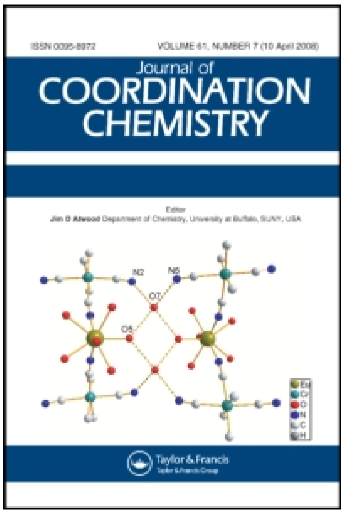

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Zofia Karwecka[a]
[a] Institute of Chemistry, University of Wroclaw, Wroclaw, Poland

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STUDIES OF THE STRUCTURE OF VANADIUM(III) COMPLEXES WITH NITROGEN CONTAINING LIGANDS IN ALCOHOLIC SOLUTIONS. I. COMPLEXES OF V(III) WITH AZOLES

ZOFIA KARWECKA

Institute of Chemistry, University of Wrocław, Wrocław, Poland

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Anhydrous vanadium trichloride reacts with azoles in low concentrated ethyl alcohol solution of V(III) to produce 1:1 electrolytic complexes of the type $[V(azole)_4Cl_2]^+$. Studies of the visible spectra of all the above complexes demonstrate that the vanadium(III) is octahedrally co-ordinated. The room temperature magnetic moments of the complexes (~ 2.8 B.M.) are consistant with the presence of two unpaired electrons per vanadium atom. At higher concn. of V(III) the polynuclear violet-red complexes probably are formed.

KEY WORDS: Vanadium(III), complexes, polynuclear complexes, azoles, alcohol solution.

INTRODUCTION

They are only a few papers dealing with the complexation reaction of V(III) with nitrogen-containing ligands in non-aqueous solution. Earlier, we examined the V(III)-pyridine[1] and V(III)-pyrazine[2] systems both in the isoamyl and ethyl alcohol solutions. We found the presence of binuclear violet complexes in the solution.

The present paper deals with the complexation of vanadium(III) with some azoles in ethyl alcohol solutions.

EXPERIMENTAL

Reagents

VCl_3(Fluka A,G), Pyrazole (E. Merck), Imidazole (E. Merck), Thiazole (Fluka A,G), primary ethyl alcohol, analytically pure (POCh Gliwice, Poland).

Apparatus

Absorption spectra were measured in a Unicam SP-700 and Unicam SP-500 spectrophotometers. Magnetic measurements were carried at room temperature 295°K by the Gouy method. Conductivity measurements at room temperature used a conductivity meter, type OK-102/1 (Radelkis).

RESULTS

During titration of alcoholic VCl_3 solution with alcoholic azole solution $[\text{ligand}] \gg [V(III)]$, the colour of solution changes from green through brown to red-violet. This violet colour is unstable at lower ligand and metal concentrations, whereas at high concentrations $[\text{ligand}] \approx 3$ M, $[V(III)] = 0.5$ M the violet colour is relatively stable. The visible absorption spectra of V(III) solutions with azoles exhibit two bands (Figure 1).

Two spin-allowed electronic transitions at about 15,000 cm^{-1} and 20,000 cm^{-1} are assigned as $^3T_{2g}(F) \leftarrow {}^3T_{1g}(F)$ at lower energies and $^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$ at higher energies.[3]

In the spectra of solutions with higher V(III) concentration the second *d-d* band coincides with the charge-transfer band ($\bar{\epsilon} > 500$). The splitting parameters, $10\,D_q$, Racah Coefficient B and the nephelauxetic ratio ($\beta_{55} = B_k/B_g$), were calculated from the formulae for term energies for the d^2 electronic configuration. The results are shown in Table I.

The values of β_{55} and B_k for V(III) in the complexes are lower than the corresponding values of the V(III)ion in ethyl alcohol. A decrease in these parameters accompanies a decrease in the electrostatic interaction resulting from an increase of visicity of the complex ion.[5] This change in parameters might also result from the formation of polynuclear complexes in solution.

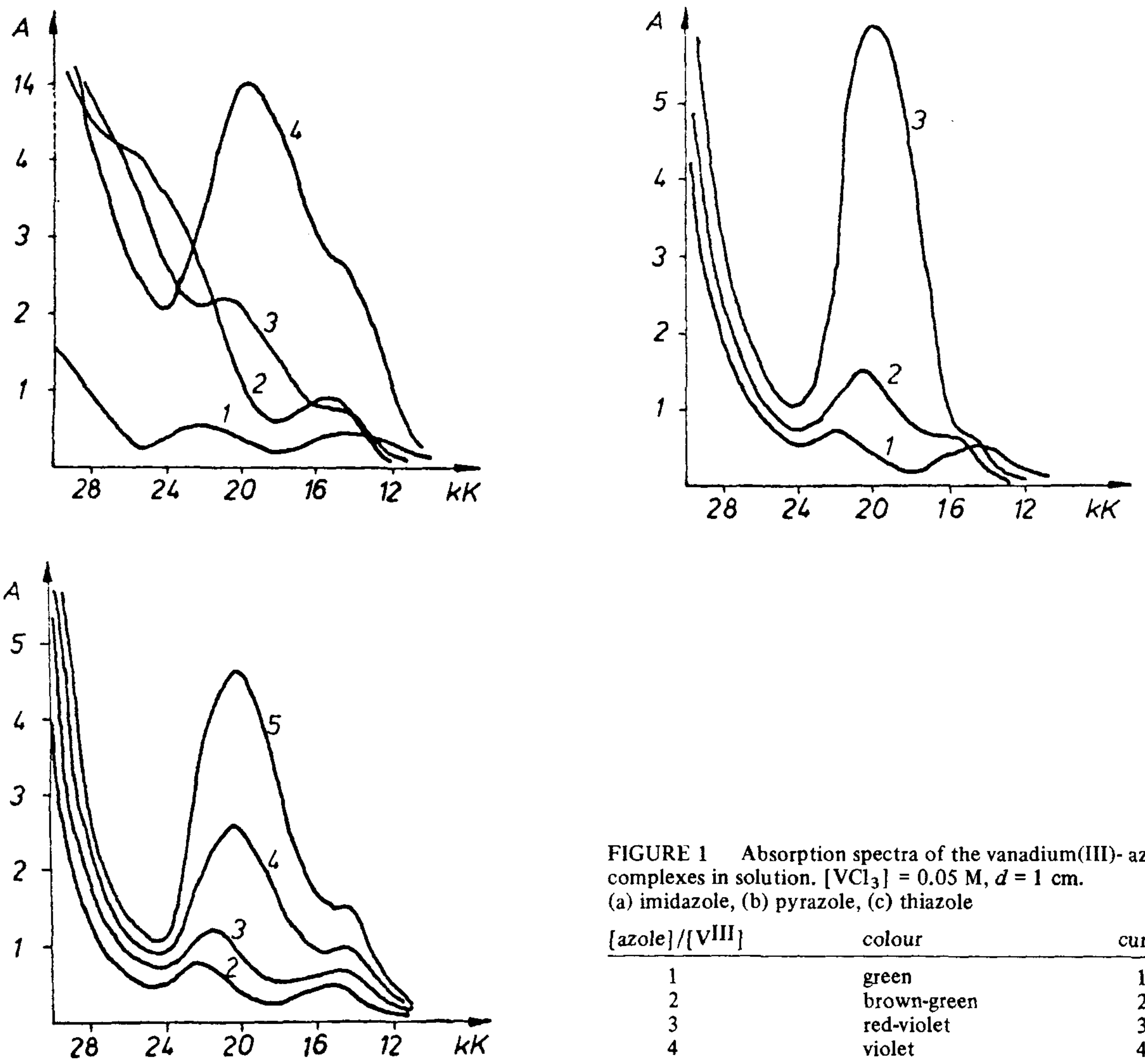


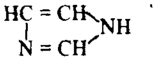
FIGURE 1 Absorption spectra of the vanadium(III)- azole complexes in solution. [VCl_3] = 0.05 M, d = 1 cm.
(a) imidazole, (b) pyrazole, (c) thiazole

[azole]/[V^{III}]	colour	curve
1	green	1
2	brown-green	2
3	red-violet	3
4	violet	4
5	violet	5

TABLE I
Spectral parameters of the mononuclear V(III) complexes in solution [V(III)] = 5.10^{-2} M, [lig]/[met] = 3, B_g = 860 cm^{-1}

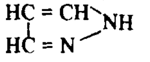
Compounds	λ_1 cm^{-1}	λ_2 cm^{-1}	D_q cm^{-1}	B_k cm^{-1}	β_{55}
[$V(C_2H_5OH)_4Cl_2$]Cl[4]	14,800	21,800	1591	548	0.635
[V pz_4Cl_2]Cl	15,000	19,800	1611	369	0.430
[V im_4Cl_2]Cl	15,000	20,900	1636	454	0.528
[V th_4Cl_2]Cl	14,600	20,400	1595	445	0.518

imidazole (im)



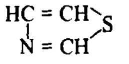
$$\begin{array}{l} HC=CH\diagdown NH \\ N=CH\diagup \end{array}$$

pyrazole (pz)



$$\begin{array}{l} HC=CH\diagdown NH \\ HC=N\diagup \end{array}$$

thiazole (th)



$$\begin{array}{l} HC=CH\diagdown S \\ N=CH\diagup \end{array}$$

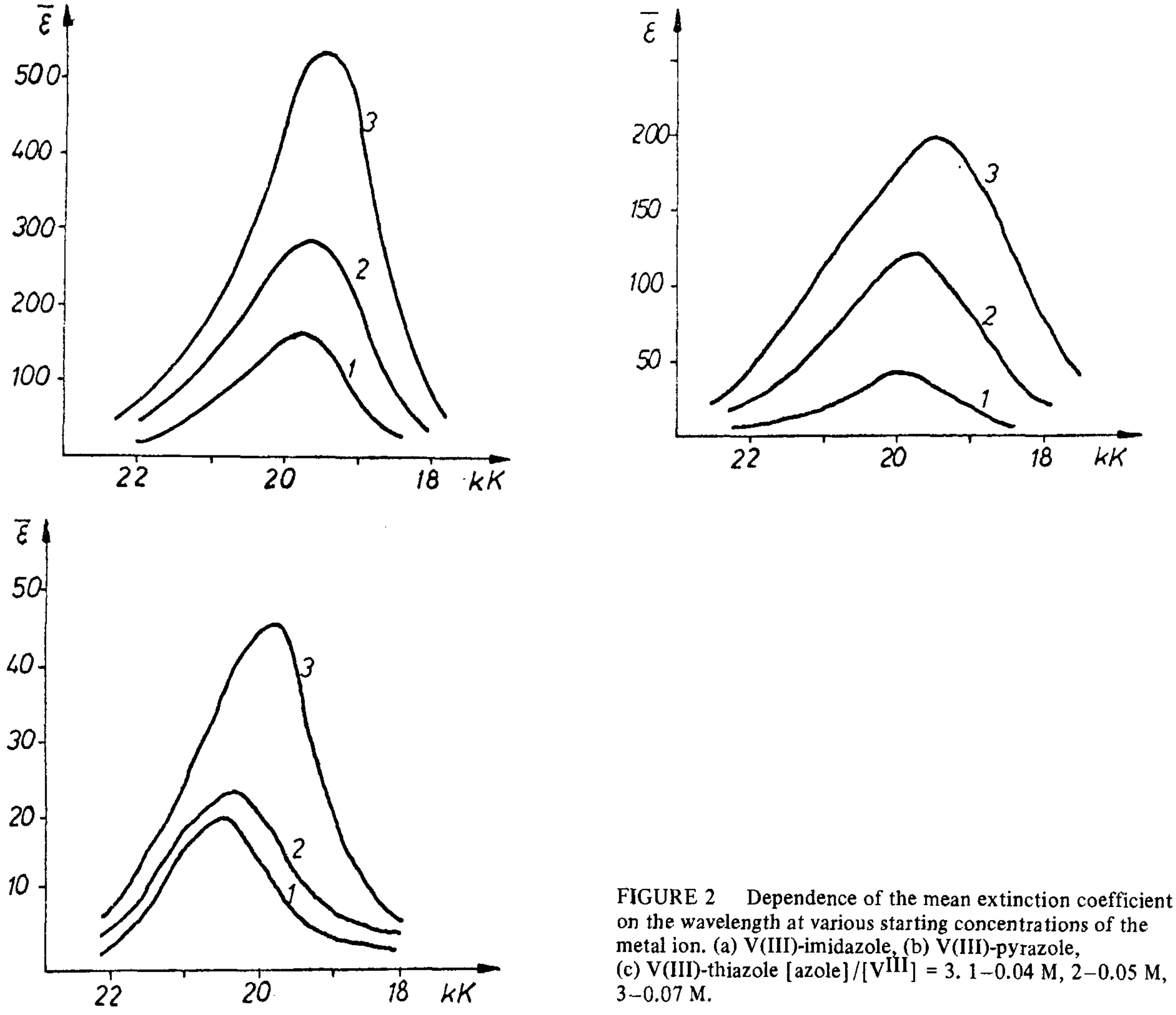


FIGURE 2 Dependence of the mean extinction coefficient on the wavelength at various starting concentrations of the metal ion. (a) V(III)-imidazole, (b) V(III)-pyrazole, (c) V(III)-thiazole [azole]/[V^{III}] = 3. 1–0.04 M, 2–0.05 M, 3–0.07 M.

In our case the second band at about 20,000 cm^{-1} is shifted towards longer wavelengths with the increasing molar ratio [lig]/[V(III)].

In order to find out if mononuclear complexes only are formed in solution, the average extinction coefficient ($\bar{\varepsilon}$) was measured as a function of total metal concentration (Figure 2).

A considerable increase in $\bar{\varepsilon}$ indicates that at least one red-violet polynuclear complex is formed in solution of V(III) with azole. The compositions of these complexes were investigated by the Job method, the corrections for band shifts were taken into account,[6] (Figure 3).

The peaks on these curves indicate that the complexes with molar ratio [azole] : [V(III)] = 4:1 are formed.

The results obtained by the spectrophotometric method were confirmed by the conductometric titration method and also by the Feltham and Hayter[7] method which is used to determine the type of electrolytes in non-aqueous solutions (Figure 4).

The plots presented (Figure 4) show a clear break in the curves at a molar ratio of 4 for the complexes with azoles. In the case when the vanadium(III) is titrated with imidazole a maximum is observed on the corresponding titration curve before the equilibrium point. This must be related to the formation of a certain transitional compound of complex salt which is fairly well dissociated.[8-10] Such conductivity maxima in the curves are found independently of vanadium(III) concentration. The conductivity is found to decrease considerably

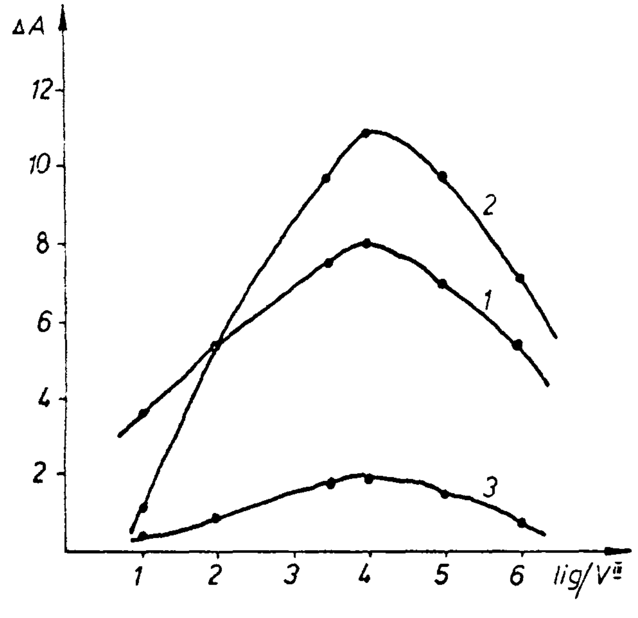


FIGURE 3 Dependence of ΔA (difference between product extinction and substrate extinction in the reaction) on the composition of the solution for systems V(III)-azole. 1-imidazole, 2-pyrazole, 3-thiazole. $\lambda = 21{,}000\ \text{cm}^{-1}$, $d = 1$ cm.

with the increasing [lig] / [V(III)] ratio. This is related most probably to the formation of less dissociated polynuclear ions of larger charges. In the case of pyrazole and thiazole which have similar basic natures (pK_b of pyrazole = 11.47, thiazole = 11.48, imidazole = 6.97) much higher ligand and metal concentrations are required to obtain polynuclear complexes. Therefore the conductivity is found to be constant over the equilibrium point. Conductivity measurements at higher V(III) concentrations are highly erroneous because of the formation of large number of ionic pairs and, therefore, it is not possible to check the complex ion charge. It is only possible to check the type of electrolyte at lower concentrations where mononuclear complexes prevail.

To study this effect series of conductivity measurement were performed on solutions of various V(III) concentrations at a molar ratio [Lig] / [V(III)] = 4 for the complexes with azoles.

The plots of molar conductivities λ_m versus $\sqrt{C_m}$ were extrapolated to infinite dilution to find the limiting conductivity λ_o and then from the plot of $\lambda_o - \lambda_m / \sqrt{C_m}$ the value of slope was found from which the type of electrolyte may be determined by comparing with the known compound.[7] The data are summarized in Table II and compared with those of VCl_3 in ethyl alcohol obtained by Casey and Clark.[4] They found the 1:1 electrolyte in solution

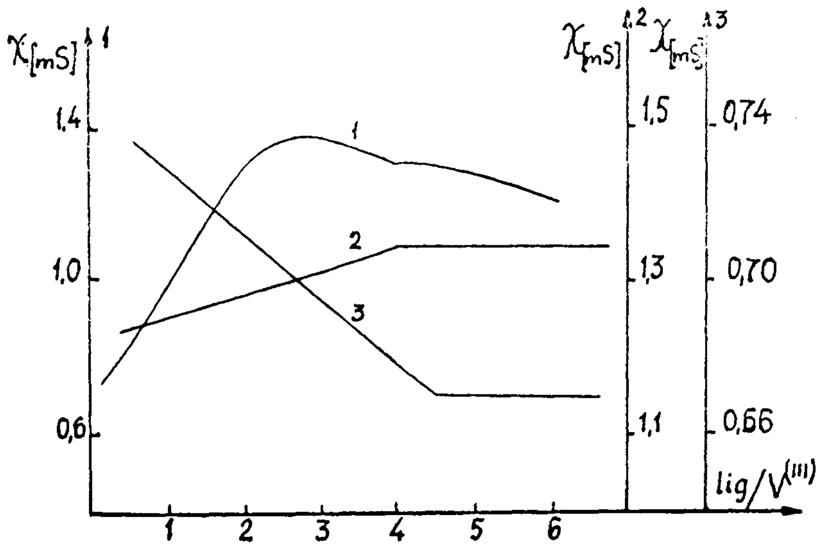


FIGURE 4 Conductometric titration of a solution of VCl_3 with azole solution. Solvent: ethyl alcohol:

1–imidazole + V(III) concn. V(III) = 2.10^{-2} M
2–pyrazole + V(III) concn. V(III) = 4.10^{-2} M
3–thiazole + V(III) concn. V(III) = 2.10^{-2} M

TABLE II

Experimental values of λ_0 and $\lambda_0-\lambda_m/\sqrt{C_m}$ for the complexes in ethanol at room temperature

Compound	Concn. range m/l	λ_0 [ohm^{-1}]	$\lambda_0-\lambda_m/\sqrt{C_m}$
$[V(C_2H_5OH)_4Cl_2]Cl$	$1-5.10^{-2}$	57	130
$[V\ im_4Cl_2]Cl$		85	143
$[V\ pz_4Cl_2]Cl$	$1-5.10^{-2}$	60	150
$[V\ th_4Cl_2]Cl$		55	137
$[V(C_2H_5OH)_4Cl_2]Cl$ [4]	$1-16.10^{-3}$	54	180

is formed what confirms the presence of the $[V(alc)_4Cl_2]^+$ cation in solution.

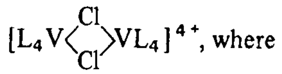
The results presented in Table II confirm the presence of 1:1 electrolytes at lower V(III) concentrations. In the case of higher concentrations where probably the polynuclear complexes are formed the above mentioned method could not be used for investigation of the type of electrolyte and, hence, the complex ion charge.

Magnetic properties in solution were investigated by the Gouy method at room temperature. The results indicate that these compounds are paramagnetic with the magnetic moment of about 2.8 BM per 1 vanadium atom.

CONCLUSION

During studies of the complexation process of V(III) with the azoles it was found that at lower V(III) concn. ($[V^{III}] < 5.10^{-2}$ M) mononuclear complexes of the type $[V(azole)_4Cl_2]^+$ are formed in solution.

The complexation process of vanadium(III) is directly visible from the absorption spectra in the visible region. The second band appearing in the spectra at about 20,000 cm^{-1} (Figure 1) is shifted towards longer wavelengths as the molar ratio of components increases. The average extinction coefficients (Figure 2) increase considerably with the increasing vanadium concentration what indicates that probably polynuclear complexes were formed in solution. Recently, we obtained a navy-blue complex in solid state from the solution of V(III) with pyrazole and thiazole.[11] These complexes were binuclear with two chloride bridges:



$$[L_4V\overset{Cl}{\underset{Cl}{<>}}VL_4]^{4+}$$, where L = azole.

The red-violet polynuclear complexes in solution are unstable and under the influence of air undergo hydrolysis and oxidation of V(III) to V(IV) with precipitation of a green-blue V(IV) complex with the above-mentioned azoles.

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