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# Synthesis, Spectral and Thermal Investigations of Some Oxovanadium(IV) Complexes of Hydrazones of Isonicotinic Acid Hydrazide

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A new series of 12 complexes of oxovanadium(IV) with hydrazones of isonicotinic acid hydrazide, namely N-isonicotinamido-3', 4', 5'-trimethoxybenzalaldimine (INH-TMB) and N-isonicotinamido-2'-furaldimine (INH-FUR) with the general formula  $VOX_2 \cdot nL$  ( $X = Cl, Br, I, NCS, NO_3, n = 1; X = ClO_4, n = 2; L = INH-TMB \text{ or } INH-FUR$ ) were synthesized and characterized on the basis of analytical, conductance, molecular weight, magnetic moment, infrared and electronic spectral data. The infrared data of the complexes reveal the bidentate nature of both ligands and coordination to carbonyl-oxygen and azomethinic-nitrogen atoms. The probable coordination number of the central metal is 5. Thermal stabilities of the complexes were studied through thermogravimetric analysis.

**Key Words:** Oxovanadium(IV), Hydrazones, Coordination compounds.

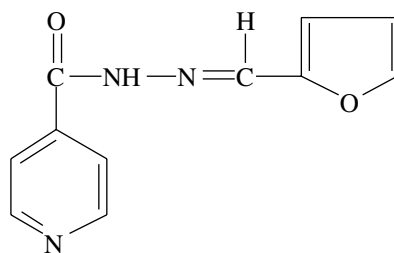
## Introduction

Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions in the periodic table. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species. The remarkable biological activity of acid hydrazides  $R-CO-NH-NH_2$ , a class of Schiff base, their corresponding aroylhydrazones,  $R-CO-NH-N=CH-R'$  and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest in the past<sup>1-4</sup>. The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors<sup>5</sup> and are useful due to their pharmacological applications<sup>6-8</sup>. Isonicotinic acid hydrazide (INH) is a drug of proven therapeutic importance and is used against a wide spectrum of

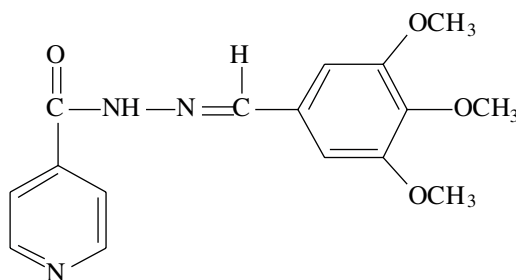
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bacterial ailments, *e.g.*, tuberculosis<sup>9</sup>. Hydrazones derived from condensation of isonicotinic acid hydrazide with pyridine aldehydes have been found to show better antitubercular activity than INH<sup>10</sup>. In the past Agarwal *et al.*<sup>11</sup> have investigated the coordinating ability of INH-derivatives with metal ions. In the present investigation we describe the synthesis and characterization of some oxovanadium(IV) complexes of N-isonicotinamido-2'-furanaldimine (INH-FUR) (1) and N-isonicotinamido-3', 4', 5'-trimethoxybenzalaldimine (INH-TMB) (2).



1. Structure of N-isonicotinamido-2'-furanaldimine (INH-FUR).



2. Structure of N-isonicotinamido-3', 4', 5'-trimethoxybenzalaldimine (INH-TMB).

## Experimental

### Materials

Oxovanadium(IV) chloride and bromide were prepared by treating vanadium pentaoxide with conc. hydrochloric or hydrobromic acid respectively in the presence of a few drops of ethanol<sup>12</sup>. Oxovanadium(IV) perchlorate was prepared by the method described by Patel<sup>13</sup>. Oxovanadium(IV) iodide in solution was prepared by treating an alcoholic solution of  $\text{VOCl}_2$  with KI in a 1:2 equimolar ratio and the reaction mixture was stirred on a magnetic stirrer for about 1 h. The precipitated KCl was filtered off and the filtrate containing  $\text{VOI}_2$  was used for complexation. Oxovanadium(IV) thiocyanate solution was prepared by treating an aqueous solution of oxovanadium(IV) perchlorate with potassium thiocyanate. The clear blue filtrate obtained after removal of the solid was concentrated by passing through dry air when syrupy green solution was obtained. Oxovanadium(IV) nitrate was prepared by treating a solution of oxovanadium(IV) chloride with silver nitrate solution.

The ligands N-isonicotinamido-3', 4', 5'-trimethoxybenzalaldimine and N-isonicotinamido-2'-furanaldimine were synthesized in the laboratory as follows. Isonicotinic acid hydrazide (1.1 mmol) was dissolved in 20 mL of 95% ethanol. To this solution, the corresponding aldehyde, *i.e.* 3,4,5-trimethoxybenzaldehyde/furfural (1 mmol), was added in 95% ethanol (20 mL). The reaction mixture was refluxed on a water bath for ca.

2 h. The partial removal of solvent on a water bath followed by cooling on ice produced a yellow crystalline product, which was suction filtered, washed with cold alcohol and dried under vacuum over  $P_4O_{10}$ .

### Synthesis of the complexes

All the complexes of oxovanadium(IV) of hydrazones were synthesized by the following general method. To a hot solution of the respective oxovanadium(IV) salt in ethanol was added a sufficient amount of 2,2'-dimethoxypropane (a dehydrating agent). This solution was mixed with a required stoichiometric amount of the respective ligand in hot methanol. The resulting mixture was refluxed for about 1 h and then concentrated to half of its volume. On cooling, a crystalline product was obtained, which was filtered, washed with organic solvents and dried in a vacuum desiccator over  $P_4O_{10}$ .

All the physico-chemical studies of the complexes were performed as reported earlier<sup>14,15</sup>.

## Results and Discussion

The reaction of  $VO^{2+}$  salts in non-aqueous solvents with INH-TMB or INH-FUR resulted in the formation of  $VOX_{2.n}L$  ( $X = Cl, Br, I, NCS, NO_3, n = 1; X = ClO_4, n = 2; L = INH-TMB$  or  $INH-FUR$ ). The analytical data of these complexes are presented in Table 1. All the complexes are fairly stable and can be stored for long periods at room temperature. The complexes are generally soluble in common organic solvents. The molar conductance values of all the complexes determined in nitrobenzene at room temperature are given in Table 1. The molar conductance values of halo, pseudohalo and nitrato complexes suggest the non-electrolytic nature of these complexes, while the perchlorato complexes behave as 1:2 electrolytes. The molecular weight of the complexes as determined cryoscopically in freezing nitrobenzene are in good agreement with the conductance data. The magnetic moments of these complexes were found to be in the 1.67-1.78 B.M. range. These magnetic moments are close to spin-only values expected for  $3d^1$  (VO)(IV) complexes with normal magnetic properties<sup>14,15</sup>.

### Infrared spectra

A study and comparison of the infrared spectra of the ligands and their  $VO^{2+}$  complexes imply that both ligands are bidentate, with the carbonyl-oxygen and azomethinic-nitrogen as the 2 coordination sites. The presence of various ring vibrations and C-H absorption makes the spectra fairly complicated for complete assignments of individual bands. The partial infrared data are presented in Table 2. The amide-I band in both INH-derivatives appears in the  $1680-1665\text{ cm}^{-1}$  region. In the infrared spectra of the complexes a considerable negative shift in  $\nu$  (C=O) is observed, indicating a decrease in the stretching force-constant of the C=O bond as a consequence of coordination through the carbonyl-oxygen atom of the free base. The amide-II band appears at the normal position in the N-H deformation frequency mode. In both INH-derivatives, the absorption in the  $1565-1560\text{ cm}^{-1}$  region was assigned to amide-II absorption. The band due to NH-stretching in free ligands occurs in the  $3350-3230\text{ cm}^{-1}$  region and remains unaffected after complexation<sup>16</sup>. This precludes the possibility of coordination through the imine-nitrogen atom. Another important band, which occurs at  $ca\ 1600\text{ cm}^{-1}$ , is attributed to  $\nu$  (C=N) (azomethine) mode<sup>17,18</sup>. In the spectra of all the complexes, this band is shifted to lower frequency and appears in the  $1570-1555\text{ cm}^{-1}$  region, indicating the involvement of the N-atom of the azomethine group in coordination<sup>17,18</sup>.

**Table 1.** Analytical, conductivity and molecular weight and magnetic data of oxovanadium(IV) complexes of INH-TMB and INH-FUR.

Complex	Colour Yield (%)	Analysis: Found (Calcd.) %			Mol. WT. Found (Calcd.)	$\Omega_M$ (Ohm cm <sup>2</sup> mol <sup>-1</sup> )	Electrolytic Nature	$\mu_{\text{eff}}$ (B.M.)
		V	N	Anion				
VOCl <sub>2</sub> (INH-TMB)	Greenish yellow (70)	11.12 (11.25)	9.18 (9.27)	15.53 (15.67)	448 (453)	2.9	Non-electrolyte	1.67
VOBr <sub>2</sub> (INH-TMB)	Deep yellow (68)	9.30 (9.40)	7.65 (7.74)	29.39 (29.52)	537 (542)	3.3	Non-electrolyte	1.78
VOI <sub>2</sub> (INH-TMB)	Dark yellow (70)	7.96 (8.01)	6.52 (6.60)	39.76 (39.93)	628 (636)	5.1	Non-electrolyte	1.71
VO(NO <sub>3</sub> ) <sub>2</sub> (INH-TMB)	Greenish yellow (72)	9.98 (10.07)	13.72 (13.83)	- -	501 (506)	4.3	Non-electrolyte	1.74
VO(NCS) <sub>2</sub> (INH-TMB)	Greenish yellow (70)	10.15 (10.24)	13.89 (14.05)	23.03 (23.29)	494 (498)	3.7	Non-electrolyte	1.77
VO(ClO <sub>4</sub> ) <sub>2</sub> ·2(INH-TMB)	Yellow (65)	5.60 (5.69)	9.28 (9.37)	21.90 (22.20)	298 (896)	53.6	1:2	1.69
VOCl <sub>2</sub> (INH-FUR)	Yellowish green (70)	14.32 (14.44)	11.77 (11.89)	19.89 (20.11)	348 (353)	3.3	Non-electrolyte	1.74
VOBr <sub>2</sub> (INH-FUR)	Yellowish green (68)	11.42 (11.53)	9.41 (9.50)	35.89 (36.19)	436 (442)	4.1	Non-electrolyte	1.77
VOI <sub>2</sub> (INH-FUR)	Dark yellow (70)	9.43 (9.51)	7.77 (7.83)	47.09 (47.38)	530 (536)	5.3	Non-electrolyte	1.67
VO(NO <sub>3</sub> ) <sub>2</sub> (INH-FUR)	Bright yellow (72)	12.43 (12.56)	17.01 (17.24)	- -	401 (406)	4.2	Non-electrolyte	1.77
VO(NCS) <sub>2</sub> (INH-FUR)	Greenish yellow (70)	12.69 (12.81)	17.23 (17.58)	28.87 (29.14)	393 (398)	3.8	Non-electrolyte	1.7
VO(ClO <sub>4</sub> ) <sub>2</sub> ·2(INH-FUR)	Yellow (65)	7.27 (7.32)	11.91 (12.06)	28.23 (28.59)	230 (696)	53.8	1:2	1.73

**Table 2.** Infrared absorption frequencies ( $\text{cm}^{-1}$ ) of VO(IV) complexes INH-TMB and INH-FUR.

Compound	$\nu$ (NH)	Amide-I	$\nu$ (C=N) azomethinic	$\nu$ (V=O)	$\nu$ (V-N)/ $\nu$ (V-O)
INH-TMB	3320m, 3230m	1665s	1600vs	—	—
VOCl <sub>2</sub> (INH-TMB)	3325m, 3230m	1640s	1565s	962m	485m, 410w
VOBr <sub>2</sub> (INH-TMB)	3325m,br	1645m	1570s	975m	495m, 400w
VOI <sub>2</sub> (INH-TMB)	3322m, 3228m	1642s,br	1572s	965m	492m, 405w
VO(NO <sub>3</sub> ) <sub>2</sub> (INH-TMB)	3320m, 3225m	1640m, 1610sh	1565s	960m	488m, 405w
VO(NCS) <sub>2</sub> (INH-TMB)	3325m, 3230m	1655m, 1620vs,br	1570s	968m	490m, 400w
VO(ClO <sub>4</sub> ) <sub>2</sub> 2(INH-TMB)	3322m, 3220m	1645m	1565s	970m	480m, 405w
INH-FUR	3350m,br	1680vs, 1650s	1595s	—	—
VOCl <sub>2</sub> (INH-FUR)	3350m,br	1660vs, 1630s	1560s	975m	492m, 415w
VOBr <sub>2</sub> (INH-FUR)	3345m, 3330m	1655vs, 1625s	1565s	960m	490m, 398w
VOI <sub>2</sub> (INH-FUR)	3350m, 3335m	1658vs, 1628s	1535s	970m	485m, 400w
VO(NO <sub>3</sub> ) <sub>2</sub> (INH-FUR)	3355m,br	1650s, 1630s	1560s	975m	480m, 398w
VO(NCS) <sub>2</sub> (INH-FUR)	3350m	1655s 1632s	1562s	970m	485m, 400w
VO(ClO <sub>4</sub> ) <sub>2</sub> 2(INH-FUR)	3355m,br	1650s, 1635s	1558s	965m	480m, 402w

The strong bands observed at 1575-1520  $\text{cm}^{-1}$  and 1080-1000  $\text{cm}^{-1}$  are tentatively assigned<sup>19,20</sup> to asymmetric and symmetric  $\nu$  (C=C) and  $\nu$  (C=N) of pyridine ring and pyridine ring breathing and deformations respectively. These bands remain practically unchanged after complexation. These observations suggest the non-involvement of pyridinic-nitrogen in complex formation. The overall infrared spectral evidence suggests that both ligands act as bidentate ligands and coordinate through amide-oxygen and azomethinic-nitrogen atoms, forming a 5-membered chelate ring. The far infrared spectral bands in the ligands are practically unchanged in these complexes. However some new bands with medium to weak intensities appear in the region 490-395  $\text{cm}^{-1}$  in the complexes under study, which are assigned to  $\nu$  (V-N)/ $\nu$  (V-O) (metal-ligand) modes<sup>14,15</sup>.

In all the complexes of VO<sup>2+</sup>, the V=O (oxovanadium) stretching frequency occurs in the range 975-960  $\text{cm}^{-1}$ . These values are in the range observed for monomeric VO<sup>2+</sup> complexes<sup>14,15</sup>.

## Anion

The thiocyanate complexes show 3 bands at ca 2060, 865 and 465  $\text{cm}^{-1}$  assignable to

$\nu$  (CN),  $\nu$  (CS) and  $\delta$  (NCS) vibrations, respectively, in the case of N-coordinated thiocyanate

groups<sup>21</sup>. In the nitrate complexes, the absence of the  $\nu_3$  band of ionic nitrate ( $D_{3h}$ ) around  $1360\text{ cm}^{-1}$  and the occurrence of 2 strong bands at  $1510$  and  $1300\text{ cm}^{-1}$  due to the split  $\nu_3$  mode in the lower symmetry indicate a coordinated nitrate group<sup>22,23</sup>. Distinction between monodentate and bidentate nitrate is usually difficult. However, by applying Lever's separation method<sup>24</sup>, a separation ( $20\text{-}25\text{ cm}^{-1}$ ) in combination bands ( $\nu_1 + \nu_4$ ) shows monodentate nitrate coordination. Other bands appeared at ca.  $1035$  ( $\nu_2$ ),  $805$  ( $\nu_6$ ) and  $735\text{ cm}^{-1}$  ( $\nu_3/\nu_5$ ) due to nitrate groups. In the perchlorato complexes the  $\nu_3$  and  $\nu_4$  bands of the perchlorato group appear at ca  $1095$  and  $630\text{ cm}^{-1}$ , respectively. This indicates that the  $T_d$  symmetry has not been disturbed in these complexes and all the perchlorato ions are present outside the coordination field<sup>13</sup>.

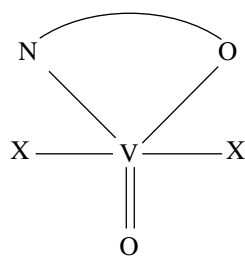
## Electronic spectra

All the oxovanadium(IV) complexes studied herein exhibited 2 bands in the  $12,000\text{-}18,000\text{ cm}^{-1}$  region. These bands were not well developed. In some complexes (Table 3) a weak, but well developed band at ca.  $23,000\text{ cm}^{-1}$  was also observed. The assignments of electronic spectral bands of  $\text{VO}^{2+}$  complexes have been a matter of controversy<sup>25,26</sup>. Ballhausen and Gray (BG)<sup>27</sup> have provided a convenient energy level scheme for these complexes. In general, oxovanadium(IV) complexes display 3 low intensity bands in the  $10,000\text{-}30,000\text{ cm}^{-1}$  range. According to the BG scheme, the first and subsequent charge transfer transitions are predicted to occur at higher energies (beyond  $30,000\text{ cm}^{-1}$ ) and often band III is not observed, but is thought to be buried beneath the low energy tail of the much more intense charge transfer band. Following the ordering of energy levels (BG scheme), the first band, which is centered at ca  $13,000\text{ cm}^{-1}$ , is assigned to an unresolved band resulting from the  $d_{xy} \rightarrow d_{xz} \rightarrow d_{yz}$  ( ${}^2B \rightarrow {}^2E$ ) transition. The second band (in region  $15,000\text{-}16,000\text{ cm}^{-1}$ ) is attributed to  $d_{xy} \rightarrow d_{x^2-y^2}$  ( ${}^2B_2 \rightarrow {}^2B_1$ ) transitions. The band at about  $23,000\text{ cm}^{-1}$  may either be assigned to the  $d_{xy} \rightarrow d_{z^2}$  ( ${}^2B_2 \rightarrow {}^2A_1$ ) transition or thought to be a low energy charge transfer band.

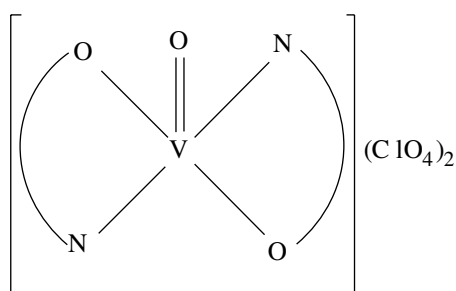
In conclusion, due to steric interactions of the large size of the ligands the coordination number 5 was been assigned to these complexes. The 5-coordinated hydrazone complexes of  $\text{VO}^{2+}$  may have the usual tetragonal pyramidal structure.

**Table 3.** Electronic spectral data ( $\text{cm}^{-1}$ ) of  $\text{VO}^{2+}$  complexes of INH-TMB and INH-FUR.

Complex	Band-I	Band-II	Band-III
	$d_{xy} \rightarrow d_{xz}, d_{yz}$	$d_{xy} \rightarrow d_{x^2-y^2}$	$d_{xy} \rightarrow d_{z^2}$
$\text{VOCl}_2(\text{INH-TMB})$	14,300	15,300	22,900
$\text{VOBr}_2(\text{INH-TMB})$	14,700	15,900	—
$\text{VOI}_2(\text{INH-TMB})$	14,500	15,800	23,100
$\text{VO}(\text{NO}_3)_2(\text{INH-TMB})$	13,900	15,700	22,700
$\text{VO}(\text{NCS})_2(\text{INH-TMB})$	14,000	16,000	—
$\text{VO}(\text{ClO}_4)_2 \cdot 2(\text{INH-TMB})$	13,300	15,250	23,000
$\text{VOCl}_2(\text{INH-FUR})$	13,900	16,050	—
$\text{VOBr}_2(\text{INH-FUR})$	13,700	15,800	23,200
$\text{VOI}_2(\text{INH-FUR})$	13,900	15,700	—
$\text{VO}(\text{NO}_3)_2(\text{INH-FUR})$	13,500	15,600	22,900
$\text{VO}(\text{NCS})_2(\text{INH-FUR})$	13,800	15,500	22,700
$\text{VO}(\text{ClO}_4)_2 \cdot 2(\text{INH-FUR})$	13,600	15,900	—

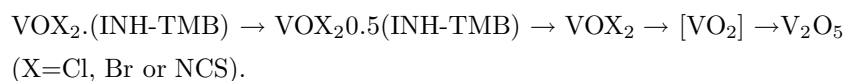


X = Cl, Br, I, NCS or NO<sub>3</sub>)



### Thermal studies

The results of thermal analysis of INH-TMB complexes of VO<sup>2+</sup> are summarized in Table 4. The TG curves of these complexes show the absence of water molecules either inside or outside the coordination sphere and the complexes degrade to the stable V<sub>2</sub>O<sub>5</sub> in air over the temperature range 210-620 °C. The TG curves show essentially 3-step processes for these complexes, as indicated by the following general equations:



**Table 4.** Thermoanalytical results of VO<sup>2+</sup> complexes of INH-TMB.

Complex	Sample Mass (mg)	Residual Mass (mg)	Moss Loss (%)				Residual (%)	
			220-325 °C		360-430 °C		~650 °C	
			Theor. <sup>a</sup>	Exp.	Theor. <sup>b</sup>	Exp.	Theor. <sup>c</sup>	Exp.
VOCl <sub>2</sub> (INH-TMB)	18.40	3.74	34.76	34.32	69.53	68.95	20.08	20.36
VOBr <sub>2</sub> (INH-TMB)	20.60	3.51	29.05	28.82	58.11	57.85	16.78	17.04
VO(NCS) <sub>2</sub> (INH-TMB)	22.80	4.21	31.62	31.29	63.25	62.87	18.27	18.49

a - Calculated for loss of a 0.5 mol of INH-TMB

b - Calculated for total loss of INH-TMB.

c. - Calculated as V<sub>2</sub>O<sub>5</sub>.



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