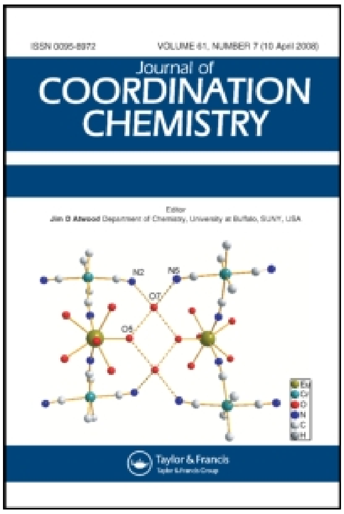

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VANADIUM(III) AND VANADIUM(IV) COMPLEXES WITH PYRAZINE IN ALCOHOL SOLUTION

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The V(III)-pyrazine system was examined spectroscopically in the isoamyl alcohol solution. An unstable, violet-red, binuclear vanadium(III) complex $[V_2(\mathrm{pyraz})Cl_4]^{2+}$ was found to be formed. On exposure to air it was slowly converted into a sparingly soluble green vanadium(IV) compound, $[VO(\mathrm{pyraz})OH]Cl.H_2O$. This compound was examined by the analytical, spectroscopic (electronic and infra-red spectra) and magnetic methods.

KEY WORDS: vanadium(III), vanadium(IV), complexes, pyrazine, alcohol solutions.

INTRODUCTION

Vanadium(III) does not form any stable complex compounds with both aliphatic and cyclic amines.

In one of our earlier works some unstable V(III) complexes with pyridine were investigated in the isoamyl alcohol solution.[1] Rupp[2] obtained solid V(III) complexes with ethylenediamine and pyridine which on exposure to air yielded stable $VOCl_2.5Py$ and $VOCl_2.2Py$ complexes. There are no data available on the complexation of vanadium(III) and vanadium(IV) with pyrazine.

In the present paper we examined the V(III)-pyrazine system in the isoamyl as well as in the ethyl alcohol solutions.

EXPERIMENTAL

Reagents

Pyrazine (E. Merck), $VCl_3.6H_2O$ was prepared by electrolytical reduction of vanadium pentoxide (analytically pure) in hydrochloric acid, precipitation of the crystalline trichloride with gaseous hydrogen chloride and drying over solid KOH in a desiccator.[3] Primary isoamyl alchohol, analytically pure (POCH Gliwice)

Apparatus

Diffuse reflectance spectra in the visible range were recorded in a Unicam SP-700 spectrophotometer over the 12000–30000 cm^{-1} region with MgO as a reflection reference.

Absorption spectra were measured in a Unicam SP-700 spectrophotometer. Infra-red spectra were measured between 200 and 4000 cm^{-1} in Nujol in a Perkin-Elmer spectrophotometer.

Magnetic measurements were carried out between 77 and 295°K using a Gouy balance.

RESULTS

Spectroscopic Measurements of the Vanadium(III)-Pyrazine System

By titrating the alcohol $VCl_3.6H_2O$ solution with alcoholic pyrazine solution ($[\mathrm{pyraz}] \gg [V(III)]$) the solution is found to change its colour from green through brown to red-violet. The absorption spectra of the alcoholic V(III) solution with pyrazine, like those of alcoholic V(III) solution, exhibit three bands.

The two spin-allowed bands assigned to the $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ transitions appear at $\lambda_1 = 14600$ cm^{-1} and $\lambda_2 = 20000$ cm^{-1}.[4] The third very weak band appears at $\lambda_3 = 28000$ cm^{-1} and is assigned to the $^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ transition.

An increase in the molar ratio $[\mathrm{pyraz}]/[V(III)]$ results in the second band being shifted towards longer wavelengths (Table I). In order to find out if only mononuclear or also polynuclear complexes are formed in solution, the average extinction was measured as function of total metal concentration (Figure 2). The above figure indicates that at least one violet-red polynuclear complex is formed in solution. The composition of the complex formed was examined by the "straight-line" method[5] (Figure 3a

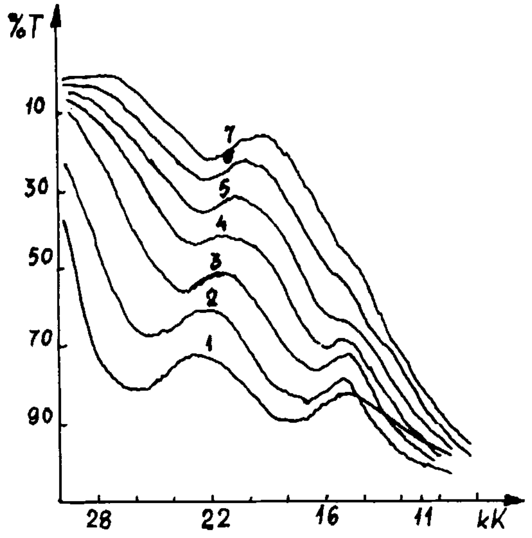


FIGURE 1 Absorption spectra of the vanadium(III)–pyrazine complex in solution. $[VCl_3] = 0.075$ M, (d = 0.1 cm)

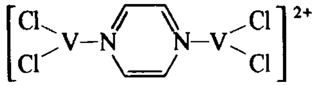
[Pyraz]/[V(III)]	Curve	1–VCl_3
0.5	2	
1	3	
2	4	
2.5	5	
3	6	
4	7	

TABLE I
The dependence of the position of the second absorption band on the [pyraz] : [V(III)] ratio. $[VCl_3] = 0.075$ M, (d = 1 cm).

[Pyraz] : [V(III)]	σ cm^{-1}	A
0	22,400	1.55
0.5	22,000	2.28
1	21,600	2.92
1.5	21,400	3.18
2	21,000	3.77
2.5	20,800	4.43
3	19.800	6.39
4	19,200	7.21

and 3b). Straight lines indicate the number of nuclei and number of members in the A_mB_n complex.

The above data show that in the system under investigation a binuclear complex is formed of the following formula:



Investigation of the Vanadium(IV)–Pyrazine System

The vanadium(III) complex is unstable and decomposes on exposure to air. The extinction is found to decrease in time (Figure 4), the solution changes its colour through green to pale yellow and a crystalline

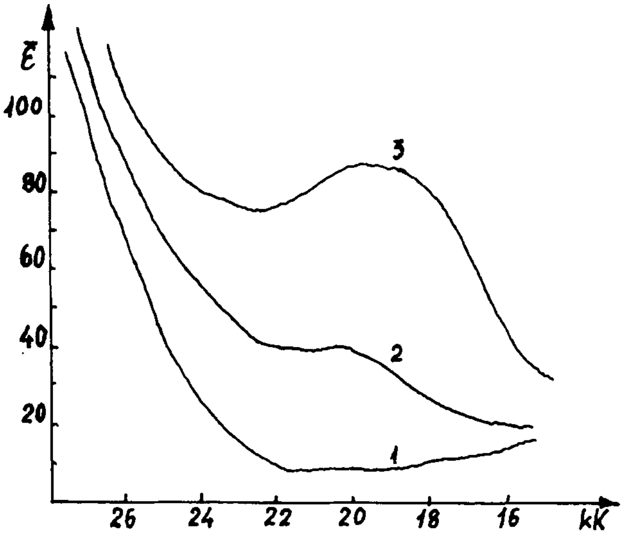


FIGURE 2 Dependence of the mean extinction coefficient on the wavelength at various starting concentrations of the metal ion. [Pyraz]/[V(III)] = 3, 1–0.0375 M, 2–0.0477 M, 3–0.075 M.

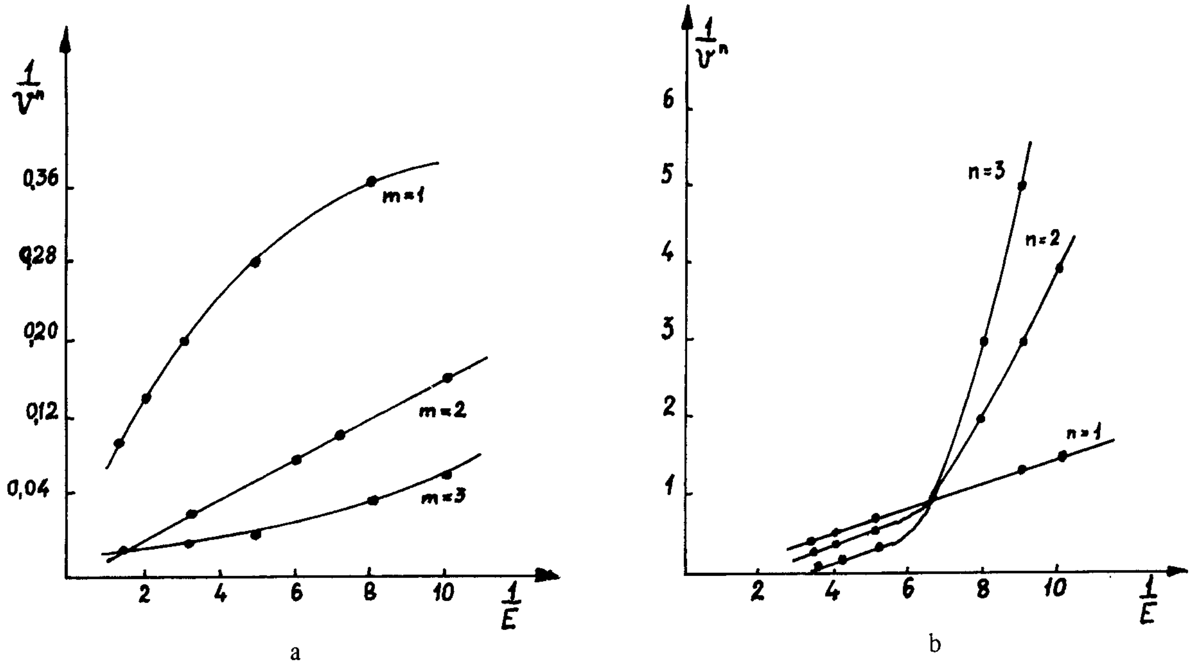


FIGURE 3 The use of the straight-line method for the system V(III)–pyrazine. (a) excess of vanadium(III), (b) excess of pyrazine.

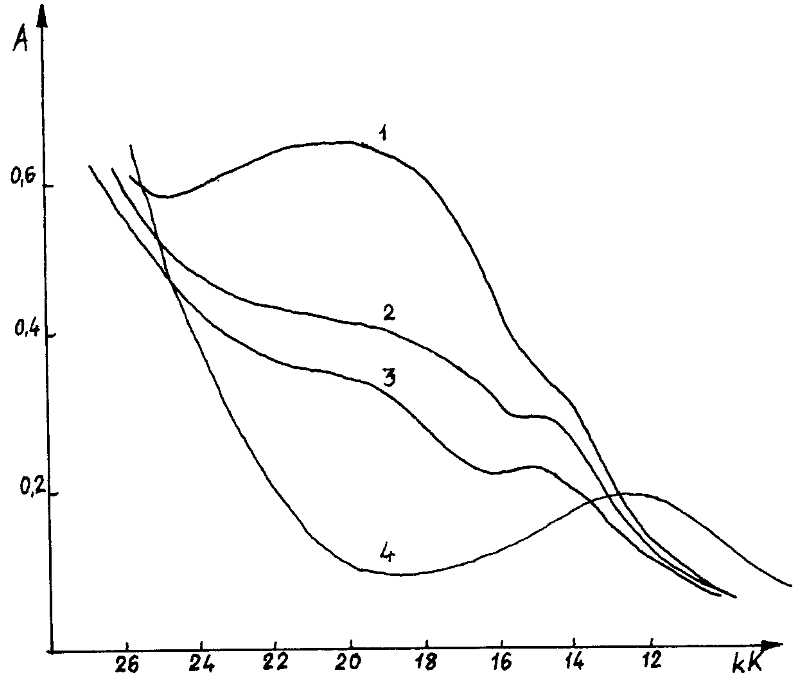


FIGURE 4 Extinction change of the violet solution containing 0.075 M $VCl_3.6H_2O$ and 0.225 M pyrazine with time. (d = 0.1 cm). 1–t = 0, 2–t = 0.5 h, 3–t = 4.5 h, 4–t = 24 h (d = 1 cm).

TABLE II
Observed energy in cm^{-1} for 0.04 M aqueous solution of $[VO(pyraz)OH]Cl.H_2O$ complex and for $[VO(H_2O)_5]^{2+}$.

Band	Observed energy complex	Observed energy[6] $[VO(H_2O)_5]^{2+}$	M.O. Assignment the symmetry C_{4v}
I	12,900	13,000	$^2B_2 \rightarrow {}^2E$
II	16,000	16,000	$^2B_2 \rightarrow {}^2E_1$
III	23,000		$^2B_2 \rightarrow {}^2A_1$

green precipitate is formed which is very stable in air. The decomposition of the violet complex is accompanied by the oxidation reaction of vanadium(III) to vanadium(IV). The presence of vanadium(IV) is confirmed by the appearance of a band (Figure 4) at $\lambda = 12800\ cm^{-1}$ corresponding to the d–d transition in the VO^{2+} ion.[6]

Vanadium(IV) co-ordinates one molecule of pyrazine and precipitates from the solution as green crystals. Analytical results indicate a formula $[VO(pyraz)OH]Cl.H_2O$.

Analysis: % calculated: V 23.45, N 13.3, C 22.1, H_2O 16.1; % found: V 23.50, N 13.5, C 22.5, H_2O 16.0.

Chlorine was detected by reaction with the Ag^+ ions. Derivatographic analysis confirmed the composition of this compound. Between 100 and 150°C a loss in water is found. The compound becomes fully decomposed at about 290°C exothermic peak on the curve.

Electronic Spectra

A diffuse reflectance spectrum was measured for $[VO(pyraz)OH]Cl.H_2O$ (Figure 5). The spectrum of this compound shows two broad bands at about $12800\ cm^{-1}$ and $22800\ cm^{-1}$ corresponding to the $b_2 \rightarrow e_\pi^*$ and $b_2 \rightarrow a_1^*$ transitions, respectively.

At about $15200\ cm^{-1}$ a shoulder is observed due to a $b_2 \rightarrow b_1^*$ transition.

Infra-red Spectra

Infra-red spectra were measured in Nujol between 200 and 4000 cm^{-1}. The frequencies found for the complex and ligand are summarized in Table III. A broad strong band between 3400 and 3500 cm^{-1} corresponds to the free –OH group. The frequency of the V=O group is shifted towards longer wavelengths as compared with other vanadium(IV) compounds and appears at 820 cm^{-1}.

The absorption bands resulting from the valence and stretching vibrations of the pyrazine complex in the complex are shifted towards shorter wavelengths as compared with pyrazine.

A new band resulting from the VO–N bond appears at 245 cm^{-1}.

Magnetic Measurements

Magnetic measurements were carried out between 77 and 295°K. The results summarized in Table IV indicate that this compound is paramagnetic with a lowered magnetic moment.

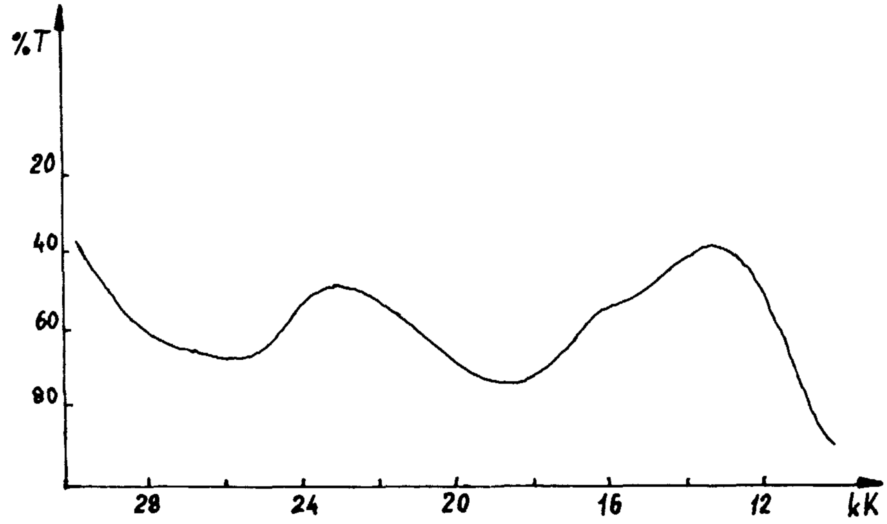


FIGURE 5 Reflectance spectra of complex $[VO(pyrax)OH]Cl.H_2O$.

TABLE III
Observed frequencies in cm^{-1}

Pyrazine	$[VO(pyraz)OH]Cl.H_2O$	Tentative assignments
	3460 m	ν O–H
1590 m	1610 vs	ν C=N
1460 bs	1460 bs	δ C=C
1410 s	1418 s	vibrations of the pyrazine ring
1380 s	1380 m	
1305 w	1305 w	
1165 bw	1165 s	
1150 s	1150 s	ν C–N
1130 w	1120 s	
1060 s	1075 vs	ν C–H
1020 vs	990 w	ring deformation
	965 vs	
	820 s	ν V=O
785 vs	770 w	ring deformation
415 vs	495 vs	δ C=C
	350 bs	ν VO–Cl
	320 m	ν VO–Cl
	245 m	ν VO–N

TABLE IV
Magnetic data at various temperature of complex $[VO(pyraz)OH]Cl.H_2O$

T_0K	$10^6 \cdot \chi_M$	$\mu_{B.M.}$
77	3765.0	1.173
100	3232.5	1.337
126	2532.0	1.378
153	2073.1	1.441
180	1611.9	1.414
206	1509.6	1.486
233	1326.9	1.503
262	1194.2	1.533
284.5	1107.2	1.548
295.5	1063.7	1.501

DISCUSSION

The vanadium(III)–pyrazine system was examined in isoamyl alcohol containing the amount of water necessary for the formation of a hexahydrated hydration sphere around the V^{3+} ion. The required amount of water was introduced as crystallization water contained in the compound.

Introduction of water bound in the hydrated crystal does not result in hydrolysis of vanadium(III). The spectra of vanadium(III) trichloride hexahydrate in isoamyl alcohol exhibit the absorption bands almost identical with those reported by Hartmann and Schlafer[7] in the spectra of anhydrous VCl_3 in isoamyl alcohol. According to the spectrophotometric data one should assume that the system under investigation contains the hexasolvate $[V(alc)_6]Cl_3$.

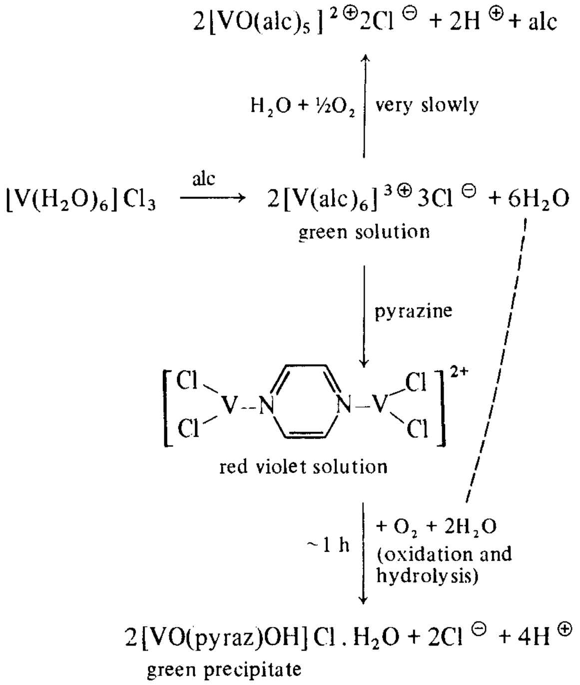
In the present paper investigations of the vanadium(III)–pyrazine system in isoamyl alcohol are described but a similar red-violet colour was also observed for the vanadium(III)–pyrazine–dioxane and vanadium(III)–pyrazine–acetone systems. This leads to a univocal conclusion that the characteristic red-violet colour results from the complex forming reaction of vanadium with pyrazine and not from the formation of alkoxides. Moreover, these compounds are green and only slightly soluble in alcohol.[8]

The complexation of vanadium(III) is directly noticeable in the absorption spectra over the visible range (Figure 1, Table I). The presence of a binuclear complex $[V_2(pyraz)Cl_4]^{2+}$ was detected by the "straight-line" method.

The pyrazine molecule is linked to the vanadium(III) atoms through its nitrogen atoms.

The complex formed is unstable. The violet-red colour disappears gradually and a crystalline green precipitate is formed of a formula $[VO(pyraz)OH]Cl.H_2O$.

The processes taking place in the vanadium(III)–pyrazine may be expressed by the following pattern:



The results of our further studies which will be published in more detail soon, indicate that vanadium(III) has a general tendency to form polynuclear complexes with single-ring azoles. Like pyrazine, vanadium(III) forms red-violet polynuclear complexes with pyrazole, imidazole, thiazole, triazole and with picolines and their single-ring derivatives. The same family of polynuclear complexes includes also a red-violet complex of vanadium(III) with pyridine, assumed by us previously as a mononuclear one. Some additional studies carried out by us now indicate that the vanadium(III) complexes with pyridine are fully analogical with those mentioned above.

In spite of the fact that, as shown above, a number of polynuclear vanadium(III) complexes are found to exist, a general conclusion suggested by Morris[9] that the red colour of the vanadium(III) complexes is related to the polynuclear character of its complexes, is not always correct. As an example one may quote the vanadium(III) complexes with dipyridyls, phenanthroline and with diamines which, as we have found, in spite of their deeply red colour have a constant average molar absorption coefficient in solution, independent of total vanadium(III) concentration, which indicates rather doubtlessly their mononuclear nature.

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