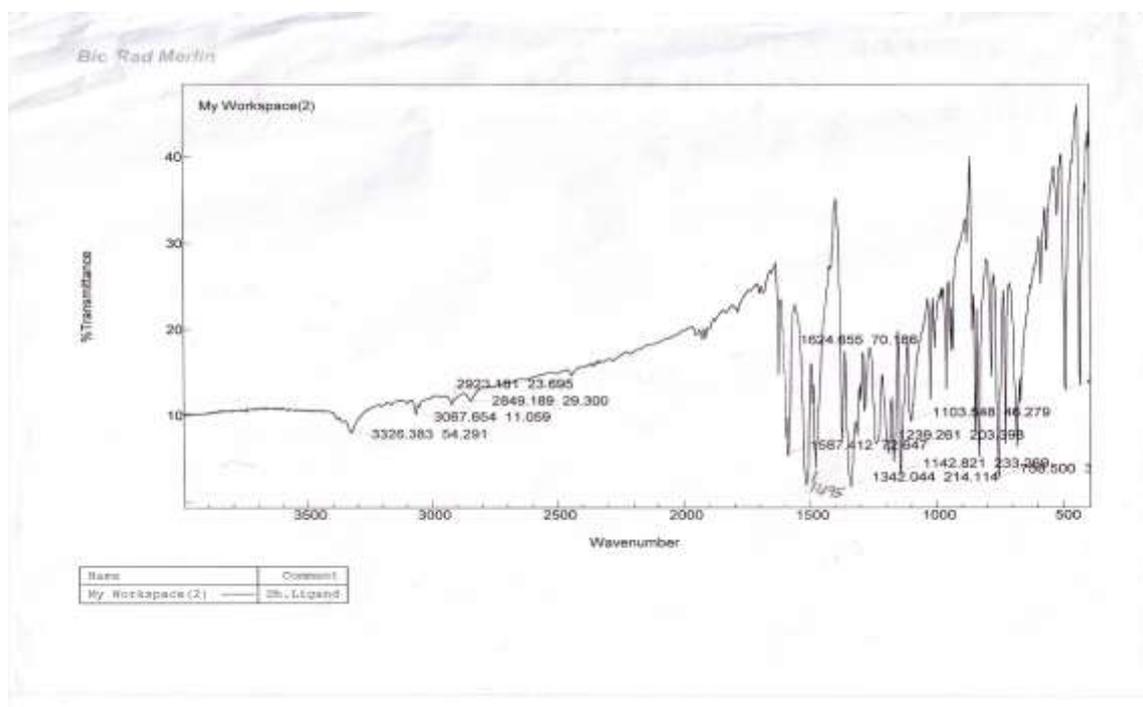


Fig.1. Infrared spectrum of Schiff base .

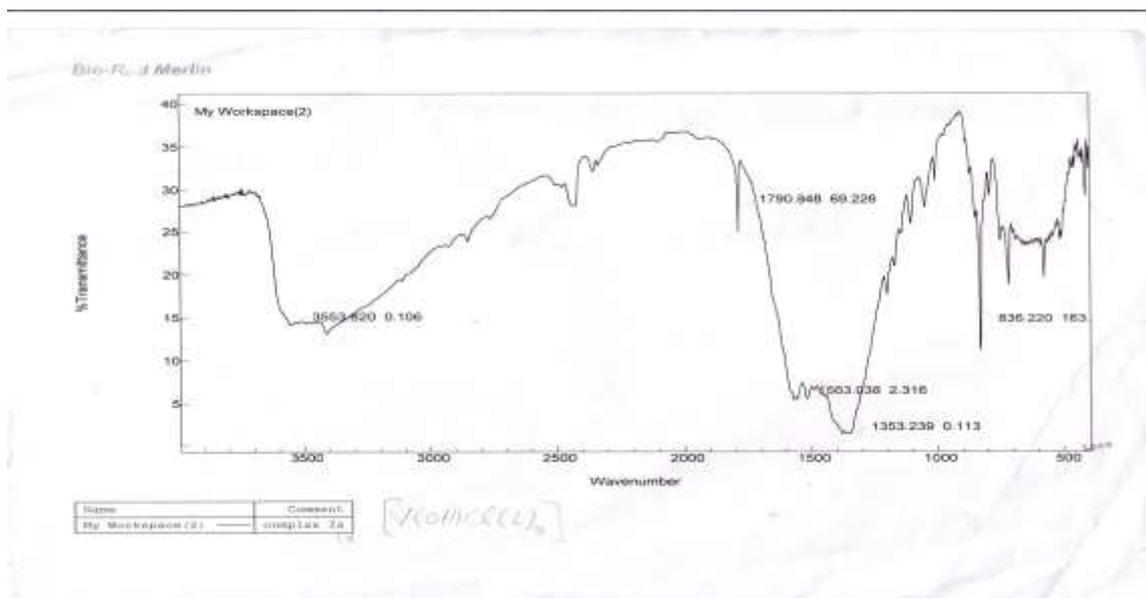


Fig.2. Infrared spectrum of V(IV) Schiff base complex $[V(OH)Cl(L)_2] \cdot 1$

Anti fungal studies

Antifungal activity of a representative complex was done successfully. The radial growth and paper disc methods were used to evaluate antifungal activity[13,14]. The activity was checked on peronospora sp. and Elbugo sp. Two fungi which are grown on PDA culture on living host tissue i.e. Brassica compestris. Inoculation was made from infected inflorescences of Brassica sp. In petriplates containing PDA medium, 10mm paper disc dipped in solution of complex in DMF in varied concentrations[15,16].

They were put on petriplates before inoculating them with the fungus. The plates containing unamended PDA were maintained as control. The inoculated plates were incubated at $25^{\circ} \pm 1C^{\circ}$ for 5 days. The radial growth of

the fungal colonies were measured on 6th day and the data was statistically analyzed[17,18]. Table (3) shows the effect of the complex on the mean radial growth (in cms). of fungus. The control Petri plates which does not contain any paper disc of complex solution shows the radial growth of (4.0-4.5)cm for fungal colonies. In order to get anew biological active complexes it was thought proper to study the biological activity for the synthesized complexes. The synthesized complexes were subjected to screening them for their antimicrobial sensitivity against two types fungal peanospora sp. and Elbugo sp. The screened results showed that the prepared complexes are sensitive against both types of fungi.

Table 3: Effect of varied concentration of Vanadyl(IV) complexes on the mean radial growth(in cms)of fungal colonies.

Complex	<u>Peanospora sp.</u>			<u>Elbugo sp.</u>		
	30mg/10ml	20mg/10ml	10mg/10ml	30mg/10ml	20mg/10ml	10mg/10ml
V(OH) I (L) ₂	0.7	1.0	1.7	0.8	0.9	1.5

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تحضير ودراسة الفعالية البايولوجية لبعض معقدات الفناديل (IV) مع قواعد شيف

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الخلاصة

يتناول البحث تحضير معقدات (قواعد شيف) مع الأملاح الفلزية للفناديل (IV) كل من الكلورايد و الأيويد و الأزوتايوسانات و النيترات ، وبعد تحضير المعقدات الناتجة درست بوساطة الطرق الطيفية و القياسات التوصيلية المولارية وتم تقدير نسبة النايروجين بطريقة (كيلدال) وتم أيضا دراسة عدد من الخواص الكيميائية الفيزيائية للمركبات المحضرة. تم التعبير عن صيغ المعقدات بالصيغ الآتية. $[V(OH)_2(NO_3)(L)]$, $[V(OH)X(L)_2]$ X= Cl, I or NCS⁻ يتصرف الليكاند (قاعدة شيف) كثنائي السن الذرات المانحة فيها هي N,O تظهر ذرة الفناديوم المركزية تناسق سداسي في هذه المعقدات. ولقد تم دراسة المعقدات من حيث الفعالية البايولوجية أيضا.