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Synthesis and characterization of oxo-peroxo vanadium(V)–ortho hydroxyacetophenone isonicotinoylhydrazone complexes

Arjun Kumar De[1*], Susanta Das Baishnab[1], Dibakar Deb[2]

[1]Department of Science & Humanities, Tripura Institute of Technology, Narsingarh, Tripura, India

[2]Department of Science & Humanities, Techno College of Engineering, Agartala, Tripura, India

**Corresponding author's at: [1]Department of Science & Humanities,*

Tripura Institute of Technology, Narsingarh, Tripura, India

E-mail address: arjuntit12@gmail.com(Arjun Kumar De)

ABSTRACT

The synthesis and characterization of oxo-peroxo complexes derived from ortho hydroxy acetophenone isonicotinoylhydrazone (H_2ohih) have been described in the present paper. The complexes have been isolated from reaction of V_2O_5 dissolved in 30% H_2O_2 and hydrazone in ethanol either as such or in the presence of alkali metal hydroxide or ammonium hydroxide or pyridine or substituted pyridines. The complexes have been found to have different composition: $H_2[VO_2(O_2)(Hohih)]$ (**1**), $K_2[VO_2(O_2)(Hohih)].2H_2O$ (**2**), $Na_2[VO_2(O_2)(Hohih)].2H_2O$ (**3**), $(NH_4)_2[VO_2(O_2)(Hohih)].2H_2O$ (**4**), $(PyH)_2[VO_2(O_2)(Hohih)]$ (**5**), (3-picH)$_2[VO_2(O_2)(Hohih)]$ (**6**) and (4-picH)$_2[VO_2(O_2)(Hohih)]$ (**7**). The complexes are orange, brown, reddish brown, dark brown to black brown. The complexes (**1**) and (**5**) to (**7**) are soluble in methanol and DMSO, while the complexes (**2**) to (**4**) are soluble in water, DMF and DMSO. All of the complexes are insoluble in other common organic solvents. These complexes have zero magnetic moment indicating their diamagnetic character. This suggests that vanadium is present as V(V) in each of them. The molar conductance value for the complexes (**2**) to (**4**) in water and for complexes (**5**) to (**7**) in methanol indicate their 2:1 electrolyte nature. However, the molar conductance value for the complex (**1**) has been related to its 4:1 electrolytic nature. The ^{1}H NMR spectral features as well as the significant features of the IR spectra of the complexes evidences regarding the coordination of ligands to the metal centre through phenolate oxygen atom, carbonyl oxygen atom, azomethine nitrogen atom and pyridyl nitrogen atom. All of the complexes have been proposed to have eight coordinate vanadium atoms.

Keywords: *hydrazone, isonicotinoylhydrazone, oxo-peroxo, phenolate, tetradentate*

1. INTRODUCTION

Vanadium is involved in biotic as well as abiotic systems [1]. It is an element with wide range of chemical properties. Vanadium is essentially present in the active site of metalloenzymes [2], haloperoxidases [3] and alternative nitrogenases [4]. Vanadium shows multiple and complex roles as inorganic cofactor sustaining diverse physiological activities in lower and higher organisms, including humans. Most notable among such activities are its antitumorigenicity [5], mitogenicity [6] and inhibition of key metabolic enzymes such as phosphoglucomutases and others [7]

Peroxovanadium(V) species have attracted the attention of pharmacologists with respect to their insulin mimetic functions [8,9], namely, vanadium(V) exerts insulin mimetic activities in a synergic manner with peroxide [10]. Peroxovanadium(V) species formed in vivo have been considered to be relevant to insulin mimesis [11]. It has been demonstrated that discrete peroxovanadium(V) complexes are also effective insulin mimics [12,13,14]. However, it is anticipated that the chemistry of the insulin mimetic activities of peroxovanadium(V) complexes is also very much complicated. In order to understand the complex physiological behaviour of peroxovanadium(V) complexes, it is necessary to know the properties of peroxovanadium (V) complexes in solution as well as in solid state. One of the most interesting features of peroxovanadium(V) complexes in solution should be their self-decomposition reactions. The stability of peroxovanadium (V) complexes strongly depends on the coexisting hetero ligand. It has been shown that peroxovanadium (V) complex $[VO(O_2)(pda)]^-$ (pda = N-pyridylmethyliminodiacetate) is very stable in an acidic solution while $[VO(O_2)(cmhist)]^-$ (cmhist = N-carboxymethylhistidine) slowly decomposes under the same condition, though the complexes have a similar donor atom set [14]. It has been shown that the latter complex exhibits weak but definitive insulin - mimetic activity in vitro while the former complex never does [14]. This finding suggested that the products formed in the self-decomposition reaction may be relevant to the insulin mimetic activity of the peroxovanadium (V) complexes previously studied.

Vanadium is not only the essential cofactor in enzymes, but also plays an important role in the action of hydrogen peroxide towards bromide oxidation [15]. cis-Dioxovanadium(V) in acidic solution coordinates one or two equivalents of hydrogen peroxide, forming the monoperxo, $VO(O_2)^+$ or diperoxo $VO(O_2)^{2-}$ species, both of which oxidize bromide. The oxidized bromine equivalent can then brominate an organic substrate or oxidize a second equivalent of H_2O_2 forming O_2. This VO_2^+ is a functional mimic of vanadium bromo peroxidase (V-BrPO) although it functions in acid and at much lower turnover rates [15]. Vanadium has been investigated for a long time in some marine organisms and plants [16] but its biochemistry still remains poorly understood [17,18]. Vanadium(V) has been used in homogeneous catalysis of oxygen transfer and oxidation reactions involving organic substrates and various peroxides. Peroxo and diperoxo vanadium(V) species have been used to convert sulphides to sulphoxides [19,20,21]. Other vanadium peroxo species hydroxylate benzene [22,23] and oxygenate olefins and acetylenes [24]. Vanadium complexes of alkyl hydroperoxides derived from variety of ligands epoxidize olefins [25]. The wide spectrum of activities exhibited by vanadium undoubtedly arises as a result of complex interactions of the metal ion in its predominant oxidation states +4 and +5. The stereochemical non-rigidity of V(V) and its ability to display coordination ranging from tetrahedral and octahedral to trigonal [26] and pentagonal bipyramidal [27] combines V(V)/V(IV) redox interplay. The formation of intermediates of different thermodynamic and kinetic stability, leading to catalytic conversions [25,28] is a logical consequence of these properties.

Hydrazones derived from isonicotinic acid hydrazide and their metal complexes have been shown to have biological activity specially, the enhanced antitubercular activity [29]. Further, the related hydrazones formed from pyridoxal and isonicotinic acid hydrazide (pyridoxal isonicotinoyl hydrazone, $pyrinhH_2$), ($pyrinhH_2$) has recently been shown to be an effective chelator of iron (III) and thus has potential to be used to mobilize iron from tissues that are overloaded with iron and may find applications in the treatment of thalassemia [30,31]. The potential of pyrinhH_2 has been examined and confirmed in a variety of biological and biochemical assays [32–37]. Recent studies have shown that salicylaldehyde isonicotinoyl hydrazone and 3-hydroxy isonicotinaldehyde isonicotinoylhydrazone also show appreciable activity in hepatocyte assay. Further, it has been found that aroyl hydrazones are potent inhibitor of DNA synthesis in a variety of cultured human and rodent cells and that their copper complex produces significant inhibitor of DNA synthesis and tumor growth when given to mice bearing a transplanted fibrosarcoma [37]. Copper complexes were found to be more potent than the unbound moiety. This, therefore, led to the suggestion that the metal chelates are the bioactive form of the drug. Accordingly, the present paper describes the synthesis of oxo-peroxo vanadium complexes of the title hydrazone and their characterization by various physico - chemical techniques. An effort has been made to establish their structure by IR spectroscopic study.

2. Experimental

2.1. Materials and methods

V_2O_5 of E. Merck, grade was employed. Organic chemicals such as isonicotinoylhydrazine and ortho hydroxyacetophenone were E. Merck reagents. The organic solvents viz. Ethanol, methanol, chloroform, benzene, diethyl ether, acetone, methylene chloride, acetonitrile, dimethyl sulphoxide and dimethyl formamide were purified by standard literature procedures. C, H and N were determined by Heraeus Carbo Erba 1108. Room temperature magnetic susceptibility measurements were made on a Sherwood Scientific Magnetic Susceptibility Balance. The molar conductance of the complexes at 10^{-3} M dilution in DMSO were measured on a Direct Reading Conductivity meter-303 with a dip type conductivity cell at room temperature. IR spectra were recorded on a Perkin-Elmer Spectrophotometer in the range 4000-450cm^{-1} in KBr discs. The ^{1}H NMR spectra were recorded on EM, 90 MHz spectrometer in DMSO-d_6 solution using TMS as an internal standard. The ESR spectra of the compounds in powdered form at room temperature and liquid temperature were recorded at X-band frequency on a Variance E-112X/2 band spectrometer, DPPH was used as an internal field marker.

2.2. Synthesis

2.2.1. Synthesis of ligand (H_2ohih)

To prepare hydrazone, ethanol solutions (100mL, 100mmol) of isonicotinoylhydrazine in hot conditions were allowed to interact with a slightly larger amount of ortho hydroxy acetophenone (105mL, 100 mmol) than required for a 1:1 molar ratio. The reaction mixture was refluxed for about 1h. The precipitate thus obtained on cooling the solutions to room temperature were filtered by suction, washed with ethyl alcohol and recrystallized from ethanol and dried in an electric oven maintained at ca 70^{O}C. Yield 75%. Anal. Calcd. for $C_{14}H_{13}N_3O_2$: C, 66.30; H, 5.04; N, 16.07. Found: C, 65.88; H, 5.09; N, 16.47.

2.2.2. Synthesis of complexes

2.2.2.1. Synthesis of $H_2[VO_2(O_2)$ (Hohih)] (1)

V_2O_5 (0.36g, 2 mmol) was suspended in ethanol (20 mL) and stirred for about 10 minutes to make it homogeneous. To this suspension, 7 mL 30% H_2O_2 was added accompanied by gentle stirring. This mixture was stirred for another 10 minutes. A vigorous reaction occurred. The reaction mixture was filtered to remove any undissolved material. This resulted a clear dark red solution. H_2ohih (1g, 4 mmol) was dissolved in ethanol (120 mL) by boiling. The hot H_2ohih solution was added slowly to V_2O_5 solution accompanied by slow stirring. This gave a brown-coloured solution. Stirring was continued for 15 - 20 minutes accompanied by cooling to room temperature. This precipitated a blackish brown compound after 1hr which was filtered, washed with ethanol and dried at ambient temperature over anhydrous $CaCl_2$.

2.2.2.2. Synthesis of $A_2[VO_2(O_2)$(Hohih)].$2H_2O$. [A=K(2), Na(3) and NH_4(4)]

In order to prepare $Na_2[VO_2(O_2)$(Hohih)].$2H_2O$, V_2O_5 (0.36g, 2 mmol) was suspended in ethanol (20 mL) and stirred for about 10 minutes. 10 mL 30% H_2O_2 was added to this suspension accompanied by stirring. This mixture was stirred for about 10 minutes and a vigorous reaction occurred. The reaction mixture was filtered to remove any undissolved material. H_2ohih (1g, 4 mmol) was dissolved in 120 mL ethanol by boiling. The resulting hot solution was added slowly to V_2O_5 solution accompanied by gentle stirring. Stirring was continued for 15 - 20 minutes accompanied by cooling to room temperature. This gave a brown-coloured solution. To this solution, 10% NaOH in water was added drop by drop bringing pH to 6.5. The reaction mixture was stirred for another 30 minutes. This precipitated an orange-coloured compound which was then filtered, washed with ethanol and dried over anhydrous calcium chloride.

The compounds $K_2[VO_2(O_2)$(Hohih)].$2H_2O$ and $(NH_4)_2$ $[VO_2(O_2)$(Hohih)].$2H_2O$ were also prepared by essentially the above procedure by using KOH and NH_4OH instead of NaOH.

2.2.2.3. Synthesis of $(BH)_2$ $[VO_2$ (O_2) (Hohih)], [BH = pyH (5), 3-picH (6) and 4 - picH (7)]

In order to prepare $(3\text{-picH})_2$ $[VO_2(O_2)$(Hohih)], V_2O_5 (0.36g, 2 mmol) was suspended in 20 mL ethanol and stirred for about 10 minutes. 10 mL 30% H_2O_2 was added to this suspension accompanied by gentle stirring. This mixture was stirred for about 10 minutes. Any undissolved material was removed by filtration. H_2sinh (1g, 4 mmol) was dissolved in ethanol (120 mL) by boiling. The resulting hot solution of H_2ohih was added slowly to V_2O_5 solution accompanied by gentle stirring. The solution was cooled to room temperature followed by addition of 3-picH (1.8 mL) accompanied by stirring for one hour. The colour of the solution changed to brown and then precipitated a redish brown coloured compound. The precipitate was filtered and washed with ethanol and isolated in the usual way.

The compounds $(pyH)_2[VO_2(O_2)$(Hohih)] (**5**) and $(4\text{-picH})_2$ $[VO_2(O_2)$(Hohih)] (**7**) were also prepared by essentially the above procedure by using 1.8 mL each of pyridine (pyH) and 4 - picoline (4- picH), respectively, instead of 3-picoline (3-picH).

3. Result and discussion

3.1. Synthesis, analytical data and the physical properties

The reaction of a solution of V_2O_5 and H_2O_2 in ethanol with preformed ligand (H_2ohih) yielded the peroxo complex $H_2[VO_2(O_2)(Hohih)]$ (**1**). On the other hand, when alkali metal hydroxide and ammonium hydroxide were added separately to the above reaction mixture and pH was raised to 6.5 –7.0, the complexes $A_2[VO_2(O_2)(Hohih)].2H_2O$ [A = K(**2**), Na(**3**) and NH_4(**4**)] were obtained. Further, the reaction of the reaction mixture consisting of V_2O_5, H_2O_2 and H_2ohih with pyridine and substituted pyridines instead of metal hydroxide and ammonium hydroxide, gave complexes of the composition $(BH)_2[VO_2(O_2)(Hohih)]$ [BH = pyH (**5**), 3-picH (**6**) and 4-picH(**7**)].

The reaction of dark red solution of V_2O_5 in 30% H_2O_2 in ethanol with ortho hydroxy acetophenone isonicotinoyl hydrazone results in the formation of dark brown to reddish brown to black brown to orange oxoperoxo complexes of vanadium. The complexes have been found to have the following composition:

$H_2[VO_2(O_2)$ (Hohih)] (**1**) and $A_2[VO_2(O_2)$ (Hohih)].nH_2O (n = 2, 0)

[A = K(**2**), Na (**3**), NH_4(**4**), pyH (**5**), 3-picH (**6**) and 4-picH(**7**)]

The complexes are orange, redish brown, dark brown to black brown. The complexes (**1**), (**5**) to (**7**) are soluble in methanol and DMSO, while the complexes (**2**) to (**4**) are soluble in water and DMSO. All of the complexes are insoluble in other common organic solvents.

The complexes along with their analytical data and molar conductance have been set out in the **Table 1**. These complexes are quite stable at room temperature. The complexes (**2**) to (4) lose weight when heated at 110°C but other complexes show no loss of weight at this temperature. When the vapours evolved from these complexes are allowed to pass through a trap containing anhydrous $CuSO_4$, it turns blue. But when these vapours are passed through pyrogallol solution, it does not turn brown. This suggests that these vapours contain water molecules only but no oxygen molecules. The loss of weight at 110°C corresponds to two water molecules in the complexes (**2**) to (**4**) which suggests that they contain two water molecules in their lattice structure. The absence of loss of weight at 110°C in other complexes dismisses the possibility of presence of water molecules in their lattice structure. The unaltered colour of the pyrogallol solution rules out the possibility of loss of active oxygen at 110°C. This suggests that the peroxo group in these complexes are quite stable. However, when these complexes are heated at 160°C, all of them show loss of weight corresponding to half oxygen molecule. Moreover, none of the complexes shows loss of weight due to water molecule at 160°C which rules out the possibility of presence of water molecules in their coordination sphere.

All these complexes possess zero magnetic moment, indicating their diamagnetic character. This suggests that vanadium is present as V(V) in each of them. These complexes decompose in dilute sulphuric acid with quantitative liberation of H_2O_2. The results of estimation of vanadium and peroxo group in these complexes are consistent with 1:1 stoichiometry of V : $O2^{2-}$.

3.2. Molar Conductance

The molar conductance values for all of the complexes have been set out in **Table 1**. The molar conductance values for complexes (**2**) to (**4**) have been recorded in H_2O while those of the remaining complexes in methanol because of the solubility reason. The molar conductance values falling in the region 206.8 - 220.9 ohm $^{-1}$ cm^2 mol^{-1} in the complexes (**2**) to (**4**) indicate their 2:1 electrolytic nature in aqueous medium. On the other hand, the molar conductance values for the remaining complexes (**5**) to (**7**) fall in the range 130.7 -135.9 ohm $^{-1}$ cm^2 mol^{-1} in methanol. The standard values of molar conductance for 2:1 electrolyte in methanol falls in the range 160 - 220 ohm^{-1} cm^2 mol^{-1}. However, the observed values of molar conductance in the present case are much less than lower limit reported for 2:1 electrolyte. The observed values suggest that these complexes are approaching to 2:1 electrolytic nature. The lower values than the lower limit of the molar conductance for 2:1 electrolyte may be attributed to the low ionic mobility of cationic coordination sphere, because the molar conductance values for the complexes (**2**) to (**4**) containing the same anionic coordination sphere fall in the normal range reported for 2:1 electrolyte in water. However, this comparison remains tentative because of the different media in which the molar conductivity data have been recorded in the two cases. On the other hand, the complex (**1**) has exceptionally very high value of the molar conductance 346 ohm^{-1} cm^2 mol^{-1}. This value definitely rules out the possibility of 2:1 electrolytic nature of the complex, because the reported value for such complexes falls in the range 160 - 220 olm $^{-1}$ cm^2 mol^{-1}. The molar conductance values for 3:1 electrolyte lie in the range 290 - 350 olm^{-1} cm^2 mol^{-1} in methanol while the reported value for 4:1 electrolyte is around 450 ohm^{-1} cm^2 mol^{-1}. The observed value for the complex approaches the upper limit for 3:1 electrolyte albeit slightly less. But keeping in view the 2:1 electrolytic nature of the other complexes, it may safely be attributed to be 4:1 electrolyte in methanol. The value lower than the value required for 4:1 electrolyte may be attributed to large size of the anionic coordination sphere.

Table 1: Analytical data and the physical properties of the oxoperoxo vanadium(V) complexes derived from 2-hydroxy acetophenone isonicotinoylhydrazone

Sl. No.	Complex	Colour/ Yield (%)	Elemental analyses Calculated (Found)					Molar conductance ohm^{-1}cm^{2}mol^{-1}
			V	O_2^{2-}	C	H	N	
(**1**)	$H_2[VO_2(O_2)(Hohih)]$	Black brown (63.0)	14.00 (13.75)	8.86 (8.62)	44.83 (45.28)	3.72 (3.77)	10.94 (11.32)	346.5
(**2**)	$K_2[VO_2(O_2)(Hohih)].2H_2O$	Orange (69.5)	11.00 (10.56)	6.69 (6.92)	34.34 (34.78)	2.43 (2.48)	9.00 (8.69)	206.8
(**3**)	$Na_2[VO_2(O_2)(Hohih)].2H_2O$	Orange (70.8)	11.00 (11.31)	7.32 (7.09)	37.69 (37.25)	2.70 (2.66)	9.13 (9.31)	220.9
(**4**)	$(NH_4)_2[VO_2(O_2)(Hohih)].2H_2O$	Dark brown (64.5)	11.24 (11.56)	7.50 (7.26)	38.49 (38.09)	4.57 (4.53)	16.23 (15.87)	209.8

(**5**)	$(PyH)_2[VO_2(O_2)(Hohih)]$	Orange (66.7)	9.19 (9.64)	6.41 (6.05)	54.90 (54.44)	4.50 (4.54)	13.00 (13.23)	130.7
(**6**)	$(3\text{-}picH)_2[VO_2(O_2)(Hohih)]$	Redish brown (57.2)	9.41 (9.16)	5.62 (5.74)	56.49 (56.01)	5.08 (5.03)	12.22 (12.57)	135.9
(**7**)	$(4\text{-}picH)_2[VO_2(O_2)(Hohih)]$	Redish brown (58.3)	8.92 (9.16)	5.59 (5.74)	55.60 (56.01)	4.98 (5.03)	12.82 (12.57)	132.7

3.3. Magnetic and ESR spectral studies

These complexes possess zero magnetic moment. This suggests their diamagnetic nature consistent with the presence of vanadium in these complexes in +5 oxidation state. This is also confirmed from ESR spectral studies of the complex (**1**), recorded as representative sample, which is ESR silent.

3.4. IR Spectra

The structurally significant IR bands for ligand and complexes have been set out in **Table. 2**. The IR spectrum of hydrazone and complexes (**1**), (**2**), (**4**) and (**5**) to (**7**) have been shown in the **Fig. S1-8**.

The significant feature of the IR spectra of the complexes involve absorptions due to coordinated peroxide, hydrazone in the keto form, lattice water and VO_2^{+1} group in the complexes (**2**) to (**4**) while coordinated peroxide, hydrazone in the keto form and VO_2^{+1} group in the complex (**1**) and coordinated peroxide, hydrazone in the keto form, VO_2^{+1} group and protonated pyridine, 3-picoline and 4-picoline in the complexes (**5**) to (**7**).

The IR spectrum of the hydrazone shows a medium intensity band at 3400 cm^{-1} and strong bands at 3118 cm^{-1} and 3058 cm^{-1}. The band at 3400 cm^{-1} is assigned to arise from stretching vibration of ortho hydroxy group, while the bands at 3118 and 3058 cm^{-1} are assigned to arise from stretching vibration of secondary - NH group. The position of these bands suggests the presence of strong intramolecular H-bonding between secondary amine hydrogen, phenolic -OH hydrogen and >C=O and >N-H groups. The ligand shows strong bands at 2952 cm^{-1}, 2853 cm^{-1} and 2800 cm^{-1}. These bands are attributed to arise from C - H stretching vibrations of either - CH_3 group or phenyl group or pyridyl group. The IR spectrum of the complex (**2**) shows bands at 3535, 3416 and 3197 cm^{-1} and that of the complex (**4**) shows band at 3413, 3310 and 3270 cm^{-1}. On the other hand, the sodium oxoperoxo vanadate complex (**3**) shows a single broad band centred at 3443 cm^{-1}. The bands observed at 3535 cm^{-1} and 3413 cm^{-1} in the complexes (**2**) and (**4**) are assigned to arise due to stretching vibration of - OH group of lattice water molecule. The bands at 3416, 3197 cm^{-1} in complex (**2**) and 3310, 3270 cm^{-1} in the complex (**4**) are attributed to arise due to - NH vibrations of secondary - NH group of hydrazones. In case of ammonium complex (**4**) the band at 3310 and 3270 cm^{-1} may have contribution due to stretching vibration of NH_4^+ group. The position of these bands rules out the possibility of coordination of secondary -NH nitrogen of the hydrazone to the metal centre. On the other hand, the IR spectrum of the sodium oxoperoxo vanadate (V) complex (**3**) shows a strong broad in the region 3100 - 3500 cm^{-1} centred at 3443 cm^{-1}. It appears that the band due to lattice water molecule and secondary -NH group are merged giving rise to a single broad band. The ammonium oxoperoxo vanadate(V) complex (**4**) shows a medium broad band centred at 2700 cm^{-1}. This band may arise due to involvement of NH_4^+ group in strong intramolecular H - bonding.

The complexes (**5**) to (**7**) also show a strong broad band in the region 3100 - 3550 cm^{-1}. However, this band shows weak splitting into two bands with their centres occurring in the regions 3375 - 3409 cm^{-1} and 3290 - 3344 cm^{-1}, respectively. These bands may essentially be correlated to the stretching vibrations of >NH groups arising from secondary >NH group of the hydrazone and -NH group of the protonated pyridyl nitrogen atom. Because of the complex nature of the bands in this region, we have refrained from drawing any conclusion regarding involvement of secondary - NH nitrogen atom in coordination or otherwise.

In the IR spectrum of the free hydrazone a very strong band is observed at 1686 cm^{-1} which is assigned to ν(C=O) stretching vibrations. This band shows a negative shift to lower frequency by 33 - 50 cm^{-1} and appears in the region 1636 - 1653 cm^{-1} accompanied by simultaneous decrease in intensity. This suggests the coordination of carbonyl oxygen atom to the metal centre.

The ligand shows a strong band at 1606 cm^{-1}. This band is assigned to stretching vibration of >C=N group. The band remains almost unshifted in position in the complex (**2**), while shifts to lower frequency by 6 - 16 cm^{-1} in the remaining complexes. Such a feature associated with the ν(>C=N) band in the complexes (**1**) and (**3**) to (**7**) indicates coordination of azomethine nitrogen atom to the metal centre. However, in the complex (**2**), the ν(C=N) band does not lead to the metal centre. Such a feature associated ν(C=O) band in the complex (**1**) is, in fact, due to two opposing effects:

(i) The effect of coordination on >C=N group would cause a vibrational shift to lower frequencies.

(ii) The effect of breaking intramolecular H-bonding between >C=N and -OH groups would cause a vibrational shift to higher frequencies.

If both these effects were equal, the position of ν(C=N) band would remain unchanged and the intensity would remain unaltered. The shift of ν(C=N) band to lower position by 6 - 16 cm^{-1} in the complexes (**1**) and (**3**) to (**7**) indicates that the >C=N group is involved in coordination and that the effect of coordination in lowering of the ν(C=N) band is more than that of H - bonding. However, in the complex (**2**) the effect of coordination in lowering of the ν(C= N) band is almost same as that of H - bonding i.e. non - shift of ν(C=N) band may be related to the difference of bonded species to the azomethine group i.e. >C= N - H to $>C=N\rightarrow M$.

The uncoordinated ligand shows a strong band at 1281 cm^{-1}. This band is assigned to bending vibration of phenolic C-O group. The band is shifted to higher frequency in the metal complexes by 33 - 51 cm^{-1} and appears in the region 1314 - 1332 cm^{-1}. This indicates the involvement of phenolic C-O group in bonding with metal centre [38].

In the ammonium complex (**4**) a sharp strong band is observed at 1440 cm^{-1}. Although a band of medium intensity also appears at almost at the same position in the other complexes, yet this band in the ammonium complex (**4**) is identified to arise due to - NH deformation mode of ammonium ion keeping in view of its intensity. The ν(N-H) modes arising from ammonium ion could not be identified clearly due to their overlapping of ν(N-H) mode originating from the lattice water and the ν(N-H) mode originating from the secondary NH group of coordinated hydrazones.

The IR spectra of the complexes show two strong bands in the region 908 - 950 cm^{-1} and another medium intensity band in the region 835 - 864 cm^{-1}. The two bands observed in the region 908 - 950 cm^{-1} indicate the presence of cis – VO_2^+, while the medium intensity band observed in the region 835 - 864 cm^{-1} is asigned to ν(o-o) of coordinated peroxide. The two strong band in the region 908 - 950 cm^{-1} are assigned to symmetric and asymmetric stretching vibration of cis – VO_2^+. The band due to ν(o-o) of coordinated peroxide occurs exactly in the region stipulated for μ_2-bonded peroxo group. Hence, it is inferred that the peroxo ligand in the complexes is bonded in the triangular bidentate manner [39]. The complexes show two medium intensity bands in the region 637 - 645 cm^{-1} and 539 - 591 cm^{-1}, respectively. These bands are assigned to $\nu_3(\nu_{V-O2})$ and $\nu_2(\nu_{V-O2})$ modes of coordinated peroxide group, respectively.

The IR spectra of the complexes do not show any new band in the region 1200 - 1300 cm^{-1}. This shows the absence of additional band in the complexes characteristic of $\nu(N\rightarrow O)$ which might result from oxidation of pyridyl nitrogen. This rules out the possibility of oxidation of pyridyl nitrogen atom to pyridyl N- Oxide in these complexes.

The participation of pyridyl nitrogen of hydrazone in the complexes (**1**) to (**7**) in coordination is evident from the fact that pyridyl ring breathing vibration appearing at 996 cm^{-1} as a medium intensity band in the free ligand shifts to higher frequency by 2 – 19 cm^{-1} in the complexes (**1**) to (**7**).

Table 2: Structurally Significant IR Bands of H_2ohih and its peroxovanadium complexes

Sl No	Complex/Ligand	ν(NH) + ν(OH)	ν (C=O)	ν (C=N)	Amide II + ν(C–O) Phenolic	β(C–O) Phenolic	ν (V=O)	ν (O–O)	ν_2 (V–O_P)	ν_3 (V–Op)	Pyridine breathing vibration
	H_2ohih	3400 m 3118 s 3058 s	1686 vs	1606 s	1540 s	1281 s	-	-		-	996 w
(**1**)	$H_2[VO_2(O_2)(Hohih)]$		1639 m	1593 vs	1540 m	1320 m	940 s 910 vs	837 m	-	640 m	1003 w
(**2**)	$K_2[VO_2(O_2)(Hohih)].2H_2O$	3535 s 3416 s 3197 s	1653 m	1606 vs	1533 s	1314 s	950 s 910 s	864 m	539 w	638 m	1015 wsh
(**3**)	$Na_2[VO_2(O_2)(Hohih)].2H_2O$	3443 s	1636 m	1600 s	1540 m	1321 m	943 s 917 s	849 m	532 w	638 w	1009 w
(**4**)	$(NH_4)_2[VO_2(O_2)(Hohih)].2H_2O$	3413 s 3310 s 3270 s	1639 m	1600 s	1540 m	1321 m	945 s 917 s	844 m	585 m	645 m	1009 w
(**5**)	$(pyH)_2[VO_2(O_2)(Hohih)]$	3363 s	1636 m	1590 s	1530 m	1332 m	940 s 908 vs	835 m	591 m	637 w	1001 w
(**6**)	$(3\text{-}picH)_2[VO_2(O_2)(Hohih)]$	3409 s	1636 m	1590 s	1543 m	1325 m	940 s 908 s	835 m	591 m	637 w	998 w

(**7**)	$(4\text{-picH})_2[VO_2(O_2)(Hohih)]$	3290 s	1636 m	1590 s	1530 m	1325 m	940 s 908 s	835 m	584 m	637 w	999 w

3.5. ^{1}H NMR Spectra

An effort was done to characterize the hydrazone and complexes by ^{1}H NMR spectroscopy. The hydrazone and the complex (**1**) gave resolved spectra in DMSO - d_6 whereas the remaining complexes gave featureless spectra due to their insufficient solubility in this medium. The ^{1}N HMR spectral data of the hydrazone H_2ohih and complex (**1**) have been given in **Table 3**. Their ^{1}H NMR spectra have been given in **Fig. S9-10.**

The ^{1}H NMR spectrum of H_2ohih shows signals at δ13.45 and δ11.83 ppm downfield of TMS which are assigned to δOH and δNH protons respectively [40]. Further, it shows doublet at δ 9.10 ppm whereas a multiplet in the region 6.77 - 8.23 ppm. While the signal at 9.10 ppm is assigned to arise due to protons ortho to pyridyl nitrogen, the multiplet in the region 6.77 - 8.23 ppm is assigned to have contribution from the remaining protons of the pyridyl ring and phenyl protons. An intense signal at 2.47 ppm is attributed to - CH_3 group bonded to >C=N group.

The proton NMR spectrum of the complex (**1**) does not show any signal in the region 13 - 15 ppm. This suggests the absence of signal arising from phenolic - OH protons indicating involvement of phenolate oxygen atoms in bonding to the metal centre via deprotonation.

However, the ^{1}H NMR spectrum of the complex shows a weak broad signal centred at 11.84 ppm. This signal appears almost at the same position as the signal due to secondary -NH proton in the uncoordinated hydrazone [40]. Hence, this signal is assigned to arise due to secondary - NH proton. This observation corroborates the IR evidences regarding coordination of hydrazone to the metal complexes in keto form. The broadness of -NH proton signal may be attributed to coupling between quadrupolar nitrogen nucleus and proton. The signal at 2.47 ppm in the uncoordinated hydrazone shifts down field by 0.14 ppm and appears at 2.57 ppm in the complex. This indicates coordination of azomethine nitrogen to the metal centre.

The doublet appearing at 9.10 ppm due to ortho pyridyl protons shifts upfield by 0.13 ppm and appears at 8.97 ppm in the complex. This indicates coordination through pyridyl nitrogen to the metal centre. The multiplet falling in the region δ6.77 - 8.23 ppm in the uncoordinated ligand appears in the region 6.43 - 8.33 ppm in the complex. It is to be noted that the resonance due to pyridyl and phenyl protons are broadened in the complex (**1**) as compared to that in the uncoordinated ligand. This may be due to partial decomposition and solvolysis of complex in DMSO.

Table 3: ^{1}H NMR spectral data for H_2ohih and its Vanadium(V) complexes

Sl No	Complex/Ligand	Chemical Shift (in δ)				
		Pyridyl + Phenyl	$-CH_3$	–NH	–OH	2,6 Pyridyl-H
1	H_2ohih	6.77 – 8.23(m)	2.47(s)	11.90(s, br)	13.52(s)	9.10(d)

2	$H_2[VO_2(O_2)(Hohih)]$ **(1)**	6.43 – 8.33(m)	2.57(s)	11.84(s)	-	8.97(s)

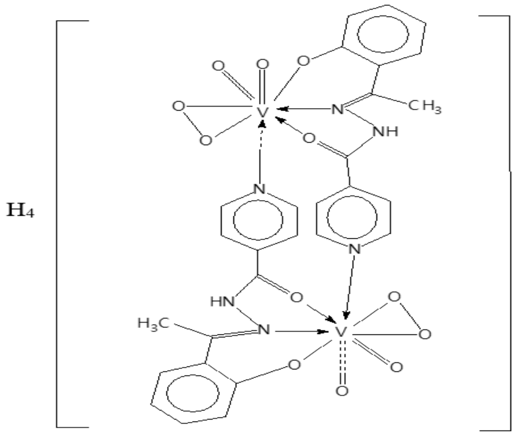

Fig. 1. Suggested structure for H_2 [$VO_2(O_2)$(Hohih)] **(1)**

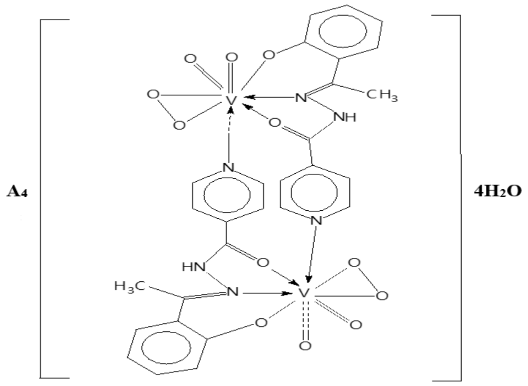

Fig. 2. Suggested structure for A_2 [$VO_2(O_2)$(Hohih)]. $2H_2O$ [A= K**(2)**, Na**(3)** and NH_4**(4)**]

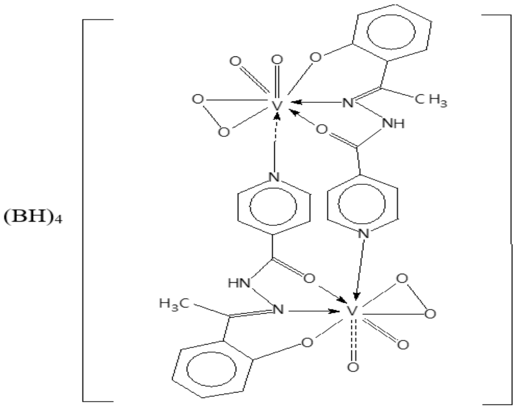

Fig. 3. Suggested structure for $(BH)_2$ [$VO_2(O_2)$(Hohih)]. [BH = pyH **(5)**, 3-picH **(6)** and pyH **(7)**]

4. Conclusion

On the basis of various physico – chemical and spectral studies, it is concluded that the ligand coordinates as a monobasic tetradentate ligand through carbonyl oxygen, azomethine nitrogen, phenolate oxygen and pyridyl nitrogen atom to the metal centre in all of the complexes. On the steric ground it can be argued that all the four coordinating atoms in the complexes cannot coordinate to the same metal ion. Hence, it is suggested that in these complexes, the carbonyl oxygen, azomethine nitrogen and phenolate oxygen atom coordinate to one metal centre, while pyridyl nitrogen atom coordinates to the other metal centre. Further, the peroxo group acts as a bidentate chelating ligand towards the metal ion. Keeping in view the fact that ortho hydroxyl acetophenone isonicotinoylhydrazone (H_2ohih) acts as a monobasic tetradentate bridging ligand, the presence of bidentate peroxo group, two oxo groups, all of the complexes may tentatively be suggested to be dimeric with eight coordinate vanadium atoms as shown in **Fig. 1-3.**

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