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Synthesis and Physico-Chemical Studies of Some Penta-Coordinated Oxovanadium(IV) Complexes of N-Isonicotinamido-2-Hydroxy-1-Naphthalidimine†

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In the present work, we have synthesized a series of six complexes of the general composition $VOX_2 \cdot n(INH\text{-}Naph)$ ($X = Cl^-$, Br^-, I^-, NO_3^- or NCS^-, $n = 1$; $X = ClO_4^-$, $n = 2$; INH-Naph = N-isonicotinamido-2-hydroxy-1-naphthalidimine). The complexes were characterized through elemental analysis, conductance, molecular weight, magnetic moment, infrared and electronic spectral data. The IR data of the complexes indicate the bidentate nature (N, O) of the ligand. The suggested coordination number is five in these complexes. T.G.A. of the complexes were also studied.

INTRODUCTION

Although Agarwal *et al.*[1–3] have recently reported Schiff bases complexes of oxovanadium(IV). But no report on oxovanadium(IV) complexes of N-isonicotinamido-2-hydroxy-1-naphthalidimine (INH-Naph) is available in literature. Thus it is worthwhile to study the ligational behaviour of N-isonicotinamido-2-hydroxy-1-naphthalidimine towards oxovanadium(IV) salts.

EXPERIMENTAL

Various oxovanadium(IV) salts were prepared as reported in literature[4]. The ligand INH-Naph was prepared in the laboratory similar to other ligands[5]. All the complexes were synthesized by the following general method. To a hot solution of the respective oxovanadium(IV) salt in ethanol a sufficient amount of 2,2′-dimethoxypropane (a dehydrating agent) was added. This solution was mixed with a stoichiometric amount of the ligand in hot ethanal. The resulting mixture was refluxed for *ca.* $\frac{1}{2}$ h and then concentrated to half of its volume. On cooling crystalline products were obtained which were filtered, washed with organic solvents and dried in vacuum desiccator over P_4O_{10}.

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IR spectra (in KBr pellets) were recorded on a Perkin-Elmer 5998 (4000–200 cm^{-1}) spectrophotometer and all other physico-chemical measurements were done as reported earlier[6] and vanadium is estimated as V_2O_5.

RESULTS AND DISCUSSION

The analytical data of these complexes are presented in Table-1. All the complexes have general composition $VOX_2 \cdot n$(INH-Naph) ($X = Cl^-, Br^-, I^-, NO_3^-$ or NCS^-, n = 1; $X = ClO_4^-$, n = 2). The complexes are generally soluble in common organic solvents. The electrical conductances measured in nitrobenzene are consistent with the non-electrolytic nature of nitrato, halo and thiocyanato complexes. While the perchlorato complex behaves as 1 : 2 electrolyte. The magnetic moments of these complexes were measured at 312 K, The values lie in the range 1.72–1.82 B.M. (Table-1). These values are well within the range observed for the VO(IV) complexes and correspond to one unpaired spin per vanaduim atom, demonstrating the tetravalency of vanadium in the complexes[7, 8].

TABLE-1
ANALYTICAL, CONDUCTIVITY, MOLECULAR WEIGHT AND MAGNETIC MOMENT DATA OF VO^{2+} COMPLEXES OF INH-Naph

Complex	Yield (%)	Analysis, Found (Calcd.)			Mol. wt Found (Calcd.)	Λ_m (ohm^{-1} cm^2 mole^{-1})	μ_{eff} (B.M.)
		V	N	Anion			
$VOCl_2 \cdot$INH·Naph	75	11.76 (11.88)	9.70 (9.79)	16.41 (16.55)	421 (429)	2.9	1.72
$VOBr_2 \cdot$INH·Naph	70	9.75 (9.84)	8.02 (8.10)	30.76 (30.88)	511 (518)	3.1	1.76
$VOI_2 \cdot$INH·Naph	70	8.25 (8.33)	6.79 (6.86)	41.32 (41.50)	607 (612)	3.3	1.82
$VO(NO_3)_2 \cdot$INH·Naph	80	10.47 (10.58)	14.39 (14.52)	— —	476 (482)	2.7	1.81
$VO(NCS)_2 \cdot$INH·Naph	72	10.64 (10.75)	14.59 (14.76)	24.33 (24.47)	468 (474)	2.9	1.74
$VO(ClO_4) \cdot 2$(INH·Naph)	65	5.95 (6.01)	9.81 (9.90)	23.29 (23.46)	278 (848)	52.9	1.78

Infrared

The comparison of the infrared spectra of the ligand and the complexes suggests that the ligand is bidentate with the carbonyl-oxygen and azomethine-nitrogen as two coordinating sites. In INH-Naph the —OH group is not taking part in the coordination. The partial IR data are presented in Table-2. The presence of various ring vibrations and C—H absorptions make the spectra fairly complicated for complete assignments of individual bands. The amide-I band in INH-naph appears at 1660 cm^{-1}. In the IR spectra of the complexes a considerable negative shift in ν(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[5]. The amide-II band appears at the normal position in the NH-deformation frequency mode. In INH-Naph, the absorption at 1560 cm^{-1} has been assigned to amide-II absorption. The band due to NH stretching in free ligand occurs[10] at 3290 and 3225 cm^{-1} and remains unaffected after complexation. This precludes the possibility of coordination through imine nitrogen atom. Another important band which occurs at 1590 cm^{-1} is attributed to ν(C═N) (azomethine) mode. In the spectra of all the complexes this band is shifted to lower frequency and appears in the 1570–1545 cm^{-1} region indicating the involvement of the N-atom of the azomethine group in coordination[9]. The strong bands observed at 1570–1522 cm^{-1} and 1080–1000 cm^{-1} are tentatively assigned[11, 12] to antisymmetric and symmetric ν(C═C) and ν(C═N) of pyridine ring and 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 band at 3500–3400 cm^{-1} is attributed to ν(OH). In all the complexes, the —OH group frequency appears at the same region as in the free ligand clearly indicating that the —OH group is not taking part in the coordination. The overall IR-spectral evidence suggests that the ligand acts as bidentate ligand and coordinate through amide-oxygen and azomethine-nitrogen atoms forming a five membered chelate ring. In far IR region the bands in 445–375 cm^{-1} are assigned to ν(V—O)/ν(V—N) modes[1-3].

TABLE-2

KEY IR BANDS (cm^{-1}) OF VO^{2+} COMPLEXES OF INH-Naph

Compounds	ν(NH) (asym. & sym.)	Amide-I	ν(C═N)	ν(V═O)	ν(V—O) ν(V—N)	ν(V—Cl)
INH-Naph	3290 m 3225 m	1660 vs	1590 s	—	—	—
$VOCl_2 \cdot (INH\text{-}Naph)$	3292 m 3216 s	1635 s 1610 m	1552 m	970 m	445 w 378 w	272 w
$VOBr_2(INH\text{-}Naph)$	3290 m 3230 s	1636 s	1570 s	972 w	430 m 380 w	—
$VOI_2(INH\text{-}Naph)$	3292 m 3225 m	1635 s	1567 s	965 m	435 m 375 w	—
$VO(NO_3)_2(INH\text{-}Naph)$	3292 m 3240 m	1630 s 1605 s	1545 s	960 m	425 m 382 w	—
$VO(NCS)_2(INH\text{-}Naph)$	3290 m 3230 m	1638 m 1608 s	1560 s	972 m	430 m 385 w	—
$VO(ClO_4)_2 \cdot 2(INH\text{-}Naph)$	3292 m 3225 m	1632 s	1555 s	970 m	425 m 375 w	—

In all the complexes of VO^{2+} under discussion, the V═O stretching frequency occurs in the 972–960 cm^{-1} region. These values are in the range observed for monomeric VO^{2+} complexes[1-3].

In $VO(NO_3)_2 \cdot (INH \cdot Naph)$, the absence of ν_3 band of ionic nitrate D_{3h} around 1360 cm^{-1} and the occurrence of two strong bands at 1520 and 1305 cm^{-1} due to the split ν_3 mode in the lower symmetry indicate a coordinated nitrato group[13, 14]. By applying Lever's separation method[15], a separation of 25 cm^{-1} in combination bands ($\nu_1 + \nu_4$) concludes the monodentate nitrate coordination. Other bands appeared at 1030 (ν_2), 805 (ν_6) and 725 cm^{-1} (ν_3/ν_5) due to nitrate groups. In the perchlorate complex, the ν_3 and ν_4 bands of the perchlorato group appear at 1080 and 622 cm^{-1} respectively. This indicates that the T_d symmetry has not been disturbed in the complexes and all the perchlorate ions are present outside the coordination field[1–3]. The thiocyanate complexes show three bands at 2045, 855 and 460 cm^{-1} assignable to ν(CN), ν(CS) and δ(NCS) vibrations respectively, in the case of N-coordinated thiocyanate groups[16].

TABLE-3
ELECTRONIC SPECTRAL BANDS (cm^{-1}) OF VO^{2+} COMPLEXES OF INH·Naph

Complex	$d_{xy} \rightarrow d_{xz}, d_{yz}$	$d_{xy} \rightarrow d_{x^2-y^2}$	$d_{xy} \rightarrow d_{z^2}$
$VOCl_2 \cdot (INH \cdot Naph)$	14700	17500	23000
$VOBr_2 \cdot (INH \cdot Naph)$	14800	16000	—
$VOI_2 \cdot (INH \cdot Naph)$	13900	17100	22900
$VO(NO_3)_2 \cdot (INH \cdot Naph)$	13300	16500	22600
$VO(NCS)_2 \cdot (INH \cdot Naph)$	13700	16800	—
$VO(ClO_4)_2 \cdot 2(INH \cdot Naph)$	14100	17300	—

Electronic spectra

The VO^{2+} complexes show two bands in 13300–17500 cm^{-1} region. These bands are not well developed. In some complexes, a weak but well developed band in 22600–23000 cm^{-1} region has also been observed (Table-3). According to Ballhausen and Gray scheme[17], the first and subsequent charge transfer transitions are predicted to occur at higher energies and often band-III is not observed but is believed 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 (13300–14800 cm^{-1}) is assigned to an unresolved band resulting from the $d_{xy} \rightarrow d_{xz} \rightarrow d_{yz}$ ($^2B_2 \rightarrow {}^2E$) transition. The second band (in the region of 16000–17500 cm^{-1}) is attributed to $d_{xy} \rightarrow d_{x^2-y^2}$ ($^2B_2 \rightarrow {}^2B_1$) transitions. The band at *ca.* 23000 cm^{-1} may either be assigned to the $d_{xy} \rightarrow d_{z^2}$ ($^2B_2 \rightarrow {}^2A_1$) transition or believed to be lower energy transfer band.

Thermal studies

The t.g. curves of these complexes show the absence of water molecule either in or out of the coordination sphere and the complexes degrade to the stable V_2O_5 in air over the temperature range 240–630°C. The t.g. curves show essentially three steps process for these complexes as indicated by the following general equations:

$$VOX_2\cdot(INH\cdot Naph) \rightarrow VOX_2\cdot 0.5\cdot(INH\cdot Naph) \rightarrow VOX_2 \rightarrow [VO_2] \rightarrow V_2O_5.$$

($X = Cl^-, Br^-, NO_3^-$ or NCS^-)

$$[VO(INH\cdot Naph)_2](ClO_4)_2 \rightarrow [VO(INH\cdot Naph)](ClO_4)_2 \rightarrow VO(ClO_4)_2 \rightarrow [VO_2] \rightarrow V_2O_5.$$

In conclusion, due to steric interactions of the larger size of the ligands the lower coordination number five has been assigned to these complexes. The five coordinated VO^{2+} complexes may have the usual tetragonal pyramidal structure.

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