

Oxovanadium(IV) Complexes: Synthesis, Spectral and Antimicrobial Studies Derived from Dibasic Tridentate (ONO) Donor Aroylhydrazone Schiff's Bases

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Abstract: The biologically active oxovanadium(IV) (I-IV) complexes are synthesized by condensation of VO(IV) salt with aroylhydrazone schiff's base ligands, 1-(1-hydroxynaphthalen-2-yl)ethanone-2-chlorobenzoylhydrazone (H_2L^1), 1-(1 - hydroxynaphthalen-2-yl) ethanone -4-chloro benzoyl hydrazone (H_2L^2), 1-(1-hydroxynaphthalen-2-yl)ethanone-2,4-chlorobenzoylhydrazone (H_2L^3) and 1-(1-hydroxynaphthalen-2-yl) ethanone-2-iodobenzoylhydrazone (H_2L^4). These chelating agents are synthesized from 2-acetyl-1-naphthol and substituted benzohydrazides by conventional method. All synthesized oxovanadium (IV) complexes are characterized by elemental analysis, solid reflectance, IR studies and thermal analysis (TGA). Further magnetic moment and molar conductance of complexes (I-IV) are also measured. According to received physicochemical data it was observed that all chelating agents behave dibasic tridentate (ONO) (enol form) towards VO(IV) ion. The analytical data along with electronic, magnetic and thermal studies suggested that all VO(IV) complexes have monomeric structures with square pyramidal geometry. Study of antimicrobial test against some bacteria and fungi are also carried out which shows significant activity of VO(IV) complexes (I-IV) in comparison with their respective ligands. Most of the VO(IV) complexes exhibited more than 90% reduction in growth against *A. niger* and *F. moniliforme* fungal strains as compared to their respective ligands.

Keywords: ONO Donar Hydrazone Chelates, VO(IV) Complexes, Spectral, Thermal and Antimicrobial Studies.

I. INTRODUCTION

In coordination compounds, chelate systems having electronegative atoms like nitrogen and oxygen increases denticity and ultimately increases stability of metal complexes [1]. In this class hydrazones possess a special place due to presence of $-CO-NH-N=C<$ moiety in their structure [2]. Another interesting feature of hydrazone is to exhibit *amido-iminol* tautomerism, further increases electron delocalization and offer different donor sites [3,4]. Hydrazones and their metal chelates have growing importance because of the wide spectrum of their biological applications like antimicrobial, antiinflammatory, antifungal, antitubercular, and anticancer activities [5-8].

Now a day's oxovanadium complexes have place attention due to their ability to uptake and transport of metals inside the cells in living organism [9]. The coordination chemistry of oxovanadium(IV) have many applications in biological field as antibacterial, anti-inflammatory, antiviral, antifungal, anticancer and antipyretic properties [10-12]. A number of oxovanadium(IV) complexes with hydrazone ligands have been reported for their insulin mimetic properties [13]. Several bio-medical application of vanadium complexes are also reviewed [14,15].

The present study is the extension of our previous work on aroylhydrazone transition metal complexes [16-18]. From the above said applications of oxovanadium(IV) complexes, in this paper we are interested in synthesis, spectral, thermal and antimicrobial studies of VO(IV) aroylhydrazone complexes (I-IV). The purpose of this study is to analyze structure and compare antimicrobial activity of aroylhydrazone ligands with newly synthesized VO(IV) complexes along with standard drugs.

II. EXPERIMENTAL

2.1 Materials and Methods

Solvents and chemicals used in synthesis of ligands and metal complexes are of AR grade and used as it purchased from S.D. fine. Metal salt Vanadylsulfate pentahydrate ($\text{VO}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$) is commercially available and purchased from Sigma Aldrich. The elemental analysis of carbon, hydrogen and nitrogen were done by Elemental Analyser (Thermo Scientific) FLASH- 2000. Chlorine was analyzed by conventional method for chlorine estimation [19]. The metal content in the complexes was estimated by classical oxide method [20]. The diffuse reflectance spectra of synthesized compounds are recorded on Jasco spectrophotometer, model no.V-670 in measurement range 1000-200 nm. The infrared spectra of ligands and their metal complexes were recorded on IR Spectrophotometer model RZX (Perkin Elmer) in the $4000\text{--}400\text{ cm}^{-1}$ region using KBr pellets. The $^1\text{H-NMR}$ spectra of H_2L^4 ligand was recorded using FT-NMR Cryo-magnet Spectrometer 400MHz (Bruker) with deuterated DMSO as solvent and TMS as internal standard. Molar conductivity of complexes was measured by using Elico CM-180 conductivity bridge in DMF (10^{-3}M) at room temperature. Magnetic susceptibility at room temperature was measured by Gouy's method. TG analyses of complexes were carried out on TG Instrument, model – SDT Q600 V20.9 Build 20 at a heating rate of 20°C per minute in an atmosphere of nitrogen, within temperature range from room temperature to 800°C .

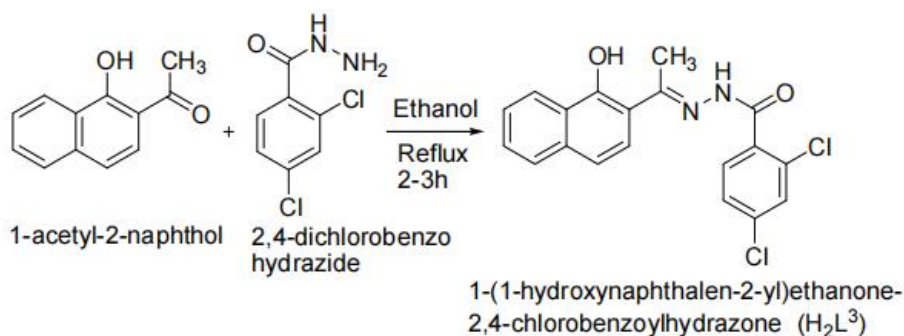
Method of synthesis and spectral analysis of 1-(1-hydroxynaphthalen-2-yl) ethanone-2-chlorobenzoylhydrazone (H_2L^1) [16], 1-(1-hydroxynaphthalen-2-yl) ethanone-4-chloro benzoylhydrazone (H_2L^2) [17] and 1-(1-hydroxynaphthalen-2-yl) ethanone-2-iodobenzoyl hydrazone (H_2L^4) [18] aroylhydrazone (H_2L^1 , H_2L^2 & H_2L^4) ligands from condensation of 2-acetyl-1-naphthol with 2-chloro, 4-chloro and 2-iodo substituted benzohydrazides was already studied in our previous work. While $^1\text{HNMR}$ study and synthesis of 1-(1-hydroxynaphthalen-2-yl)ethanone-2,4-chlorobenzoylhydrazone(H_2L^3) ligand is discussed in this paper. Starting materials 2,4-dichlorobenzohydrazide [21] and 2-acetyl-2-naphthol for synthesis of H_2L^3 ligand are prepared by procedure given in literature [22].

2.1.1 Synthesis of 1-(1-hydroxynaphthalen-2-yl)ethanone-2,4-chlorobenzoylhydrazone (H_2L^3)

To hot ethanolic solution (15ml) of 2,4dichlorobenzohydrazide (0.01mol), hot ethanolic solution (15ml) of 2-acetyl-1-naphthol was added with continuous stirring and reaction mixture was allow to heat under reflux on water bath for 2-3 h [Scheme 1]. After cooling, the solution was allowed to evaporate resulting in yellow coloured solid product, washed with ethanol and recrystallized from DMF/ethanol (1:4 v/v) and dried under vaccum of CaCl_2 . Yield – 75%, Melting point - 170°C .

2.1.2 Synthesis of VO(IV) Complexes

To a hot DMF solution (5ml) of organic ligands ($\text{H}_2\text{L}^1 - \text{H}_2\text{L}^4$) (0.01mol), a hot DMF solution (5ml) of the appropriate salt $\text{VO}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (0.01mol) solution was added under continuous stirring. The mixture was refluxed on sand bath for 5-6h. The resultant solution was digested to half of its volume; on cooling solid product was obtained. The product was washed with ethanol followed by petroleum ether and dried at room temperature under vaccum of CaCl_2 . Yield – 68%, Melting point $>300^\circ\text{C}$.



Scheme 1 – Synthesis of ligand 1-(1-hydroxynaphthalen-2-yl)ethanone-2,4-chlorobenzoylhydrazone (H_2L^3)

III. ANTIMICROBIAL STUDY

In the present work the method and microorganisms used to test and measure mode of action on ligands ($H_2L^1-H_2L^4$) as well as their VO(IV) metal complexes are,

3.1 Antibacterial Activity

Method used: Agar Cup Method [23]

Bacterial cultures used:

i) Gram positive: *Staphylococcus aureus*, *Bacillus subtilis*

ii) Gram negative: *Escherichia coli*, *Salmonella typhi*

Standard antibiotic used - *Penicillium*

3.2 Antifungal Activity

Method used: Poison plate method [23]

Fungal cultures used: *Aspergillus niger*, *Penicillium chrysogenum*, *Fusarium moniliforme*, *Aspergillus flavus*.

Standard antifungal used - *Gresiofulvin*

IV. RESULTS AND DISCUSSION

From analytical and physicochemical data of ligands and VO(IV) complexes given in Table 1, confirms 1:1 ligand:metal stoichiometry. A molar conductance value in range of $13.4-17.9 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in DMF at 10^{-3}M , indicates non-electrolytic nature of all complexes [24]. VO(IV) metal complexes are colored and dissolve in only DMF and DMSO solvent and insoluble in water.

4.1 Magnetic Property and Diffuse Reflectance Spectral Study

Magnetic moment of VO(IV) complexes in the present investigation were measured at room temperature. VO(IV) ion belongs to $S = 1/2$ system and its complexes exhibits magnetic moment similar or very close to spin-only moment of 1.73 BM indicating d^1 system [25] and is the characteristic value for mononuclear oxovanadium complexes. The room temperature magnetic moment values of all synthesized VO(IV) complexes are found in the range of 1.59 – 1.64 BM, which has lower value than spin only values.

Diffuse reflectance spectra of VO(IV) (1-4) complexes shows low intensities d-d bands in the ranges $11750-12500 \text{ cm}^{-1}$ due to ${}^2B_{2g} \rightarrow {}^2E_g$ transition, $15384-15873 \text{ cm}^{-1}$ due to ${}^2B_{2g} \rightarrow {}^2B_{1g}$ transition and $22321-23809 \text{ cm}^{-1}$ due to ${}^2B_{2g} \rightarrow {}^2A_{1g}$ transition in spectra. A fourth high energy band around $28571-30303 \text{ cm}^{-1}$, was observed in spectra which can be assigned as a $L \rightarrow M$ charge transfer transition. Magnetic moment values and diffuse reflectance spectra given in Table 2 indicates square pyramidal geometry around VO(IV) ion [26].

Table 1: Analytical and Physico-chemical data of ligands and VO(IV) complexes

Molecular Formula Ligand/Complex	Molecular weight	Colour	Elemental analysis %Found(Cal.)					*(Λ_m)
			C%	H%	N%	Cl%	M%	
$C_{19}H_{15}ClN_2O_2$ (H_2L^1)	338.79	Lemon yellow	67.28 (67.36)	4.18 (4.46)	7.98 (8.27)	10.49 (10.46)	---	---
$[VO(L^1)(H_2O)](1)$	421.72	Deep Olive	52.67 (54.11)	3.29 (3.59)	5.98 (6.64)	8.30 (8.41)	12.00 (12.08)	15.8
$C_{19}H_{15}ClN_2O_2$ (H_2L^2)	338.79	Dark yellow	67.01 (67.36)	3.88 (4.46)	8.08 (8.27)	10.00 (10.46)	---	---
$[VO(L^2)(H_2O)](2)$	421.72	Olive	53.77 (54.11)	3.19 (3.59)	6.38 (6.64)	8.00 (8.41)	11.90 (12.08)	17.9
$C_{19}H_{14}Cl_2N_2O_2$ (H_2L^3)	373.23	Yellow	61.16 (61.14)	3.42 (3.78)	7.21 (7.51)	18.43 (19.00)	---	---
$[VO(L^3)(H_2O)](3)$	456.17	Olivedrab	52.67	3.02	5.98	14.30	11.00	13.4

			(50.03)	(3.09)	(6.14)	(15.54)	(11.17)	
$C_{19}H_{15}N_2O_2 (H_2L^4)$	430.24	Pale yellow	52.78 (53.04)	3.04 (3.51)	6.31 (6.51)	---	---	---
$[VO(L^4)(H_2O)](4)$	513.17	Pale Olive	43.67 (44.47)	2.29 (2.95)	5.08 (5.46)	---	9.58 (9.93)	17.9

* Molar conductance values in $ohm^{-1} cm^2 mole^{-1}$

4.2 Infra-Red Spectral Study

The structurally significant IR frequency values for ligands ($H_2L^1-H_2L^4$) and their respective VO(IV) complexes have been reported in Table 3 and representative IR spectra of $[VO(L^1)(H_2O)]$ is given. The IR spectra show structurally important vibrational bands of the free hydrazone ligand and their metal complexes, which are useful for determination of mode of coordination of the ligand. The Schiff bases exhibits a medium intense band at $2995-3005 cm^{-1}$ due to the intramolecular hydrogen bonding (OH--NH) [27].

Table 2: Diffuse reflectance Spectral data and Magnetic moment of the VO(IV) complexes

Metal Complex	Absorption (cm^{-1})	Band Assignment	Magnetic Moment μ_{eff} (BM)
$[VO(L^1)(H_2O)](1)$	11750 15873 23809 28985	$^2B_{2g} \rightarrow ^2E_g$ $^2B_{2g} \rightarrow ^2B_{1g}$ $^2B_{2g} \rightarrow ^2A_{1g}$ LMCT	1.64
$[VO(L^2)(H_2O)](2)$	12500 15384 23364 28571	$^2B_{2g} \rightarrow ^2E_g$ $^2B_{2g} \rightarrow ^2B_{1g}$ $^2B_{2g} \rightarrow ^2A_{1g}$ LMCT	1.60
$[VO(L^3)(H_2O)](3)$	12195 15432 22321 30303	$^2B_{2g} \rightarrow ^2E_g$ $^2B_{2g} \rightarrow ^2B_{1g}$ $^2B_{2g} \rightarrow ^2A_{1g}$ LMCT	1.62
$[VO(L^4)(H_2O)](4)$	12019 15673 22831 29411	$^2B_{2g} \rightarrow ^2E_g$ $^2B_{2g} \rightarrow ^2B_{1g}$ $^2B_{2g} \rightarrow ^2A_{1g}$ LMCT	1.59

The absence of this band in the spectra of complexes indicates deprotonation of phenolic group and coordination of oxygen atom to metal ion. Moreover, the strong band at $1286-1309 cm^{-1}$ due to the $\nu(C-O)$ (phenolic) stretching in the ligand has been shifted to the $1305 - 1328 cm^{-1}$ region upon complexation. This shift towards higher absorption in the complexes also indicates coordination through the phenolic oxygen. The ligand exhibits strong band at $1583-1593 cm^{-1}$ due to azomethine group ($C=N$). In all complexes this band shifted to lower frequency ($6 - 20 cm^{-1}$), indicating the participation of azomethine nitrogen in coordination. A ligand spectrum exhibits band at $979-1051 cm^{-1}$ due to the (N-N) stretch [28]. This band is shifted to higher wave number in complexes also supports the coordination of azomethine nitrogen atom. The high frequency shift of the (N-N) band is expected because of diminished repulsion between the lone pairs of adjacent nitrogen atoms. The lower frequency region of the spectra also confirms the participation of the phenolic oxygen and azomethine nitrogen by the appearance of bands at $551 - 578 cm^{-1}$ and $420 - 447 cm^{-1}$ assignable to $\nu(M-O)$ and $\nu(M-N)$ respectively. The other bands observed at $3190-3211$ and $1629-1654 cm^{-1}$ in free ligand are assignable to $\nu(N-H)$ and $\nu(C=O)$ stretches respectively. The spectra of all VO(IV)(1-4) do not show the band due to $\nu(N-H)$ and $\nu(C=O)$ frequencies which indicating the coordination of ligand to metal in enol form [28]. A strong band at region $991-997 cm^{-1}$ give evidence of $V=O$ stretch [25] in all VO(IV) complex spectra. A new band at frequency $3438-3414 cm^{-1}$ and $1622-1645 cm^{-1}$ confirms coordination of water molecule to metal in complex.

Table 3: IR Spectral data (cm^{-1}) of ligands and its VO(IV) complexes

Sr. No.	Compound	$\nu\text{OH} + \nu\text{NH}$ (HO----NH)	N-H	C=O	C-O Phenolic	C=N	N-N	C-O enolic	M-O	M-N	V=O
1.	H_2L^1	2995	3190	1653	1288	1589	1020	---	---	---	---
2.	H_2L^2	3005	3211	1633	1286	1593	979	---	---	---	---
3.	H_2L^3	2995	3207	1629	1309	1587	1051	---	---	---	---
4.	H_2L^4	2997	3194	1654	1288	1583	1014	---	---	---	---
5.	$[\text{VOL}^1(\text{H}_2\text{O})]$	---	---	---	1309	1575	1022	1249	553	420	991
6.	$[\text{VOL}^2(\text{H}_2\text{O})]$	---	---	---	1315	1573	1024	1255	570	447	995
7.	$[\text{VOL}^3(\text{H}_2\text{O})]$	---	---	---	1328	1581	1059	1253	578	443	995
8.	$[\text{VOL}^4(\text{H}_2\text{O})]$	---	---	---	1305	1575	1018	1253	551	426	997

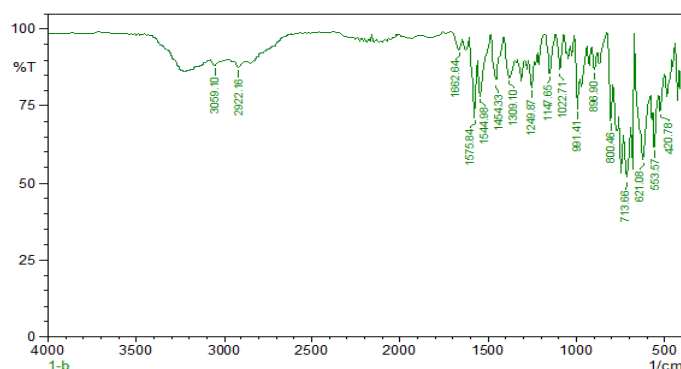


Figure 1: Infra-red spectra of $[\text{VO}(\text{L}^1)(\text{H}_2\text{O})](1)$ complex

4.3 Thermogravimetric Analysis

Thermal decomposition involves the breaking of bonds between the metal ion and ligands in metal complex which is utilized to study thermal stability of complexes. Thermogravimetric analysis of VO(IV) (3) was studied as representative compound in the temperature range of 30-800°C in nitrogen atmosphere at a heating rate of 20°C/min. In the present study thermogram of VO(IV) complex shows two step decomposition pattern, first stage starts from 147.03°C with estimated loss 3.432% attributed to the loss of one coordinated water molecule [29]. In the second stage decomposition within temperature range 168-448°C with the mass loss of 41.14% was due to partial decomposition of ligand. Above 450°C decomposition of organic part was continued with weight loss about 18.20% and having high residue 37.24% indicate some organic part along with metal oxide. (Fig.2).

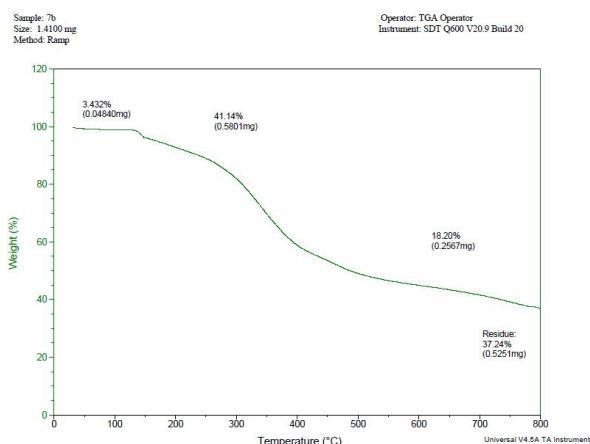


Figure 2: Thermogravimetric analysis curve of $[\text{VOL}^3(\text{H}_2\text{O})](3)$ complex

4.4 ¹H NMR Study of ligands

¹H NMR spectral data of ligands H₂L¹ [16], H₂L² [17] and H₂L⁴ [18] are studied in our previous work. The proton NMR spectrum of 1-(1-hydroxynaphthalen-2-yl)ethanone-2,4 chlorobenzoylhydrazone(H₂L³) ligand is recorded in DMSO-d₆ (Fig.3). In the proton NMR spectrum a singlet signal at δ 14.75 ppm assigned for phenolic -OH proton. Another singlet signal is observed at δ 11.73 ppm attributes to the imino -NH proton. A high intensity singlet signal at δ 2.51 ppm is assigned for three protons of methyl group. A multiplet peaks due to protons of naphthalene and phenyl rings are in the range of δ 7.58-8.36 ppm are assigned.

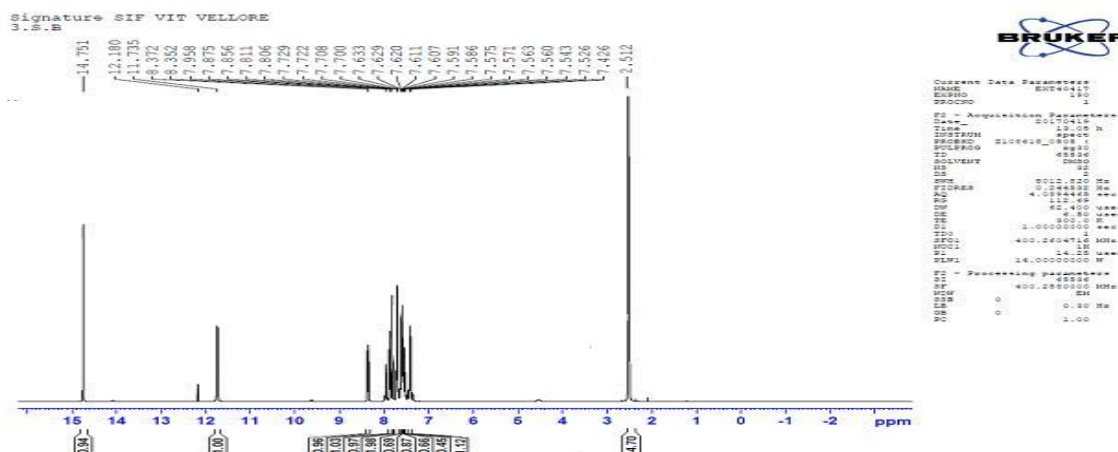


Figure 3: ¹H NMR spectra of Ligand H₂L³.

4.5 Antimicrobial Study

From the antibacterial and antifungal activity of ligands and their respective VO(IV) complexes represented in Table 4, reveals that ligand on complexation with metal ion increases their activity against bacteria and fungi. This increased activity of complex can be explained on the basis of overtone's concept and Tweedy chelation theory [30]. It was observed that all ligands and VO(IV) complexes are very active against *E. Coli* bacteria and exhibited higher activity than standard *penicillin*. All ligands are inactivity against *S. typhi* bacteria while their respective VO(IV) complexes shows activity against *S. typhi* bacteria. Most of the VO(IV) complexes exhibited more than 90% reduction in growth against *A. niger* and *F. moneliforme* fungal strains as compared to their respective ligands. Generally ligand H₂L³ which contain more -Cl group shows higher antibacterial activity than other ligands [31]. Presence of naphthalene ring in the complexes increases their liophilicity. Due to coordination the polarity of the ligand and the central metal ion are reduced through the lipid layer of the bacterial cell membrane [32].

Table 4: Antibacterial and antifungal activity of ligands H₂L¹-H₂L⁴ and its VO(IV) complexes(1-4)

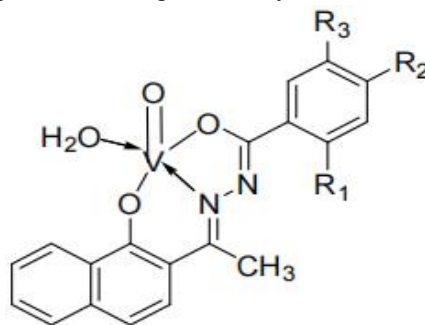
Sample Code No.	Antibacterial activity(mm)				Antifungal activity			
	Gram -ve		Gram +ve					
	<i>E. coli</i>	<i>S. typhi</i>	<i>S. aureus</i>	<i>B. subtilius</i>	<i>A. niger</i>	<i>P.chryso genum</i>	<i>F.moneli forme</i>	<i>A. flavus</i>
H ₂ L ¹	15	n.a.	15	11	RG	RG	RG	+ve
VO(IV) (1)	22	19	25	28	-ve	RG	RG	-ve
H ₂ L ²	12	n.a.	12	10	RG	+ve	RG	RG
VO(IV) (2)	17	16	20	20	-ve	RG	RG	RG
H ₂ L ³	16	n.a.	16	15	RG	RG	RG	RG
VO(IV) (3)	20	19	29	28	-ve	RG	-ve	RG
H ₂ L ⁴	14	n.a.	15	n.a.	RG	RG	-ve	RG

VO(IV) (4)	20	18	25	27	-ve	RG	-ve	RG
<i>Penicillin</i>	11	24	36	30	--	--	--	--
<i>Griseofulvin</i>	--	--	--	--	-ve	-ve	-ve	-ve

n. a.- No activity, +ve – Growth (Antifungal Activity absent), -ve – No Growth (More than 90% reduction in growth, Antifungal Activity present), RG – Reduced Growth (More than 50% and less than 90% reduction in growth)

V. CONCLUSION

Due to stability of all newly synthesized VO(IV) (1-4) complexes and halosubstituted ligands $H_2L^1-H_2L^4$ in solid state and in solvent, they are characterized and their antimicrobial activity is also studied in this paper. From analytical data and physicochemical properties reveals 1:1 ligand:VO(IV) complex ratio. Spectroscopic properties confirms dibasic tridentate ONO enolic ligation of ligands towards metal ion in complexes. Square pyramidal geometry of all VO(IV) complexes was also confirmed from their magnetic moment, diffuse reflectance spectra and IR spectral studies. Thermogravimetric analysis of all VO(IV) (1-4) complexes gives information about presence of one coordinating water molecule at coordination site of metal. The tentative structure of $[VO(L)(H_2O)]$ complex is given in Fig. 4. Study of antimicrobial activity of ligands and metal complexes proves moderate to good activity against some bactericides and fungicides. Obviously all VO(IV) complexes show higher activity due to chelation as compare with ligands.



Where, -	R ₁	R ₂	R ₃
1	-Cl,	-H	-H
2	-H	-H	-Cl
3	-Cl	-H	-Cl
4	-H	-H	-I

Figure 4: Tentative structure of $[VO(L)(H_2O)]$ (1-4) complexes

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