

Pyrazole and Imidazole Complexes of Vanadium(II) Chloride

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Complexes of vanadium(II) chloride with pyrazole and imidazole of the type $VCl_2(\text{pyrazole})_4$ and $VCl_2(\text{imidazole})_6$ were prepared. The complexes are unstable in air and substitution labile in solution. The electronic spectra of their methanolic solutions suggest octahedral symmetry. The participation of methanol in the first coordination sphere appears to be a function of the concentration of the ligand in solution. The values of Dq and B are calculated. The far infrared spectrum of the pyrazole complex in the crystalline state indicates a trans configuration. Magnetic measurements give values for the magnetic moments lower than the spin-only value.

Introduction

Until a few years ago very little had been done on the synthesis of V(II) complexes with organic ligands, except with strong chelating agents.¹

This was the case partly because these complexes are very unstable in air, but principally because the starting material, VCl_2 , was very unreactive, probably because of its polymeric structure.² In 1968, though, Seifert and Auel³ succeeded to prepare a series of V(II) complexes with organic ligands by using the complex $VCl_2 \cdot 2CH_3OH$ as starting material. This complex was proved to be quite labile to substitution. Also, at the same time, Larkworthy *et al.*⁴ prepared a series of V(II) complexes with ethylenediamine, diethylenetriamine, and γ -picoline, using hydrated V(II) halides in alcoholic media.

In the present work the imidazole and pyrazole complexes of V(II) were synthesized and isolated in our laboratory, and their electronic, infrared, and far infrared spectra were studied.

The above syntheses were done during the course of our studies on the influence of various ligands upon the behaviour of V(II) during reactions with several reducible organic molecules.⁵ Speculations on the structure and reactivity of these complexes were made, based on their magnetic and spectral properties.

The starting material was $VCl_2 \cdot 2CH_3OH$, which was prepared following a method similar to that of Seifert and Auel.³

Experimental

Materials

Vanadium(III) chloride (anhydrous), pyridine, pyrazole, and imidazole were purchased from Fluka.

Hydrogen chloride (gaseous) was also purchased from Fluka. It was dried by passing through traps of conc. sulfuric acid. Attempts to generate hydrogen chloride by adding conc. sulfuric acid to conc. hydrochloric acid did not lead to satisfactory results; chlorine was formed at the same time, which caused oxidation of the mercury in the electrolytic cell, and the product V(II) contained considerable amounts of Hg_2Cl_2 .

Methanol was dried with magnesium activated by iodine and distilled.⁶ Argon was purified from traces of water and oxygen by passing through traps of dry calcium chloride and R-3-11 catalyst of B.A.S.F., which was generated by a stream of hydrogen at 180°C. For the electrolysis, instead of the catalyst traps methanolic solutions of dry hydrochloric acid with 0.2M VCl_3 and zinc amalgam were used.

Instrumentation

The ultra-violet, visible, and near infrared spectra were obtained with a Cary 14 spectrophotometer. The infrared spectra were obtained with a Perkin-Elmer, Mod. 521 spectrophotometer, and the far infrared spectra with an FS-720 Fourier Transform interferometer of Beckman RIIC. The complexes were examined as Nujol mulls between high density polyethylene windows.

The magnetic susceptibility measurements were done with a Gouy Balance. Vanadium was determined by atomic absorption spectroscopy.

The electrolytic cell used for the reduction of V(III) was similar to that designed by Seifert and Auel,⁷ except that it was an all-glass apparatus.

Preparation of Complexes

All the manipulations were done in a glovebox or under a stream of argon.

Starting material

($VCl_2 \cdot 2CH_3OH$) Anhydrous VCl_3 was dissolved in dry methanol, to give a green solution, and dry hydrogen chloride was bubbled through for about two hours. The resulting solution contained about 8% HCl. The solution was then transferred to the electrolytic cell, and the electrolytic reduction of V(III) was done following the method of Seifert and Auel.³ The violet-blue solution of V(II) was evaporated to dryness under vacuum and the solid product was heated at 65°C for 5 hours, under vacuum. A light green powder of $VCl_2 \cdot 2CH_3OH$ was thus obtained.

 $VCl_2(pyridine)_4$

It was prepared following the method of Seifert and Auel.³ Analysis: Calcd. for $VCl_2(pyridine)_4$: V, 11.64%; C, 54.81%; H, 4.60%; N, 12.78%. Found, V, 11.6%; C, 54.8%; H, 4.59%; N, 12.8%.

 $VCl_2(pyrazole)_4$

5 g of pyrazole were dissolved in dry methanol, and 1.8 g of $VCl_2 \cdot 2CH_3OH$ were added in small portions. A yellow solution was formed, which was brought to boil for 15 min. A blue-green precipitate was formed, which was filtered out and dried in vacuum. The precipitate was pulverized and washed with ether several times, in order to eliminate the excess of pyrazole. The complex was insoluble in ether. Analysis: Calcd. for $VCl_2(pyrazole)_4$: V, 12.92%; C, 36.53%; H, 4.09%; N, 28.43%. Found, V, 12.5%; C, 36.1%; H, 4.35%; N, 28.1%.

 $VCl_2(imidazole)_6$

7 g of imidazole were dissolved in dry methanol. 2.5 g of $VCl_2 \cdot 2CH_3OH$ were added in small portions and a green solution was formed. Light green crystals precipitated shortly after. The precipitate was filtered out and washed with ether. It was dried under vacuum and subsequently ground to a fine powder and washed many times with ether, in order to eliminate the excess of imidazole. The complex was insoluble in ether. Analysis: Calcd. for $VCl_2(imidazole)_6$: V, 9.61%; C, 40.76%; H, 4.56%; N, 31.70%. Found, V, 10.2%; C, 40.5%; H, 4.55%; N, 31.3%.

Results and Discussion**Electronic Spectra**

The optical absorption spectra of methanolic solutions of the imidazole and pyrazole complexes are shown in Figure 1. They were taken with pure methanol as reference. Curves 1 and 3 correspond to pure methanolic solutions of the imidazole and pyrazole complexes, respectively, while curves 2 and 4 correspond to solutions containing also an excess of the corresponding free ligand.

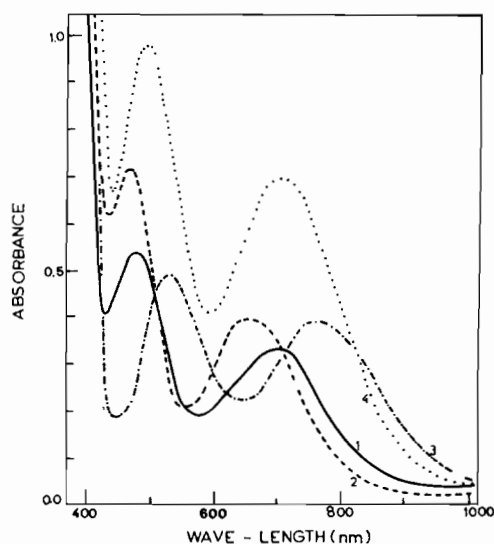


Figure 1. Electronic spectra of: (1) $VCl_2(imidazole)_6$ in pure methanol, (2) $VCl_2(imidazole)_6$ + imidazole (excess) in pure methanol, (3) $VCl_2(pyrazole)_4$ in pure methanol, (4) $VCl_2(pyrazole)_4$ + pyrazole (excess) in pure methanol.

A continuous increase of the extinction coefficient and a shift to higher wave numbers are observed for the peaks of the curves 1 and 3 when the amount of the ligand added is gradually increased. These changes continue until the final positions are reached, those shown by curves 2 and 4. Further addition of ligands does not alter the spectrum.

Due to a very intense charge transfer band no structure can be observed above 400 nm in Figure 1. On the contrary, very dilute solutions of V(II) pyrazole and imidazole complexes in pure methanol exhibit weak shoulders with ill-defined peak positions on a very intense charge transfer band, commencing at about 340 nm. These spectra do not show the peaks which are present in Figure 1. They are probably too weak to be detected. The spectra of these dilute solutions have not been drawn.

Since V(II) is known to form octahedral complexes, spectra 1, 2, 3, and 4 are attributed to the $3d^3$ configuration in octahedral symmetry. Three main transitions are, therefore, expected from ${}^4A_{2g}(F)$ ground state to the ${}^4T_{2g}(F)$, ${}^4T_{1g}(F)$, and ${}^4T_{1g}(P)$ states.⁸ The strength of the ligand field can be found from the transition ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$, which equals $10 Dq$. The value of the Racah parameter B is calculated from the matrix,⁸

$$\begin{vmatrix} 15B + 12 Dq - \sigma_{2,3} & 4 Dq \\ 4 Dq & 18 Dq - \sigma_{2,3} \end{vmatrix} = 0$$

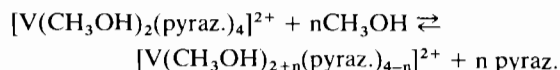
where, $\sigma_{2,3}$ denotes the energy of the transitions ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ $\{=\sigma_2\}$ and ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ $\{=\sigma_3\}$

respectively. If σ_2 or σ_3 are known, B is calculated and vice versa.

According to Seifert and Auel⁷ the chlorides of $VCl_2(CH_3OH)_4$ in methanolic solutions are substituted by methanol, which is a stronger ligand than chlorine. The latter appears to exchange for methanol in the second coordination sphere.⁶ Such an exchange, however, is expected to have no observable effect on the electronic spectra taken at room temperature.

In this work a behaviour similar to that of $VCl_2(CH_3OH)_4$ is assumed for the $VCl_2(\text{pyrazole})_4$ complex in methanolic solutions.

To explain the shift to higher wave numbers of the spectrum of $VCl_2(\text{pyrazole})_4$ with excess of pyrazole, it is proposed that an exchange reaction occurs between pyrazole and methanol in the first coordination sphere. It is taken that the two chlorides of the original complex have already been substituted by two methanols. Data from diffuse reflectance spectra should provide a definite answer for the kind of species involved.



Addition of pyrazole to the solution will drive the reaction to the left. Thus the amount of pyrazole in the first coordination sphere will be a function of the concentration C_p of the pyrazole in solution. Experimental results suggest that for a value of C_p sufficiently high the maximum possible amount of pyrazole has entered in the first coordination sphere. This could explain the observation that the spectra 2 and 4 remain unaffected when more pyrazole is added to the solution.

An argument similar to that just given could explain the shift to higher wave numbers of the spectrum of

$VCl_2(\text{imidazole})_6$ complex in pure alcohol, which is observed when imidazole is added to the solution.

The shift to higher wave numbers agrees with the fact that alcohol is a "weaker" ligand than pyrazole or imidazole.

Under these assumptions calculations of Dq and B will have a meaning only for curves 2 and 4, whereas for pure methanolic solutions, curves 1 and 3, the calculations will give only mean values.

Assuming that the low wave-number peak of the curves 2 and 4 corresponds to the ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ $\{=10 Dq\}$ transition and the high wave-number peak to the ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ $\{=\sigma_2\}$ transition, the values of Dq and B can be obtained. These are given in Table I. The values of σ_3 have been calculated and they are also given in Table I. The values of Dq for curves 1 and 3 are given in Table I also.

No attempt will be made to correlate the calculated values of σ_3 with experimental results because of lack of information in the corresponding spectral region.

In the absence of any data from diffuse reflectance spectra in the solid state no definite conclusion can be drawn for the kind of species involved.

A further support of the earlier made assumption, that in pure methanolic solutions the ligands pyrazole and imidazole, of the first coordination sphere of the complexes $VCl_2(\text{pyrazole})_4$ and $VCl_2(\text{imidazole})_6$, are in equilibrium with the solvent, comes from the values of Dq. If this assumption is correct the values of Dq must be in the order:

$$Dq' < Dq'' < Dq'''$$

where Dq' , Dq'' and Dq''' are the corresponding Dq values for the systems: (a) $VCl_2(CH_3OH)_4$ in pure methanol, (b) $VCl_2(\text{pyrazole})_4$ or $VCl_2(\text{imidazole})_6$

TABLE I. Observed and Calculated Electronic Transitions. Calculated Values of Dq and B. The Observed Transitions are also Given in nm.

Compound	Transitions			Dq cm ⁻¹	B cm ⁻¹
	Observed		Calculated		
	σ_1 cm ⁻¹ (nm)	σ_2 cm ⁻¹ (nm)	σ_3 cm ⁻¹		
$VCl_2(\text{pyrazole})_4 + \text{pyrazole} + CH_3OH/CH_3OH$	1449 (690)	20920 (478)	32586	1449	669
$VCl_2(\text{pyrazole})_4 + CH_3OH/CH_3OH$	13460 (743)	19608 (510)	30521	1346	
$VCl_2(\text{imidazole})_6 + \text{imidazole} + CH_3OH/CH_3OH$	15504 (645)	21978 (455)	34384	1550	657
$VCl_2(\text{imidazole})_6 + CH_3OH/CH_3OH$	14663 (682)	21505 (465)	33432	1466	

in pure methanol, and (c) $VCl_2(\text{pyrazole})_4$ + pyrazole (excess) or $VCl_2(\text{imidazole})_6$ + imidazole (excess) in methanol, respectively. From reference 6 and Table I one obtains:

Pyrazole complex:

$$Dq' (= 1170) < Dq'' (= 1346) < Dq''' (= 1449)$$

Imidazole complex:

$$Dq' (= 1170) < Dq'' (= 1466) < Dq''' (= 1550)$$

Magnetic Measurements

The magnetic results listed in Table II along with other related V(II) complexes show that the magnetic moments at room temperature are somewhat lower than the spin-only value expected for octahedral V(II) compounds. The discrepancies may be partly attributed to oxidation during the measurements, since these complexes are very unstable in air.

Stability of the Complexes

The pyrazole and imidazole complexes of V(II) were found to be very stable in absence of air and humidity, but they were quickly hydrolyzed in presence of traces of atmospheric air. As it was mentioned above, these complexes are quite labile in solution, the ligands being quickly substituted by methanol in methanolic solutions.

Infrared Spectra

The infrared data of $VCl_2(\text{imidazole})_6$ and $VCl_2(\text{pyrazole})_4$ in the crystalline state are summarized in Table III along with the frequencies of other related compounds.

$VCl_2(\text{imidazole})_6$

The spectrum of $VCl_2(\text{imidazole})_6$ exhibits two well-resolved absorption bands at 313 and 202 cm^{-1} of very strong intensity in the far infrared region. Assuming O_h symmetry with six imidazole ligands coordinated through the tertiary nitrogen, only one stretching mode is expected in the vanadium–nitrogen region.

The absorption peak observed at 313 cm^{-1} can be attributed to ν_3 (f_{1u}) vanadium–nitrogen asymmetric

TABLE II. Effective Magnetic Moments in B.M. at appr. 293° K.

Compound	$M_{\text{eff}} = (X \text{ mol. cor. } T)^{1/2} \mu_B$
$VCl_2(\text{imidazole})_6$	3.77
$VCl_2(\text{pyrazole})_4$	3.66
$VCl_2(\text{pyridine})_4$	3.88 ^a
$VCl_2(\text{CH}_3\text{OH})_4$	3.91 ^a
$VCl_2(\text{acetonitrile})_4$	3.82 ^a
$VCl_2(\gamma\text{-picoline})_4$	3.77 ^b

^a Ref. 3. ^b Ref. 4b.

TABLE III. Vibrational Frequencies of Pyrazole, Imidazole and Pyridine Complexes with Vanadium (II) Chloride below 400 cm^{-1} .

Compound	Metal–Nitrogen Stretch	Metal–chlorine Stretch	Further Bands
$VCl_2(\text{imidazole})_6$	312 vs ^a		203 vs 183 ^b w 144 ^b s 136 s 100 ^b w 85 ^b m 70 w 53 w
$VCl_2(\text{pyrazole})_4$	292 vs	312 vs	197 sbr 175 w 139 ^b s 93 m 70 w 43 mw
$VCl_2(\text{pyridine})_4$	276 vs	311 vs	202 s 178 m 161 m 141 s 104 w 78 w 54 m 45 w

^a vs, very strong; s, strong; sbr, strong broad; m, medium; w, weak; mw, medium weak. ^b Ligand modes.

stretch. This value is in accordance with a number of six-coordinate imidazole complexes with various divalent transition metal ions reported in the literature.^{4b, 10, 11}

The second absorption at 202 cm^{-1} is attributed to a bending mode $\delta(\text{NMN})$ rather than a band arising from the splitting of ν_3 , since it appears at much lower wavelengths (202 cm^{-1}) than ν_3 (313 cm^{-1}). This is in accordance with the assignment for $Ni(\text{NH}_3)_6\text{Cl}_2$ by Nakagawa and Simanouchi¹² (ν_3 at 330 cm^{-1} and ν_4 at 215 cm^{-1}) and other similar complexes.¹²

The possibility of a species of lower symmetry [$VCl_2(\text{imidazole})_4$], that is of D_{4h} or C_{2v} symmetry must also be excluded, since such a species requires a far greater number of fundamentals than may reasonably be found in the observed vibrational spectrum.

$VCl_2(\text{pyrazole})_4$ and $VCl_2(\text{pyridine})_4$

The far infrared spectrum of $VCl_2(\text{pyrazole})_4$ exhibits three very strong bands in the 400–200 cm^{-1} region. If we assume the presence of discrete six-coordinate octahedral species there exists the possibility of *cis* or *trans* configuration. For the *trans* configuration (D_{4h} symmetry) only one infrared-active fundamental vanadium–chlorine stretching mode is ex-

pected of symmetry type e_u . For the *cis* configuration (C_{2v} symmetry) at least two fundamentals associated with the vanadium–chlorine stretching modes are expected to be observed in the region under discussion. We can, therefore, in principle, distinguish between *cis* or *trans* configuration.

The two very strong broad bands observed at 312 and 292 cm^{-1} in the infrared spectrum of $\text{VCl}_2(\text{pyrazole})_4$ are attributed one to vanadium–chlorine and the other to vanadium–nitrogen stretching modes. A difficulty arises with the assignments of these bands, since both of them appear so close; electronegativity differences or steric factors involved could shift the vanadium–nitrogen band from 312 cm^{-1} observed in $\text{VCl}_2(\text{imidazole})_6$ to lower frequencies.

Literature reports of the infrared spectra of crystalline hexachlorovanadates¹³ indicate a strong absorption around 330 cm^{-1} and complexes of vanadium(III) chloride with various ligands, where octahedral symmetry is assumed around the vanadium(III) ion, give strong absorptions in the range 300–350 cm^{-1} , which are attributed to vanadium–chlorine stretching frequencies. By comparison of our spectra with those reported for $\text{VX}_2(\gamma\text{-pic.})_4$ (where X = Cl, Br, I),^{4b} we could tentatively attribute the band observed at 312 cm^{-1} as the vanadium–chlorine stretching mode. The second band observed at 292 cm^{-1} was attributed to the vanadium–nitrogen stretching mode in agreement with previous reports^{4b, 10, 17–19} of metal–nitrogen stretching modes.

The possibility that the band at 292 cm^{-1} arises from removal of degeneracy of the mode, and therefore is also a vanadium–chlorine vibration is very unlikely due to absence of vanadium–nitrogen bands in that case. Also a far more complicated spectrum should have been observed in the region 150–350 cm^{-1} (four metal–nitrogen and two metal–halogen absorption bands for C_{2v} symmetry).

Furthermore, the spectrum of $\text{VCl}_2(\text{pyridine})_4$ which was reported to be isostructural with $\text{NiCl}_2 \cdot 4\text{py}$ ²⁰ exhibited an infrared spectrum very similar to $\text{VCl}_2(\text{pyrazole})_4$, giving evidence that the species is a monomeric *trans* octahedral unit of D_{4h} symmetry, although further support is required from Raman data or solution spectra for the above suggestion.

All bands attributed to vanadium–chlorine or vanadium–nitrogen modes were broad and could contain several unresolved peaks, in which case some distortion from the proposed symmetries should be expected. The breadth of these absorptions is not unexpected, however, since these fundamentals are either doubly (e_u) or triply (f_{1u}) degenerate modes, and crystal effects can lower this degeneracy sufficiently to give rise to broad bands. Similar effects have been observed

in the solid state spectra involving degenerate vibrations.^{21–23}

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