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CHARACTERISATION AND THERMOGRAVIMETRIC ANALYSIS OF MIXED-LIGAND COMPLEXES OF OXOVANADIUM(IV) WITH NICOTINIC ACID AND 8-HYDROXYQUINOLINE, PIPERAZINE, α,α'-DIPYRIDYL AND β-PICOLINE

V. RAJENDRA PRASAD and M.C. SAXENA

Department of Chemistry, Dr. Hari Singh Gour Vishwavidyalaya, Sagar (M.P.) 470 003 (India)

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ABSTRACT

Four hexacoordinated oxovanadium(IV) mixed-ligand complexes, $[(VONic)HQ \cdot H_2O]$, $[(VO(Nic)_2)_2pip]$, $[VO(Nic)_2dipy]$, and $[VO(Nic)_2pic \cdot H_2O]$ (Nic = nicotinate, HQ = 8-hydroxyquinolinate, pip = piperazine, dipy = α,α'-dipyridyl, pic = β-picoline), have been prepared and characterised by means of elemental analysis, magnetic measurement, electronic, infrared and ESR spectral studies, and thermogravimetry (TG). The electronic spectra are satisfactorily explained with the help of the Ballhausen–Gray scheme. Hexacoordinated mixed-ligand complexes can be converted into the pentacoordinated complex $[VO(Nic)_2]$, which is stable over the temperature range ~ 250–350°C as revealed by TG. Thermal decomposition of all four complexes leads to the formation of V_2O_5 at ~ 560°C as final product.

INTRODUCTION

Unambiguous assignment of electronic spectral bands of the complexes of oxovanadium(IV) (vanadyl ion, VO^{2+}) and their theoretical explanation has been attempted by some earlier workers. An interesting aspect of these studies is the possibility of formation of penta- as well as hexa-coordinated complexes of the VO^{2+} ion. The complex $VO(Nic)_2 \cdot H_2O$ (where Nic = nicotinic acid) has been reported [1]. The present work describes the preparation, characterisation, and thermal behaviour of the mixed-ligand complexes of oxovanadium(IV) with nicotinic acid (Nic) as primary ligand and 8-hydroxyquinoline (HQ), piperazine (pip), α,α'-dipyridyl (dipy), and β-picoline (pic) as secondary ligands.

EXPERIMENTAL

Vanadyl sulphate pentahydrate (Merck) and nicotinic acid (Thomas Tyrer) were used for preparing complexes. Other chemicals used were of BDH

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TABLE 1

Analytical data and magnetic moments of mixed-ligand oxovanadium(IV)–Nic complexes with HQ, pip, dipy and pic

Secondary ligand	Formula of the complex [a]	Analytical data (%)								Solubility	Magnetic moment, μ_{eff} (BM)
		C		H		N		V			
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.		
HQ	$[VO(C_6H_4NO_2)(C_9H_6NO)\cdot H_2O]$	51.12	51.30	3.50	3.44	7.89	7.98	14.30	14.50	soluble in THF [b]	1.84
pip	$[(VO(C_6H_4NO_2)_2(C_4H_{10}N_2)]$	47.12	47.47	3.67	3.70	12.02	11.92	14.30	14.38	insoluble	1.62
dipy	$[VO(C_6H_4NO_2)(C_{10}H_8N_2)]$	56.60	56.57	3.45	3.45	11.80	11.99	10.85	10.91	insoluble	1.85
pic	$[VO(C_6H_4NO_2)(C_5H_4NCH_3)\cdot H_2O)]$	51.25	51.20	4.05	4.06	9.63	9.95	12.00	12.07	insoluble	1.82

[a] Nic (nicotinate) = $C_6H_4NO_2$, HQ (8-hydroxy quinolinate) = C_9H_6NO, pip = $C_4H_{10}N$, dipy = $C_{10}H_8N_2$, pic = $C_5H_4NCH_3$.
[b] THF = tetrahydrofuran.

AnalaR or Merck GR grade. Elemental analysis was done in the microanalytical section of the Indian Institute of Technology, Kanpur. Infrared spectra were recorded in KBr pellets on a Perkin-Elmer (model 521) infrared diffraction grating spectrophotometer in the range 4000–250 cm^{-1}. ESR spectra were recorded at 25°C on an X-band Varian (V-4502) EPR spectrometer provided with 100 kHz field modulation; DPPH (diphenyl picryl hydrazyl radical) was used as a field marker. Magnetic susceptibility measurements were made using a Gouy balance at 25°C and mercury tetrathiocyanato cobalt(II) as calibrant. Electronic spectra were recorded in Nujol mull using a Cary (model 14) recording spectrophotometer. TG was performed on a Cahn RG electrobalance (model 2050) at a recorder chart speed of 200 mm h^{-1} using a platinum crucible at a heating rate of 6°C min^{-1}. The TG experiments were carried out in an atmosphere of static air.

Preparation of complexes

Vanadyl sulphate pentahydrate (0.5 g), dissolved in 5 ml of distilled water, was added to a solution of nicotinic acid (0.5 g Nic in 25 ml hot rectified spirit). The pH of the mixed solution was adjusted to ~ 3.5. HQ (1 mol) in rectified spirit was then added and the contents were concentrated over a steam bath. The concentrated solution was kept overnight at ~ 0°C. A brown precipitate was obtained, which was filtered, washed and stored in a desiccator. The mixed-ligand complexes with pip, dipy and pic were obtained as above; the contents had to be refluxed on a steam bath for 1–2 h for these complexes.

The complexes were analysed for their composition. Characterisation was done with the help of electronic, IR and ESR spectral data, magnetic susceptibility measurements and TG. The solubility determinations, chemical analyses and magnetic measurements are reported in Table 1.

RESULTS AND DISCUSSION

The analytical data suggest that the mixed-ligand complexes should be hexa-coordinated, and have the formulae shown in Table 1. The Bohr magneton values correspond to a paramagnetism equivalent to one unpaired electron in a ligand field. The unusually low BM value for the piperazine complex is suggestive of the fact that the vanadium atom in this complex is in a different environment than that in the other three complexes.

Electronic spectra

The assignment of electronic spectral bands is presented in Table 2. The energy level order proposed for the penta-aquo vanadyl ion in accordance

TABLE 2

Electronic spectral data for the mixed-ligand oxovanadium(IV)–Nic complexes with HQ, pip, dipy and pic

Complex	Observed band frequency (cm^{-1})	Band assignment ($d-d$ transitions)
[(VONic)HQ·H_2O]	14510	$d_{xy} \rightarrow d_{xz}, d_{yz}$
	16960	$d_{xy} \rightarrow d_{x^2-y^2}$
[(VO(Nic)$_2$)$_2$pip]	14000	$d_{xy} \rightarrow d_{xz}, d_{yz}$
	16310	$d_{xy} \rightarrow d_{x^2-y^2}$
	23620	$d_{xy} \rightarrow d_{z^2}$
[VO(Nic)$_2$dipy]	14490	$d_{xy} \rightarrow d_{xz}, d_{yz}$
	16820	$d_{xy} \rightarrow d_{x^2-y^2}$
[VO(Nic)$_2$pic·H_2O]	13510	$d_{xy} \rightarrow d_{xz}, d_{yz}$
	15400	$d_{xy} \rightarrow d_{x^2-y^2}$
	20200	$d_{xy} \rightarrow d_{z^2}$
	24390	charge transfer

with the Ballhausen–Gray scheme [2,3] is, b_2 $(d_{xy}) < e(d_{xz}, d_{yz}) < b_1(d_{x^2-y^2}) < a_1$ (d_{z^2}). The three bands observed in the present series of vanadyl complexes may originate from the electronic transitions $^2B_2 \rightarrow {}^2E$ (band I) due to absorption allowed by the electric dipole selection rule, $^2B_2 \rightarrow {}^2B_1$ (band II), which is vibrationally allowed, and $^2B_2 \rightarrow {}^2A_1$ (band III), attributed to the dipole-forbidden transition. Although an alternative scheme has been suggested by Selbin [4], the bands in the present series of mixed-ligand complexes are satisfactorily explained on the basis of the Ballhausen–Gray scheme. The third band is not observed for the HQ and dipy complexes; perhaps it is hidden by the low energy tail of the intense charge-transfer band occurring in the UV region. An additional band for the pic complex may well be of charge-transfer origin.

Infrared spectra

The assignment of IR spectral bands requires a detailed discussion. The primary ligand Nic exists as a dimer [5]. The chief bands in its spectrum are: 2500 cm^{-1} due to stretching vibrations of the OH bond in the dimer, 1720 cm^{-1} (C=O stretch.), 1600 cm^{-1} due to pyridine ring vibrations, and 1420, 1325, 1302 and 958 cm^{-1} which are characteristic of the dimer. On complexation the band at 2500 cm^{-1} disappears and those at 1720 and 1302 cm^{-1} are shifted showing the existence of ionised carboxylate. It has been reported [6] that bidentate carboxylates have values of $\nu(OCO)_{asym.}$ and $\nu(OCO)_{sym.}$ close to those found in the corresponding free ions, whereas unidentate carboxylate has $\nu(OCO)_{asym.}$ at substantially higher frequencies. It has been noticed in the first two complexes (with HQ and pip) that the

$\nu(OCO)_{asym.}$ vibrations lie close to those found in the free ligand, their positions being 1620 and 1615 cm^{-1}, respectively. In the other two complexes (with dipy and pic) the corresponding values are substantially higher, 1650 and 1660 cm^{-1}, respectively. It may, therefore, be concluded that Nic acts as a monovalent bidentate ligand in the complexes with HQ and pip and as a monovalent unidentate ligand with dipy and pic. These conclusions are adequately supported by the work of Alyavin and Teplyakova [7].

The separately recorded spectra of the secondary ligands have been compared with the spectra of corresponding mixed-ligand complexes. The spectrum of HQ has been compared with its previously recorded IR spectrum [8]. The main IR bands in the HQ mixed-ligand complex are given below (cm^{-1}).

400(w), 460(m), 510(m), 540(w), 580(s), 620(w), 640(s), 720(m), 755(m), 780(m), 810(m), 965(vs), 1050(m), 1065(m), 1098(w), 1105(w), 1110(w), 1150(m), 1180(m), 1280(m), 1330(s), 1380(s), 1430(s), 1475(s), 1510(s), 1565(s), 1600(s), 1620(s,br), 1740(w), 3500(br).

The bands characteristic of coordinated HQ [9] have been obtained at 1565, 1510, 1475, 1430, 1380, 1280, 1150, 1105, 1098 and 780 cm^{-1}. The band at 965 cm^{-1} is assigned to $\nu(V{=}O)$ and that at 460 cm^{-1} to V–O vibrations [10]. The C–O stretching vibrations appear at 1105 cm^{-1}. The bands in the region 1600–1400 cm^{-1} may be attributed to C=N and C=C stretching vibration frequencies [11]. The ring vibrations appear at 1180 and 1150 cm^{-1} and the C–H out-of-plane deformation vibrations at 720 and 780 cm^{-1}.

The chief IR spectral bands for the pip mixed-ligand complex are as follows (cm^{-1}).

410(m), 450(w), 480(m), 490(w), 510(w), 530(s), 550(w), 565(w), 595(w), 620(s), 635, 640(s), 660(w), 710(w), 745(s), 780(s), 810(s), 820(m), 860(w), 935, 945(s), 1030(w), 1055(w), 1105, 1110(s), 1140(m), 1210(m), 1240(w), 1260(m), 1280(s), 1320(s), 1355(m), 1380(s), 1440(m), 1460(s), 1510(s), 1520(m), 1565(m), 1600(w), 1615(s), 1670(m), 2090(s,br), 2900(w), 3250(w).

The occurrence of the $\nu(OCO)_{asym.}$ stretching frequency at a lower value of 1615 cm^{-1} is indicative of the presence of chelated carboxylate in the mixed-ligand complex. The ring vibrations of the heterocyclic ring remain unaffected in the complex suggesting that the ring nitrogen of Nic is not participating in coordination. The bands at 3328 and 2941 cm^{-1} which arise due to $\nu(N{-}H)$ and $\nu(C{-}H)$ [12], respectively, in the pip spectrum are shifted to lower values of 3250 and 2900 cm^{-1} in the mixed-ligand complex. The $-CH_2$ scissoring vibrations of piperazine appear at 1460 and 1440 cm^{-1} for the complex as against 1479 and 1449 cm^{-1} for pip. The $\delta(N{-}H)$ deformation vibration is located at 1140 cm^{-1} for the complex and at 1127

cm^{-1} for pip. A strong band at 1080 cm^{-1} in the ligand is shifted to higher frequency region in the complex splitting into two strong bands at 1105 and 1110 cm^{-1}. The IR spectrum of the present Nic–pip complex resembles those of pip bridged complexes reported by Hendra and Powell [12]. The ν(V=O) stretching frequency is found to split into two and is located at 935 and 945 cm^{-1} as a strong band. This lowering of ν(V=O) indicates that the vanadium atom in the Nic–pip complex is present in a different environment as compared to other complexes of the present series. Okawa et al. have reported a lower value of ν(V=O) for some binuclear oxovanadium(IV) complexes [13]. Splitting of the ν(V=O) band may well be due to splitting of the unit cell group or a crystal packing effect which causes the vanadium atoms in a dimer to be non-equivalent [14]. The above observations lead to an inference that the present Nic–pip complex may be a bridged complex.

The main IR bands observed for the Nic–dipy complex are reported below (cm^{-1}).

415(m), 475(m), 515(w), 590(m), 640(w), 680(m), 730(w), 750(m), 790(m), 810(m), 820(s), 895(m), 980(s), 1020(w), 1080(m), 1110(m), 1160(m), 1220(m), 1260(m), 1330(s), 1390(w), 1425(m), 1455(s), 1475(m), 1500(w), 1550(m), 1580(m), 1600(s), 1650(s,br), 1710(w), 2300(w), 3100(w).

The ring vibrations of Nic remain unaffected in the mixed-ligand complex indicating that its ring nitrogen is not participating in coordination. The $\nu(OCO)_{asym.}$ and $\nu(OCO)_{sym.}$ vibrations are located at 1650 and 1425 cm^{-1}, respectively, indicating that the carboxylate group is unidentate in this complex [6]. If dipy is regarded as an *ortho*-substituted pyridine, it would be reasonable to expect the pyridine ring breathing, *ortho*-substituted pyridine vibration, and C–H out-of-plane deformation vibrations to appear in the region 1200–700 cm^{-1}.

The peak at 990 cm^{-1} is assigned to pyridine breathing mode; this shifts to 1020 cm^{-1} on chelation in the Nic–dipy complex [15]. The bands at 1080, 1220 and 1260 cm^{-1} may be a consequence of *ortho*-substituted pyridine vibrations [15]. The out-of-plane bending of the ring hydrogens of dipy are located at 750 and 730 cm^{-1} [13,16]. The bands at 1580 and 1475 cm^{-1} are characteristic of chelated dipy [17]. The C–H stretching vibrations are observed at 3100 cm^{-1}. The ν(V=O) and V–O vibrations appear at 980 and 475 cm^{-1}, respectively.

The important bands appearing in the IR spectrum of the Nic–pic mixed-ligand complex are as follows (cm^{-1}).

405(m), 410(m), 470(m), 500(w), 520(m), 560(m), 620(m), 640(w), 660(w), 720(s), 740(w), 790(s), 820(m), 840(s), 860(w), 980(s), 1040(w), 1060(w), 1100(s), 1120(m), 1180(m), 1240(m), 1280(s), 1320(m), 1360(w), 1390(w), 1420(s), 1460(s), 1470(s), 1505(w), 1590(m), 1600(s), 1660(br), 1730(w), 1760(w), 1800(w), 1830(w), 3100 (m), 3500 (br).

The spectrum of the complex contains characteristic absorption bands due to both ligands. β-Picoline shows very strong absorption at 708 and 788 cm^{-1} due to its γ(C–H) and ϕ(C–C) vibrations. The region 789–810 cm^{-1} contains an absorption band characteristic of 3-monosubstituted pyridine compounds along with an out-of-plane deformation vibration of the ring hydrogen appearing at 712 cm^{-1} [15], but these vibrations due to Nic also occur in the same region. In the Nic–pic complex strong bands at 720 and 790 cm^{-1} have been observed for the out-of-plane deformation vibrations. The bands at 1590 and 1615 cm^{-1} may be assigned to the interaction between C=C and C=N vibrations of the pyridine ring [11,14]. These, together with a band at 1505 cm^{-1}, show the presence of coordinated pic. The $-CH_3$ symmetric and antisymmetric deformation vibrations are located at 1390 and 1460 cm^{-1}. The band at $\sim$ 3100 cm^{-1} is due to the $-CH_3$ group of pic, and a broad one at $\sim$ 3500 cm^{-1} may be regarded as indicative of the presence of a coordinated water molecule, which is supported by the TG studies. The ν(V=O) and V–O vibrations appear at 980 and 470 cm^{-1}, respectively.

ESR spectra

The ESR spectrum of the (VO^{2+}–Nic–HQ) complex was recorded in THF. Spectra of the (VO^{2+}–Nic–pip), (VO^{2+}–Nic–dipy) and (VO^{2+}–Nic–pic) complexes were recorded using their polycrystalline samples. Values of the isotropic ESR parameter, g_0 (g(av)), obtained for the four complexes are 1.970, 1.965, 1.965 and 1.962, respectively. These values agree well with those of other oxovanadium(IV) complexes [18]. The spectra are shown in Fig. 1. The spectrum of the (VO^{2+}–Nic–HQ) complex gives hyperfine splitting due to interaction of the unpaired electron with the ^{51}V nucleus and the characteristic eight lines are observed. The isotropic hyperfine splitting constant is $A_0 = 101.5G$, which is less than the value reported for $VO(acac)_2$ [19]. The lower value of A_0 is associated with greater delocalisation of the electron on the metal because of the decreased electrophilic nature of the ligands and a consequent increased covalency of the (V–O) chelate bonds. The lowering of the g(av) values as compared to the free-electron value, g_e (2.002), is due to the spin–orbit interaction of the ground state d_{xy} level with low lying excited states. The absence of super-hyperfine splitting in the ESR spectrum of the HQ mixed-ligand complex (Fig. 1) may be due to large nuclear moment and spin ($I = 7/2$) causing large line width (which tends to obscure the super-hyperfine splitting). Resolution of the ^{51}V hyperfine splitting in the spectrum has not been observed for undiluted polycrystalline samples probably due to lack of magnetic dilution. A broad band has been observed for the powder spectrum of the complexes, which may be tentatively assigned to the transition $\Delta M_S = 1$.

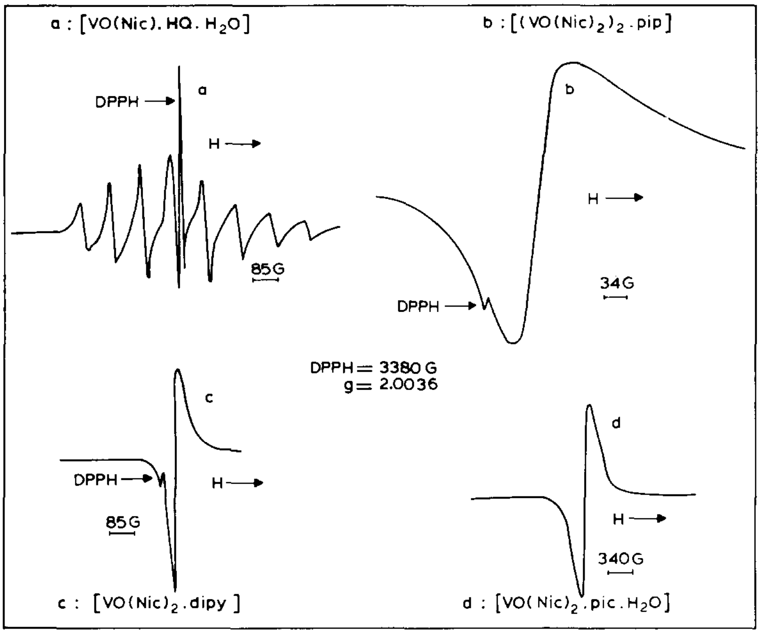

Fig. 1. ESR spectra of the oxovanadium(IV)–nicotinato complexes with (a) 8-hydroxyquinoline, (b) piperazine, (c) α,α'-dipyridyl and (d) β-picoline. (Spectrum (a) recorded in THF, spectra (b), (c) and (d) using polycrystalline samples; field modulation, 100 kHz; field marker, DPPH.)

Thermogravimetric analysis (TG)

The thermograms of the mixed-ligand VO^{2+}–Nic complexes with HQ and pip are given in Fig. 2 and those with dipy and pic in Fig. 3. The calculated and observed weight losses are presented in Table 3. The first complex (with HQ) shows a two-step thermal decomposition. The first step corresponds to the loss of one coordinated water molecule in the temperature range 160–215°C, beyond which there is a plateau up to ~ 300°C. The second decomposition step starts at this temperature and continues up to ~ 570°C, where the removal of organic matter is complete. A constant weight due to V_2O_5 is indicated after this temperature. Both the ligands decompose in overlapping steps resulting in a single-step weight loss after 300°C. The second complex (with pip) undergoes decomposition recording a weight loss in the TG curve from 180 up to 280°C corresponding to the removal of one molecule of pip from the complex. A plateau at 280–350°C indicates thermal stability of $[VO(Nic)_2]$ in this range. The second step shows a sharp weight loss at 350–360°C due to the destruction of organic matter and finally, above ~ 560°C, the residual substance (V_2O_5) leads to a constant weight.

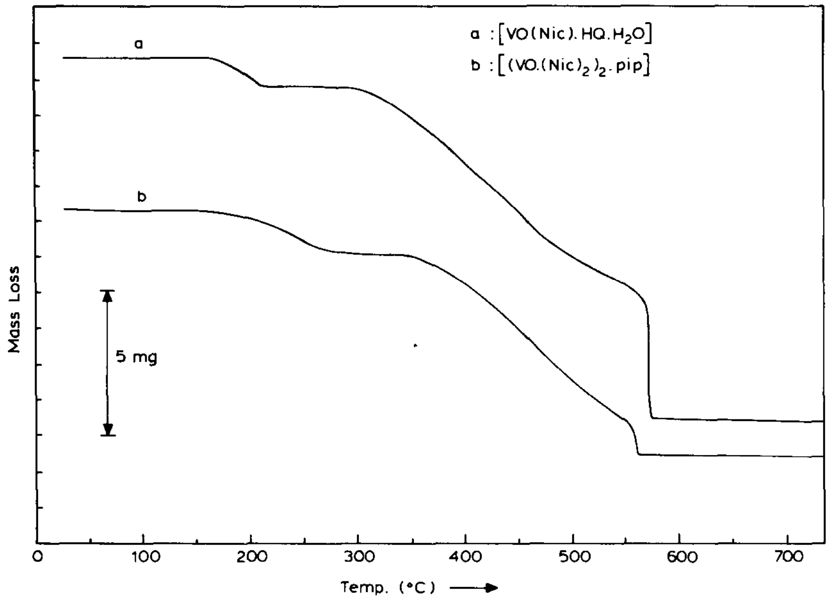

Fig. 2. TG curves of oxovanadium(IV)–nicotinato complexes with (a) 8-hydroxyquinoline and (b) piperazine. (Recorder chart speed, 200 mm h^{-1}; heating rate, 6°C min^{-1}; atmosphere, static air.)

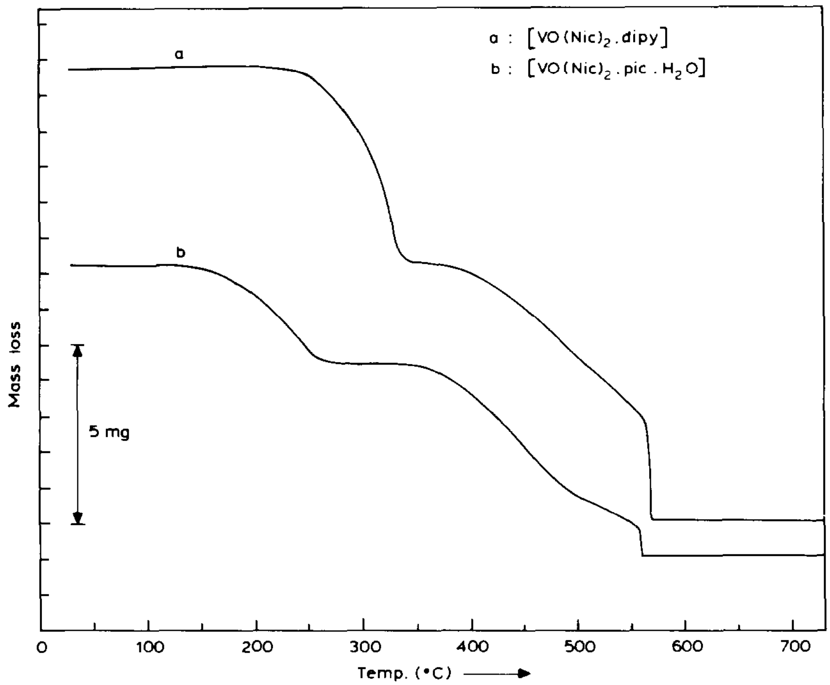

Fig. 3. TG curves of oxovanadium(IV)–nicotinato complexes with (a) α,α'-dipyridyl and (b) β-picoline. (Recorder chart speed, 200 mm h^{-1}; heating rate, 6°C min^{-1}; atmosphere, static air.)

TABLE 3

TG data on the mixed-ligand oxovanadium(IV)–Nic complexes with HQ, pip, dipy and pic (temperature ranges in which decomposition occurs are given in parentheses)

Complex (formula and name)	Initial weight (mg)	Weight loss due to H_2O (mg)		Weight loss due to pip/dipy/ (pic + H_2O) (mg)		Weight loss up to V_2O_5 (mg)	
		Calc.	Found	Calc.	Found	Calc.	Found
[(VONic)HQ·H_2O]-oxo-nicotinato(8-quinolinolato)aquo-vanadium(IV)	17.00	0.87	0.92 (160–215°C)	–	–	12.56	12.45 (300–570°C)
[(VO(Nic)$_2$)$_2$pip]-μ-piperazino-bis-[oxo-bis-nicotinato-vanadium(IV)]	11.54	–	–	1.40	1.35 (180–280°C)	8.56	8.39 (350–560°C)
[VO(Nic)$_2$dipy]-oxo-bis(nicotinato)-α,α'-dipyridyl-vanadium (IV)	15.65	–	–	5.23	5.31 (240–340°C)	12.60	12.58 (355–570°C)
[VO(Nic)$_2$pic·H_2O]-oxo-bis(nicotinato)-β-picoline-aquo-vanadium (IV)	10.20	–	–	2.68	2.72 (140–260°C)	8.00	7.98 (350–560°C)

The third complex (with dipy) shows a decomposition pattern somewhat similar to that of the second. The ligand dipy is removed in the range 240–340°C. Extension of the step up to 340°C shortens the plateau due to [VO(Nic)$_2$] to a range of ~ 10–15°C only. A fresh weight loss begins at ~ 355°C extending up to ~ 570°C due to thermal decomposition of organic matter, and once again a constant weight is recorded due to V_2O_5 residue. The first thermolysis step of the fourth complex (with pic) lies in the temperature range 140–260°C corresponding to simultaneous removal of one water molecule and one molecule of β-picoline from the complex. After this step the TG curve remains horizontal up to about 350°C; this portion, however, corresponds to the weight of the dimeric species [VO(Nic)$_2$]$_2$. The procedural decomposition occurs again with weight loss up to ~ 560°C and thereafter the thermogram records a constant weight of V_2O_5.

TG reveals that: (i) coordinated H_2O and monodentate organic ligands like pic are simultaneously driven out in the temperature range ~ 150–250°C resulting in a single-step mass loss due to these moieties; (ii) the complex [VO(Nic)$_2$] is thermally stable in the range ~ 250–350°C. At higher temperature it starts decomposing and gets converted into V_2O_5 at around 560°C;

(iii) removal of pip or coordinated H_2O also results in the conversion of the original hexa-coordinated complex into penta-coordinated $[VO(Nic)_2]$; (iv) the complex $[VO(Nic)(C_9H_6NO)]$ obtained from the original complex with HQ after removal of one coordinated water molecule is somewhat less stable compared to $[VO(Nic)_2]$.

These spectral and TG studies lead to conclusions enabling us to assign (tentative) structures to the four mixed-ligand complexes. Their formulae and names, as mentioned in the first column of Table 3, should suffice with regard to assignment of structures.

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