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Synthesis, spectroscopic and antimicrobial studies of oxovanadium (IV) complexes incorporating tridentate ONO donor hydrazones

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ABSTRACT

Oxovanadium (IV) complexes of ONO donor hydrazone ligand derived from 2-hydroxy aryl ketones and 2imidazolyl mercaptoaceto hydrazide (LH₂) have been synthesized and characterized by elemental analyses, molar conductance, magnetic susceptibilities, electronic, IR, ESR and thermal studies. Elemental analyses show 1:1 metal to ligand stoichiometry for oxovanadium (IV) complexes. The IR spectra of the complexes indicate that the ligand LH₂ acts as a dibasic tridentate nature hence the ligand exhibits in enol form in newly prepared oxovanadium (IV) complexes. Spectral data indicates that square pyramidal geometry of monomeric five coordinated oxovanadium (IV) complexes with the general formula $[VO(L)H_2O]$ is confirmed by thermal studies. The hydrazone and their complexes were screened for their invitro antibacterial activity against E.coli and S.aureus. Antifungal activity against T.polysporum and C. albicans.

Keywords: Oxovanadium (IV) complexes, Hydrazones, Spectral studies, Square pyramidal, Antimicrobial activity.

INTRODUCTION

Oxovanadium (IV) salts are known to form stable complexes with bi, tri and tetradentate schiffs bases. In these complexes V(IV) could exist in a five or six coordinated state [1-3]. A square pyramidal or distorted trigonal bipyramidal structure is observed for five coordinated complexes [4] while distorted octahedral geometry is reported for the six coordinated ones [3].

The coordination chemistry of oxovanadium (IV) (i,e VO^{+2} or Vanadyl ion) is more interesting and rather more important because of two main reasons. Firstly the vanadyl complexes are finding more and more importance in biological systems [5-7]. Secondly the coordination number and geometry of this metal is highly ligand dependent [8]. Moreover Vanadyl ion is less toxic than vanadate ion [9]. In the last years research has been directed towards the synthesis of efficient bioactive compounds with low toxicity, in order to achieve this goal the type and the position of substituent into ligand were varied.

The hydrazone derivatives are used as fungicides and in the treatment of diseases such as tuberculosis, leprosy and mental disorder [10]. The remarkable biological activity of acid hydrazides $R-CO-NH-NH_2$, their corresponding hydrazones $R-CO-NH-N=CH-R^1$ and the dependence of their mode of chelation on the transition metal ions present in the living system have offered significant interest in recent years [11-14].

In view of the fast growing interest of hydrazones on account of the structural, analytical and biological importance of their metal complexes, the synthesis of oxovanadium (IV) complexes of ONO donor hydrazones derived from 2-imidazolyl mercaptoaceto hydrazide and 2-hydroxy aryl ketones (LH₂) have been carried out and the results are presented in this paper. The 3D structure of $L^{1}H_{2}$ is shown in figure 1.



Figure.1: 3D structure of ligand L¹H₂

EXPERIMENTAL SECTION

All chemicals used for the synthesis of ligands and complexes were of reagent grade, the solvent were dried and distilled before use according to standard procedures. Vanadyl chloride is prepared from vanadium pentoxide with HCl according to the standard reported method [15]. Carbon, hydrogen and nitrogen were determined on Carlo Erba CHN analyzer. The vanadium content in all the complexes was determined by using standard procedures [16]. Conductance measurements were made using 10^{-3} M solutions of complexes in DMF using Elico conductivity bridge type CM-82 provided with a cell having cell constant 0.52 cm^{-1} . The electronic spectra of complexes in DMF were recorded on Hitachi 2001 spectrophotometer and IR spectra were recorded on Nicolet 170 SXFT-IR spectrophotometer in KBr pellets in the range 400-4000 cm⁻¹. Magnetic susceptibilities of the complexes were measured with a Faraday balance using mercury (II) tetrathiocyanatocobaltate (II) as calibrant. The est spectra of VO(IV) complexes at room temperature were recorded on Varian E-4X band EPR spectrophotometer using TCNE as the g marker. Thermograms were recorded on a Perkin Elmer analyser in N₂ atmosphere at a heating rate of 10^{0} C. Antimicrobial activities of the ligand (LH₂) and its complexes along with the standards were carried out against the pathogenic bacteria *E. coli* and *S. aureus* and antifungal activity against *T.polysporum* and *C. albicans* by cup plate method.

Preparation of 2-imidazolyl mercaptoaceto hydrazone:

To an absolute ethanolic solution (100 ml) containing sodium metal (2.8 g) was added with stirring 2-mercapto imidazole (10 g) and the resulting mercaptide was slowly treated with ethyl chloroacetate (30-40 ml). The mixture was refluxed on a steam bath for about an hour and filtered hot in a dry Buckner funnel. The alcoholic solution was concentrated to about 50% of its original volume and hydrazine hydrate was added. The solution was refluxed for about 20 h on a steam bath and cooled in ice. The separated solid was filtered, washed with water and crystallized from alcohol (yield 70-72%). Further to an ethanolic solution of 2-imidazolyl mercaptoaceto hydrazide (0.1 mol), 2-hydroxy aryl ketone (0.1mol) was added and the mixture was refluxed on a steam bath for about 3 h. The solution was filtered hot from the suspended impurities, concentrated and cooled. The separated solid was filtered, washed with water and crystallized from alcohol (yield for alcohol (yield 69 -70%).

Preparation of oxovanadium (IV) complexes:

An ethanolic solution of ligand (20 ml, 0.01mol) was added to ethanolic solution of vanadyl chloride (20 ml, 0.01mol). The mixture was refluxed in the presence of sodium acetate (1gm) for about 3 hours on a water bath. The coloured complexes thus obtained was filtered, washed with hot water, ethanol and finally dried and stored over anhydrous CaCl₂ in vacuum (66-68%).

RESULTS AND DISCUSSION

Oxovanadium (IV) complexes are green colored, stable towards air and moisture at room temperature. The complexes are generally insoluble in water, ethanol and methanol but soluble in coordinating solvents like DMF and DMSO. The analytical data of the complexes (Table 1) reveal that the complexes are of 1:1 metal to ligand stoichiometry, and can be represented by the general formula [VO(L)H₂O]. The molar conductance values of the complexes at 10^{-3} M in DMF fall in the range 7.8-11.6 ohm⁻¹ cm²mol⁻¹ indicating the non-electrolytic nature of the complexes [17].

Compound/Abbraviation	MolWt/	Viald %	Element	al analys	Molar Conductance			
Compound/Abbreviation	Colour	i leiu 70	С	Н	N	V	Wolar Conductance	
$C_{13}H_{14}N_4O_2S$	204	70	50.96	4.58	22.74			
L^1H_2	504	70	(51.32)	(4.60)	(22.92)	-	-	
$[VO(C_{13}H_{12}N_4O_2S)H_2O]$	386.94	72	39.86	3.60	18.02	13.09	10.2	
$[VO(L^1)H_2O]$	Green	12	(40.21)	(3.62)	(18.09)	(13.16)	10.5	
$C_{14}H_{16}N_4O_2S$	210	60	52.58	4.93	21.84			
L^2H_2	516	09	(52.73)	(5.01)	(22.02)	-	-	
$[VO(C_{14}H_{14}N_4O_2S)H_2O]$	400.94	60	47.37	3.43	17.27	12.58	7 0	
$[VO(L^2)H_2O]$	Green	09	(47.60)	(3.47)	(17.36)	(12.49)	7.0	
$C_{18}H_{16}N_4O_2S$	266	70	58.37	4.32	19.03			
$L^{3}H_{2}$	500	70	(59.01)	(4.37)	(19.12)	-	-	
$[VO(C_{18}H_{14}N_4O_2S)H_2O]$	448.9	71	47.72	3.06	15.31	11.22	11.6	
$[VO(L^3)H_2O]$	Dark green	/1	(48.08)	(3.02)	(15.49)	(11.28)	11.0	

Table 1: Analytical and molar conductance data of the ligands and their VO(IV)complexes.

Infrared spectra

The selected IR spectra of the ligands and their oxovanadium (IV) complexes along with the tentative assignments are reported in experimental and in Table 2. By comparing the characteristic peaks in the spectra of the ligands and their complexes in order to determine the involvement of coordination sites in chelation. The ligands show bands in the regions 3205–3190, 3060–3040 and 1705–1695 cm⁻¹ assigned to v(N-H) of hydrazide [18], v(N-H) of imidazole moiety and v(C=O) respectively [18]. The bands due to v(C=O) and v(C=N) are located in the regions 1515–1502 and 1655–1645 cm⁻¹ respectively [19]. In VO(IV) complexes, the bands due to v(NH) of hydrazide and v(C=O) are also disappear due to enolization of the ligand followed by coordination of carbonyl oxygen to the metal ion via deprotonation. This is further supported by the appearance of a new band around 1610-1605 cm⁻¹ due to >C=N-N=C<. The band due to v(C=N) also suffers a negative shift by 15-22 cm⁻¹ indicating the involvement of azomethine nitrogen in the coordination [20,21]. A noticeable change in the IR spectra of the complexes is the shift of phenolic (C-O) to higher energy side by 15-20 cm⁻¹. This large shift in the complexes probably due to increase in C-O band strength by extended delocalization of the pi-system of the azine moiety. In complexes, a medium broad band due to intramolecular hydrogen bonded phenolic -OH is disappeared, which supports the breaking of the hydrogen bonding, deprotonation of phenolic oxygen atom to the metal [22]. However, the presence of a broad band around 3440 cm⁻¹ is may be due to coordinated water molecule, this result is substantiated by TGA data. The presence of a strong band in the region of 968 - 972 cm⁻¹ in the spectra of the complexes is tentatively assigned to V=O stretching mode [23], these values are in the range observed for monomeric VO^{2+} complexes [24]. The nonligand bands appearing in the regions 525-510 and 445-435 cm⁻¹ are assigned to v(V-O) and v(V-N) modes respectively [25].

Table 2: Important IR spectral bands (cm⁻¹) of the ligands and their VO(IV) complexes

Ligand/Complex	ν(N-H)	v(C=O)	v(C=N)	v(C-O) phenolic	v(V-O)	v(V-N)	v(V=O)	
0 1	hydrazine	· ,	azomethine	· · · · ·	· · /	· · /		
L^1H_2	3199	1704	1648	1502			-	
$[VO(L^1)H_2O]$	-	-	1631	1519	517	439	969	
L^2H_2	3203	1689	1652	1508	-	-	-	
$[VO(L^2)H_2O]$	-	-	1634	1523	522	452	971	
$L^{3}H_{2}$	3192	1696	1650	1514	-	-	-	
$[VO(L^3)H_2O]$	-	-	1629	1532	512	446	968	

Table 3: Loff values, ele	lectronic spectral	bands and	assigned	transitions of	the complexes
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Complexes	$\mu_{eff(BM)}$	Band maxima(cm ⁻¹)	Transitions
		13067	$2b_{2g} \rightarrow 2e_{g^*}$
$[VO(L^1)H_2O]$	1.71	17021	$2b_{2g} \rightarrow 2b_{1g}$
		23170	$2b_{2g} \rightarrow 2a_{1g}$
$[VO(L^2)H_2O]$		12454	$2b_{2g} \rightarrow 2e_{g^*}$
	1.74	16644	$2b_{2g} \rightarrow 2b_{1g}$
		22312	$2b_{2g} \rightarrow 2a_{1g}$
$[VO(L^3)H_2O]$		12844	$2b_{2g} \rightarrow 2e_{g^*}$
	1.69	16961	$2b_{2g} \rightarrow 2b_{1g}$
		22781	$2b_{2g} \rightarrow 2a_{1g}$

Magnetic susceptibility measurements and electronic absorption spectra

The μ_{eff} values and the electronic absorption bands of the complexes along their respective assignments are given in Table 3. The room temperature magnetic susceptibilities of VO(IV) complexes were found to be in the 1.67–1.78

B.M. range, which are the characteristic values for mononuclear oxovanadium complexes with $S = \frac{1}{2}$ and a d_{xy} or $d_x 2_{-y} 2$ ground state. These magnetic susceptibilities of the complexes are consistent with square-pyramidal geometry around the central metal ion [24]. The electronic spectra of VO(IV) complexes exhibit low intensities d-d bands in the ranges 12450-13070 cm⁻¹, 16600-17025 cm⁻¹ and 22300-23200 cm⁻¹ due to ${}^{2}b_{2g} \rightarrow {}^{2}e_{g}$, ${}^{2}b_{2g} \rightarrow {}^{2}h_{1g}$ and ${}^{2}b_{2g} \rightarrow {}^{2}a_{1g}$ transitions respectively, characteristic of a square pyramidal ligand field around V⁴⁺. The electronic spectra also exhibit a fourth high energy band around 28500-29250 cm⁻¹, which can be assigned as a ligand to metal charge transfer transition which is consistent with square pyramidal geometry around the VO (IV) ion [26].

ESR spectra

The esr spectrum of VO(L¹)H₂O complex at RT shows normal eight line isotropic features (Fig.2) revealing hyperfine splitting of the ^{5I}V nucleus while its frozen solution spectrum is anisotropic showing parallel and perpendicular features separately. The absence of the super hyperfine splitting in the spectrum at RT and the trend of *g*-values calculated from the frozen spectrum ($g_{II} < g_{\perp} < 2$) show that, the unpaired electron is in the b_{2g} (d_{xy}) orbital localized on the metal [27, 28] with square pyramidal geometry around the V⁴⁺ [29, 30].



Fig 2: ESR spectrum of [VO(L¹)H₂O]

Thermal studies

The thermal analysis of the $[VO(L^1)H_2O]$ complex has been studied under dynamic air atmosphere. The hydrated water molecules are associated with the complex formation and found outside the coordination sphere formed around the central metal ion. The dehydration of this type of water takes place in the temperature range 25-220^oC. On the other hand the coordinated water molecules are eliminated at high temperature than the water molecules of hydration. The water of coordination is usually eliminated [31] in the temperature range of $100-316^{\circ}C$. The organic part of the complex may decompose in one or more steps with the possibility of the formation of one or two intermediates. These intermediates may include the metal ion with a part of the schiffs base in case of 1:1 or 1:2 complexes. These intermediates may finally decompose to stable metal oxides. The thermal decomposition of $[VO(L^1)H_2O]$ occurs in two steps. The first weight loss (obsd:4.58%) in the temperature range $146-312^{\circ}C$ corresponds to loss of one mole of coordinated water molecule (cald:4.65%). The decomposition continues with the gradual weight loss and ceases at about $524^{\circ}C$ this weight loss in the temperature range of $348-524^{\circ}C$ assuming weight loss of the organic part (L¹) of the complex. The final residue with attaining a constant weight roughly corresponds to V₂O₅.

Antimicrobial activity

Antimicrobial activity was carried out using the cup-plate method [32]. The antimicrobial activity results of the screened compounds are given in the Table 4 and Figure 3. The ligands and their oxovanadium (IV) complexes have been tested for their antibacterial activity [33] against *E.coli* and *S.aureus* and antifungal activity [34] against *T.polysporum* and *C.albicans* at four different concentrations (25, 50, 75 and 100 μ g / 0.1 cm³). The standard drugs streptomycin and griseofulvin were also tested for their antibacterial and antifungal activity at the same concentrations under the conditions similar to that of the test compounds. The activity was measured by measuring the diameter of the inhibited zone in millimetre. The activity of the complexes generally increases with increasing the concentration of the compounds. The data revealed that the activity of the ligand enhanced on complexation but

less than standard used. The VO(IV) complexes show higher antibacterial activity than the ligands. On chelation the polarity of the metal ion will be reduced to a greater extent due to overlap of the ligand orbital and partial sharing of positive charges of metal ion with donor groups. Further it increases the delocalisation of pi electrons over the whole chelate ring and enhances the lipophilicity of the complex. This again enhances the penetration of complexes into lipid membrane and blocking the metal bonding sites on enzymes of micro organisms [35].



a) Antibacterial activity of ligand and its VO(IV) complexes against E.coli



b) Antibacterial activity of ligand and its VO(IV) complexes against *S.aureus*



c) Antifungal activity of ligand and its VO(IV) complexes against *T.polysporum*





Figure 3: Biological activities of hydrazone ligands and their metal complexes

 Table 4: Antimicrobial activities of the hydrazone ligands and their VO (IV) complexes

 (Zone of inhibition in mm, Concentration in ppm)

	Antibacterial activity							Antifungal activity								
		Ε.	coli			S.aureus			T. polysporum				C.albicans			
Compound	25	50	75	100	25	50	75	100	25	50	75	100	25	50	75	100
L^1H_2	07	09	11	13	08	10	14	17	10	13	16	17	09	11	14	16
L^2H_2	08	11	12	14	09	13	15	17	09	12	16	18	10	13	15	16
$L^{3}H_{2}$	10	12	13	15	08	11	14	16	10	11	13	15	11	12	14	16
$[VO(L^1)H_2O]$	12	15	17	21	11	13	16	18	15	17	21	24	17	19	23	24
$[VO(L^2)H_2O]$	14	17	19	22	12	15	17	19	17	19	24	25	16	21	24	25
$[VO(L^3)H_2O]$	13	15	18	21	14	17	19	23	16	19	23	26	17	21	23	24
Streptomycin	28	31	33	35	26	29	31	34								
Griseofulvin									30	31	33	35	29	32	33	35

CONCLUSION

The analytical data reveal that the non-electrolytic VO(IV) complexes are of 1:1 metal to ligand stoichiometry, and can be represented by the general formula [VO(L)H₂O]. IR spectra suggest that the ligand behaves in a dibasic tridentate manner in complexes with ONO donor sequence. The monomeric five coordinate square pyramidal geometry of the complex have been proposed and figure 4 shows the proposed tentative structure of the complexes. On comparing the biological activity of the ligands and there complexes with the standard bactericide and fungicide, it is observed that the activity of the complexes generally increases with increasing the concentration of the compounds.



Figure 4: Proposed tentative structure of the complex *Where* $R = CH_3$, C_2H_5 , C_6H_5

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