906. *Some Chloro-complexes of Vanadium*(IV)

By P. A. Kilty and D. Nicholls

Hexachlorovanadates(IV) have been prepared by fission of the V=O bond in oxytetrachlorovanadates(IV) using thionyl chloride. The new complexes have been characterised and the thermal decomposition of $(pyH)_2VCl_6$ and Cs_2VCl_6 studied; the latter yields the pentachlorovanadate(III). The complex $[py_2VCl_4]$ has been obtained using an excess of vanadium(IV) chloride in toluene at −20°. The chemistry of pyridine and of some pyridine-containing vanadium(IV) compounds in liquid hydrogen chloride has been studied, and it has been shown that hexachlorovanadates(IV) can be prepared in this medium from vanadium(IV) chloride, but not from the $VOCl_4^{2-}$ complexes.

The general route available for the preparation of hexachlorometallates of Group IVA transition elements, *i.e.*, the reaction of MCl_4 ($M = Ti$ or Zr) with a chloride of a univalent cation in aqueous or ethanolic hydrogen chloride,[1] with vanadium(IV) chloride leads only to oxychloride complexes. The alternative general route [2] to hexahalogeno-complexes, *i.e.*, the high-temperature reaction between the transition-metal halide and the alkali-metal halide, is also impracticable for vanadium(IV) chloride. It is apparent therefore that hexachlorovanadates(IV) must be prepared in solvents which are incapable of solvolysing the VCl_6^{2-} ion. Conductimetric evidence has been presented for the formation of K_2VCl_6 in iodine monochloride,[3] but we have not been able to isolate a pure product from the reaction of potassium and vanadium(IV) chlorides in this solvent. While our work was in progress, the diethyl- and triethyl-ammonium hexachlorovanadates were synthesised [4] by reaction of vanadium(IV) chloride with the alkylammonium chlorides in chloroform. We have characterised [5] a variety of oxychloride complexes of vanadium(IV) and report here the conversion of oxytetrachlorovanadates into hexachlorovanadates by reaction with thionyl chloride, together with some chemistry of pyridine and vanadium(IV) chloride in liquid hydrogen chloride.

The Preparation of Hexachlorovanadates(IV) *in Thionyl Chloride*.—The green oxychlorides, M_2VOCl_4 (M = pyridinium, quinolinium, or isoquinolinium), dissolve in thionyl chloride at room temperature giving dark red solutions with evolution of sulphur dioxide,

$$M_2VOCl_4 + SOCl_2 \longrightarrow M_2VCl_6 + SO_2$$

Evaporation of the solutions give the dark red, almost black hexachlorovanadates(IV) in quantitative yield. When $M = Cs^+$, K^+, or NH_4^+, the oxychlorides are insoluble in thionyl chloride; they are, however, slightly soluble in methyl cyanide and more soluble in nitromethane. Cæsium hexachlorovanadate(IV) can thus be obtained by treating the complex oxychloride with a 20—30% solution of thionyl chloride in nitromethane and stirring

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[1] G. W. A. Fowles and D. Nicholls, *J. Inorg. Nuclear Chem.*, 1961, **18**, 130; J. E. Drake and G. W. A. Fowles, *ibid.*, p. 136.

[2] G. W. A. Fowles, " Preparative Inorganic Reactions," vol. I, Interscience, 1964, p. 130.

[3] V. Gutmann, *Z. anorg. Chem.*, 1951, **264**, 151.

[4] G. W. A. Fowles and R. A. Walton, *J. Inorg. Nuclear Chem.*, 1965, **27**, 735.

[5] P. A. Kilty and D. Nicholls, unpublished results.

the reaction mixture at room temperature for two days. In view of the use of sulphur dioxide for preparing oxychlorides, *e.g.*, the conversion of $MoCl_5$ into $MoOCl_3$,[6] we were at first surprised to find quantitative fission of the vanadium–oxygen bond. Pyridinium hexachlorovanadate(IV) gives a red solution in liquid sulphur dioxide but no reaction occurs on standing the solution for one week at 0°.

Recently, thionyl chloride has been used in the synthesis of a number of transition-metal chloro-complexes from the simple chlorides; vanadium(III) chloride reacts with tetraethylammonium chloride in the boiling solvent to form the binuclear complex $(Et_4N)_3V_2Cl_9$.[7] The fission of metal–oxygen bonds with thionyl chloride has been used in the preparation of chlorocomplexes of rhenium,[8] protactinium, niobium, tantalum,[9] and uranium [10] so that the method is becoming of quite wide application. The fission of vanadium–oxygen bonds with thionyl chloride has been used in the conversion of oxides and oxychlorides of vanadium(III) and vanadium(IV) into vanadium(III) chloride,[11] and niobium(V) chloride has been prepared similarly from hydrated niobium(V) oxide.[12]

The hexachlorovanadates(IV) (Table 1) are extremely sensitive to hydrolysis but are otherwise stable up to 50° (or higher in the case of the alkali-metal salts) in dry air. They give red solutions in methyl cyanide, and their molar conductivities are compatible with their formulation as 1 : 2 electrolytes.[13] Their room-temperature magnetic moments are close to the spin-only values and characteristic of vanadium(IV) complexes. The infrared (i.r.) spectra of the hexachlorovanadates (in the region 700—5000 cm.$^{-1}$) show only the absorption bands due to the organic cations; on allowing the specimens to hydrolyse in moist air for one minute, a strong sharp peak appears in the V=O stretching region at 970 cm.$^{-1}$. The visible spectra of solutions of $(pyH)_2VCl_6$ in methyl cyanide show two absorption maxima. The peak around 15,400 cm.$^{-1}$ ($\varepsilon_{max.} = 89$) must be due to the $^2T_{2g} \longrightarrow {}^2E_g$ transition in the octahedral d^1 anion VCl_6^{2-}. This peak is expectedly somewhat broad and asymmetric as a result of Jahn–Teller distortion of the excited state. A *Dq* value of 1540 cm.$^{-1}$ is thus obtained as compared to the hypothetical value [14] of 2000 cm.$^{-1}$ obtained using the VCl_4 tetrahedral absorption at 9000 cm.$^{-1}$ and the ionic approximation $Dq(\text{tet.}) = -{}^4/_9\, Dq(\text{oct.})$. The peak at 21,050 cm.$^{-1}$ ($\varepsilon_{max.} = 1040$) is probably due to charge transfer. Similar spectra were obtained on solid hexachlorovanadates(IV) using diffuse reflectance, but the peaks were considerably broadened.

TABLE 1

Hexachlorovanadates(IV)

	Found (%)		Theory (%)		Λ_M ohm^{-1} cm.^{2} (~10^{-3}M in MeCN)	μ_{eff} (B.M.) (at 20°)
	Cl	V	Cl	V		
$(pyH)_2VCl_6$	50·4	12·1	50·1	12·1	180	1·74
$(\text{quin H})_2VCl_6$	41·5	9·8	40·6	9·7	—	1·74
$(\text{isoquin H})_2VCl_6$	39·7	9·8	40·6	9·7	206	1·73
$Cs_2\ VCl_6$	39·6	9·7	40·2	9·6	—	1·75

py = pyridine; quin = quinoline; isoquin = isoquinoline.

On thermal decomposition to 130°, $(pyH)_2VCl_6$ evolves approximately 1 mol. of hydrogen chloride with the sublimation of a red solid of variable composition; a tensimetric study of this material in liquid hydrogen chloride (Figure 3c) shows it to be an approximately equimolar mixture of $(pyH)_2VCl_6$ and $[py_2VCl_4]$. Its i.r. absorption spectrum shows the presence of both co-ordinated pyridine (the absorption frequencies being exactly the same as

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[6] D. A. Edwards, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1198.
[7] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J.*, 1963, 2189.
[8] K. W. Bagnall, D. Brown, and R. Colton, *J.*, 1964, 3017.
[9] K. W. Bagnall and D. Brown, *J.*, 1964, 3021.
[10] K. W. Bagnall, D. Brown, and J. du Preez, *J.*, 1964, 2603.
[11] H.-J. Seifert, *Z. anorg. Chem.*, 1962, **317**, 123.
[12] D. C. Bradley, B. N. Chakravarti, and W. Wardlaw, *J.*, 1956, 2381.
[13] B. J. Hathaway and A. E. Underhill, *J.*, 1960, 3705.
[14] C. J. Ballhausen, " Introduction to Ligand Field Theory," McGraw-Hill, 1962, p. 228.

those found in [py_2VCl_4]) and the pyridinium ion. The major reaction occurring is thus:

$$(pyH)_2VCl_6 \longrightarrow [py_2VCl_4] + 2HCl$$

Some recombination then occurs in the cooler parts of the sublimation apparatus. Above 130° a small amount of unsublimed [py_2VCl_4] decomposes to [$pyVCl_3$] with evolution of pyridine and necessarily some oxidation product of pyridine (which we have not identified). Since [py_2VCl_4] is apparently unreported previously we have prepared this material by an independent route and studied its thermal decomposition (see later).

Cæsium hexachlorovanadate(IV) is much more stable thermally. Decomposition begins at 210° and by 284° one gram-atom of chlorine has been evolved per mole of Cs_2VCl_6. No further weight loss occurs on heating to 352°. The violet residue of Cs_2VCl_5 has a room-temperature magnetic moment of 2·56 B.M., confirming that reduction has occurred. Its diffuse reflectance spectrum (Figure 1a) shows a fairly sharp peak at 17,700 cm.$^{-1}$ and a weaker, broader band centred at 11,200 cm.$^{-1}$; it is sufficiently different from that of vanadium(III) chloride (Figure 1b) to rule out the formulation of " Cs_2VCl_5 " as a mixture of 2CsCl + VCl_3. Our spectrum of VCl_3 is in agreement with that recently obtained by Clark.[15] Other workers[16] have recorded the spectra of VCl_3 in the LiCl–KCl eutectic at 400° and interpret the absorptions at 18,020 and 11,000 cm.$^{-1}$ as the ${}^3T_{1g} \longrightarrow {}^3T_{1g}(P)$ and ${}^3T_{1g} \longrightarrow {}^3T_{2g}$ transitions in the octahedral VCl_6^{3-} ion. Whilst our spectrum of Cs_2VCl_5 is similar, the presence of Cs_3VCl_6 in our material would necessitate the presence of $CsVCl_4$ also. The VCl_4^- species, however, absorbs at somewhat lower frequencies (and with higher intensities) and such absorptions are absent from our spectrum. The co-ordination around the vanadium atom in the pentachlorovanadate(III) appears therefore to be approximately octahedral; there is still the possibility, however, of " Cs_2VCl_5 " being a mixture of Cs_3VCl_6 and $Cs_3V_2Cl_9$.

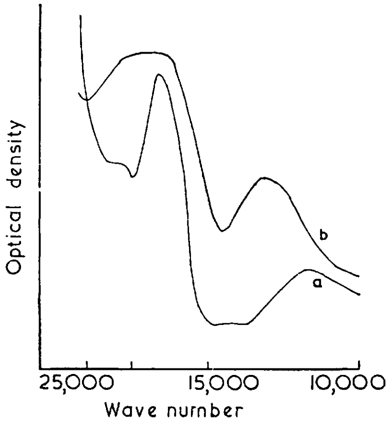

FIGURE 1. Diffuse reflectance spectra of (a) Cs_2VCl_5 and (b) VCl_3

Bis(pyridine)vanadium(IV) *Chloride*.—The reduction of highest-valency transition-metal halides with pyridine has been widely demonstrated in recent years. Thus, for example tantalum(IV) iodide can be conveniently prepared by reducing tantalum(V) iodide with pyridine to [py_2TaI_4], followed by thermal decomposition of this complex.[17] Vanadium(IV) chloride is reduced in an excess of pyridine at room temperature giving, amongst other products, [py_3VCl_3].[18] We have succeeded in isolating the dark red vanadium(IV) complex, [py_2VCl_4], by reacting a slight excess of the halide with pyridine in toluene solution at −20°. Its room-temperature magnetic moment, $\mu_{\text{eff}} = 1{\cdot}80$ B.M., and oxidation-state titration with permanganate, confirm that little or no reduction to vanadium(III) has

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[15] R. J. H. Clark, *J.*, 1964, 417.

[16] D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, 1962, **66**, 57.

[17] R. E. McCarley and J. C. Boatman, *Inorg. Chem.*, 1963, **2**, 547.

[18] M. W. Duckworth, Ph.D. Thesis, Southampton, 1962.

occurred. The infrared spectrum is typical of complexes containing co-ordinated pyridine;[19] the existence of single absorption peaks at 751 and 676 cm.$^{-1}$ suggests that the complex is *trans*-[VCl_4py_2] since these bands are split into several components in the lower symmetry *cis*-octahedral [py_2MX_4] compounds.[20]

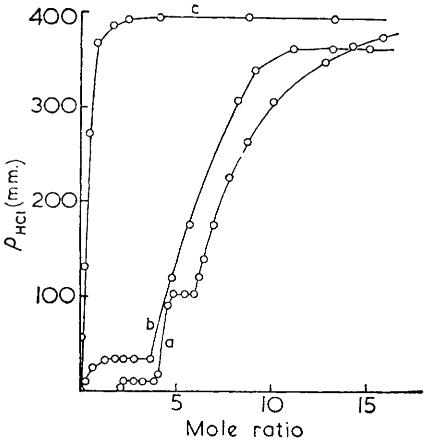

FIGURE 2. Tensimetric studies (at −96°) of the systems

(a) pyridine–HCl,
(b) VCl_4–2pyHCl–HCl, and
(c) VCl_4–HCl

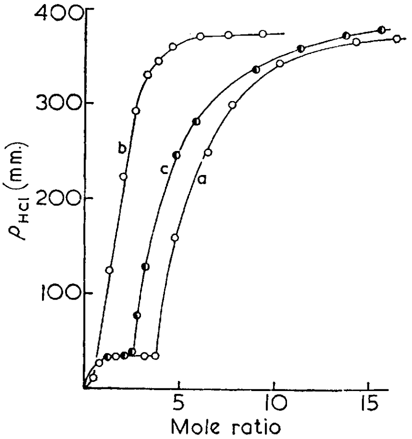

FIGURE 3. Tensimetric studies (at −96°) in the systems

(a) $(pyH)_2VCl_6$,
(b) [py_2VCl_4], and
(c) sublimate in thermal decomposition of $(pyH)_2VCl_6$

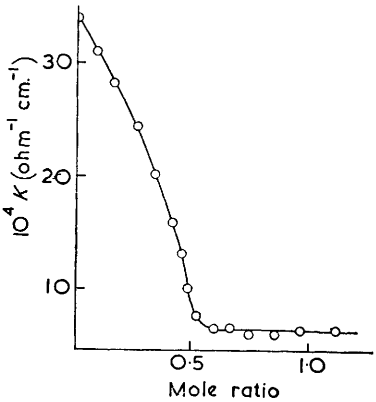

FIGURE 4. Conductimetric titration of VCl_4 against pyridine in hydrogen chloride at −96°

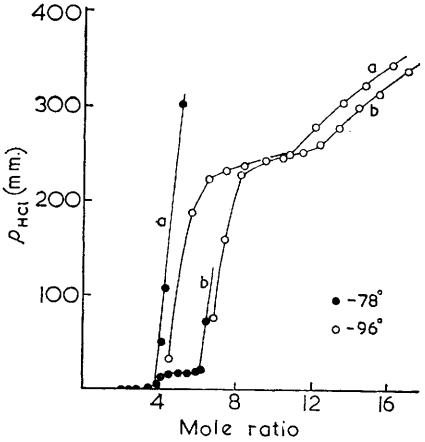

FIGURE 5. Tensimetric study of the systems

(a) $(pyH)_2VOCl_4$–HCl and
(b) $(pyH)_2VOCl_4,2H_2O$–HCl

Bis(pyridine)vanadium(IV) chloride is insoluble in benzene, toluene, and iso-octane but dissolves in acetone and thionyl chloride, and gives only feebly-conducting solutions in methyl cyanide. The diffuse reflectance and methyl cyanide solution spectra show the *d–d* transition at 15,750 cm.$^{-1}$ with a more intense charge-transfer band centred at 21,050 cm.$^{-1}$. It is not possible to resolve the *d–d* peak into the two transitions $^2B_{2g} \longrightarrow {}^2A_{1g}$

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[19] N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.
[20] G. S. Rao, *Z. anorg. Chem.*, 1960, **304**, 176.

and ${}^2B_{2g} \longrightarrow {}^2B_{1g}$, expected for the tetragonally distorted (D_{4h}) structure. Solutions in thionyl chloride show similar spectra except that the *d–d* transition is moved to slightly higher frequency and the spectra are almost identical with those of $(pyH)_2VCl_6$ dissolved in thionyl chloride; $[py_2VCl_4]$ is probably converted into $(pySOCl)_2[VCl_6]$ in this solvent.

Sublimation of $[py_2VCl_4]$ is slow at 132°/10^{-3}mm., and at higher temperatures some reduction occurs, giving a violet residue of empirical formula close to $[pyVCl_3]$. As only small quantities of this material have been produced we have been unable to characterise it fully. It does not sublime at, and is stable up to, 200° *in vacuo*.

Reaction of Pyridine and some Pyridine-containing Vanadium(IV) *Compounds in liquid Hydrogen Chloride*.—Pyridine forms a saturated solution in hydrogen chloride at —96° containing *ca.* 17 mole % of the base. The vapor pressure–composition isotherm (Figure 2a) shows the existence of two phases, py,4HCl and py,2HCl; these we believe to contain chloride ions hydrogen-bonded to hydrogen chloride molecules,[21] *i.e.*, $pyH^+(Cl,3HCl)^-$ and $pyH^+(Cl,HCl)^-$. Vanadium(IV) chloride is insoluble in and does not react with hydrogen chloride at —96° (Figure 2c). A red solution is formed, however, when vanadium(IV) chloride is condensed on to pyridinium chloride in liquid hydrogen chloride, and a mixture of pyridine and vanadium(IV) chloride (2 : 1 mole ratio) gives quite a different isotherm (Figure 2b) from that of pyridine. This isotherm is in fact identical to that of $(pyH)_2VCl_6$ (Figure 3a); the univariant portions in these isotherms being attributed to the formation of saturated solutions of the hexachlorovanadate(IV). The formation of pyridinium hexachlorovanadate(IV) in liquid hydrogen chloride is confirmed by the conductimetric titration of vanadium(IV) chloride against pyridine at —96°. Pyridinium chloride is a strong base in liquid hydrogen chloride and titration with the strong chloride-ion acceptor vanadium(IV) chloride, results in a progressive lowering of the conductivity until all the base is converted into $(pyH)_2VCl_6$. The shape of the conductimetric titration curve (Figure 4) is very similar to that obtained by Waddington and Klanberg [22] in the titration of tetramethylammonium chloride with boron trichloride. Evaporation of solutions containing an excess of vanadium(IV) chloride yields pyridinium hexachlorovanadate(IV) contaminated with some vanadium(III) chloride. A fairly pure product is obtained, however, if only a slight excess of vanadium(IV) chloride over pyridine is used. Bis(pyridine)vanadium(IV) chloride is insoluble in, and does not react with, hydrogen chloride at —96° (Figure 3b).

Both the hydrates and the anhydrous salts containing the $VOCl_4^{2-}$ anion, where the cation is a protonated aromatic amine, dissolve in liquid hydrogen chloride at —96° forming green solutions, which soon turn dark red-brown and deposit some insoluble material. Tensimetric studies in the systems $(pyH)_2VOCl_4$–HCl (Figure 5a) and $(pyH)_2VOCl_4 \cdot 2H_2O$–HCl (Figure 5b) indicate a saturated solution dissociation pressure of 240 mm., and the pressure drops below 1 mm. at a composition $(pyH)_2VOCl_4,4HCl$. The curve for the dihydrate differs from that of the anhydrous salt only in showing a univariant portion with a dissociation pressure of 16 mm. at —78° and this step corresponds therefore to the dissociation

$$H_3OCl \rightleftharpoons H_2O + HCl$$

The absence of a univariant portion at 16 mm. dissociation pressure in the $(pyH)_2VOCl_4$–HCl tensimetric indicates, therefore, that the reaction

$$(pyH)_2VOCl_4 + 2HCl \longrightarrow (pyH)_2VCl_6 + H_2O$$

has not occurred. The continued removal of hydrogen chloride from either system results in the formation of a composition $(pyH)_2VOCl_4,2HCl$ at —78°. In order to examine separately the soluble and insoluble products, we carried out the reaction between $(pyH)_2VOCl_4$ and liquid hydrogen chloride in a filtration apparatus. At —96° the reaction gives a red

[21] P. A. Kilty and D. Nicholls, *Chem. and Ind.*, 1963, 1123.
[22] T. C. Waddington and F. Klanberg, *J.*, 1960, 2332.

insoluble product (which turns violet upon losing hydrogen chloride *in vacuo*) and a pale, heterogeneous soluble product. Analysis of these materials suggests that the major reaction occurring is

$$(pyH)_2VOCl_4 \longrightarrow (pyH)VOCl_3 + pyHCl$$

The oxidation-state titrations and room-temperature magnetic moments show that some disproportionation also occurs however, so that the insoluble product contains V^{5+} and the soluble product, V^{3+}. The insoluble product is probably a mixture of $(pyH)VOCl_3$ and $(pyH)_2VOCl_5$; its colour is very similar to that of other $VOCl_3^-$ compounds and its visible spectrum has a peak at 19,000 cm.$^{-1}$, an absorption found in all $VOCl_3^-$ compounds.[5] The infrared spectrum of the insoluble product shows sharp absorptions in the V–O stretching region at 1002 and 993 cm.$^{-1}$; a further two broad bands at 903 and 880 cm.$^{-1}$ are characteristic of V–O–V stretching frequencies in polymeric $VOCl_3^-$ compounds. In view of the heterogeneous nature of these reaction products, the tensimetric study becomes difficult to interpret; the composition $(pyH)_2VOCl_4,2HCl$, stable at −78°, represents largely a mixture of $(PyH)VOCl_3,HCl$ and $(pyH)HCl_2$, but the reaction is obviously more complicated, and does not appear to involve the fission of the V–O bond in $VOCl_4^{2-}$. It is interesting to note, however, that at room temperature a green solution of $(pyH)_2VOCl_4$ in methyl cyanide turns red on saturation with dry hydrogen chloride and the resulting solution absorbs intensely at 21,000 cm.$^{-1}$ so that VCl_6^{2-} species are probably formed under these conditions.

EXPERIMENTAL

All operations were carried out under rigorously anhydrous conditions in high-vacuum apparatus or in an atmosphere of dry oxygen-free nitrogen.

Materials.—Vanadium(IV) chloride was prepared from the pure elements at 400° and fractionated *in vacuo*, prior to use, to remove vanadium(III) chloride and chlorine. Vanadium(III) chloride was prepared by thermal decomposition of vanadium(IV) chloride. Hydrogen chloride and sulphur dioxide were dried over phosphorus pentoxide prior to vacuum fractionation. Methyl cyanide was refluxed over barium oxide, distilled several times *in vacuo* from phosphorus pentoxide, and finally from pyridinium hexachlorovanadate(IV). Thionyl chloride was vacuum fractionated; pyridine was dried over bis(pyridine)silicon tetrachloride.

Analytical Methods.—Vanadium was estimated by permanganate titration; this titration was also used to estimate the oxidation state of vanadium in reaction products. Chlorine was estimated gravimetrically. Gases evolved in thermal decompositions were identified by infrared spectra and molecular-weight estimations.

Magnetic and Spectroscopic Methods.—Magnetic moments were measured by the Gouy method at room temperature using a permanent magnet of field strength 8000 gauss in conjunction with an Oertling semi-micro balance. Visible spectra were recorded on a Unicam S.P. 500 which was fitted with the standard attachment when measuring the diffuse reflectance spectra of solid samples.

Preparation of Hexachlorovanadates(IV).—(*a*) *In thionyl chloride.* In a typical reaction, $(pyH)_2VOCl_4$ (3·15 mmoles) was treated with an excess (10 ml.) of thionyl chloride *in vacuo* and the reaction mixture set aside for 12 hr. at 20°. The volatile products were then thrice fractionated through −78° traps to remove $SOCl_2$ and finally through −78° and −117° traps. The −117° trap collected 3·22 mmoles of a gas (Found *M*, 65; i.r. spectrum identical to that of SO_2). The residual dark red hexachlorovanadate (3·18 mmoles) was evacuated for several hours at 45° prior to analysis. Analytical results are presented in Table 1.

(*b*) *Using thionyl chloride in nitromethane.* The cæsium salt Cs_2VOCl_4 is insoluble in thionyl chloride but sparingly soluble in nitromethane. Accordingly, Cs_2VOCl_4 (2 g.) was stirred for 2 days at room temperature in nitromethane (20 ml.) to which thionyl chloride (6 ml.) had been added. The reaction mixture was allowed to settle for 2 hr., after which the solvent was decanted and the red-black residue of Cs_2VCl_6 evacuated at 70° for many hours.

Reaction of $(pyH)_2VCl_6$ *with Liquid Sulphur Dioxide.*—An excess (20 ml.) of sulphur dioxide was distilled on to $(pyH)_2VCl_6$ (0·594 g.), the mixture sealed in an ampoule, and kept at 0° for 1 week. Some of the solid dissolved, giving a dark red brown solution, but there was no apparent reaction, After the sulphur dioxide had been distilled off, the residue was analysed (Found: Cl, 49·2; V, 11·9. Calc. for $(pyH)_2VCl_6$; Cl, 50·1; V, 12·1%).

Thermal Decomposition of Hexachlorovanadates.—(*a*) $(pyH)_2VCl_6$. Stepwise (20° intervals) thermal decomposition of $(pyH)_2VCl_6$ (0·583 g.) to 210° *in vacuo*, gave (i), a dark red sublimate (0·445 g.), which began to appear above 56° (Found: Cl, 46·0; V, 13·4%); oxidation state of vanadium = 4·0, i.r. spectrum showing all peaks present in the spectra of $(pyH)_2VCl_6$ and $[py_2VCl_4]$; a second experiment gave a sublimate of composition Cl, 43·4; V, 12·1%): and (ii), a violet *residue* (0·046 g.) (Found: Cl, 45·7; V, 19·4%; $[pyVCl_3]$ requires, Cl, 45·0; V, 21·5%). Hydrogen chloride (0·049 g.) (Found: *M*, 38) was evolved between 100 and 130° and pyridine (0·026 g.) between 130 and 210°. Traces of sulphur dioxide and thionyl chloride were evolved between 20 and 100°; these arose from traces of thionyl chloride absorbed on the starting material.

(*b*) Cs_2VCl_6. Up to 210°, Cs_2VCl_6 (0·613 g.) lost virtually no weight *in vacuo*; by 284° there was 7·41% loss of weight (all chlorine). No further weight loss occurred on heating to 352°; the pale violet *residue* (0·568 g.) (Found: Cl, 35·5; V, 10·3. Cs_2VCl_5 requires Cl, 35·9; V, 10·3%) had μ_{eff} = 2·56 B.M. at 20°.

Preparation and Thermal Decomposition of $[py_2VCl_4]$.—Pyridine (2 mol.) was distilled on to vanadium(IV) chloride (1·1 mol.) in toluene and the reaction mixture warmed to −23°. A brick-red solid was isolated by distilling off the solvent and excess of vanadium(IV) chloride; the *product* was purified by sublimation *in vacuo* at 132° {Found: Cl, 41·5; V, 14·3%; oxidation state of V = 4·0, μ_{eff} (20°) = 1·80 B.M. $[py_2VCl_4]$ requires Cl, 40·4; V, 14·5%}.

At 174°, $[py_2VCl_4]$ (0·396 g.) gave (i) a sublimate, the upper part of which was red (0·209 g.) (Found: Cl, 41·7; V, 15·5. Calc. for $[py_2VCl_4]$: Cl, 40·4; V, 14·5%) and the lower part pale brown owing to decomposition (Found: Cl, 32·7; V, 15·8%); and (ii) a violet residue (0·056 g.) (Found: Cl, 45·9; V, 24·5. Calc. for $[pyVCl_3]$: Cl, 45·0; V, 21·5%). An unmeasured quantity of pyridine was evolved during the decomposition.

Reactions in Liquid Hydrogen Chloride.—Vapour pressure–composition isotherms were measured in a tensimeter especially designed to minimise the dead-space. Conductimetric titrations were carried out in a 25-ml. cell fitted with a vacuum-tight magnetically operated stirrer. The electrodes were of bright platinum. Waddington's method [22] of removing the solvent before each addition of titrant was used. The filtration and extraction procedures using liquid hydrogen chloride were carried out in an apparatus similar to that used previously for liquid ammonia.[23] Analytical results for the products obtained from the reaction of $(pyH)_2VOCl_4$ with hydrogen chloride at −96° are presented in Table 2.

TABLE 2

Reaction products of the $(pyH)_2VOCl_4$–HCl reaction

Insoluble product					Soluble product				
V (%)	Cl (%)	μ_{eff}	% V as V^{5+}	V : Cl	V (%)	Cl (%)	μ_{eff}	% V as V^{3+}	V : Cl
16·1	43·1		35	1 : 3·86	10·6	37·9		28	1 : 5·14
17·3	42·6	1·20	46	1 : 3·53	10·9	38·9	1·96	13	1 : 5·12

The i.r. spectra of both products show all the absorptions associated with the pyridinium ion and, in addition, the insoluble product has absorptions at 1002vs, 993vs, 903vs, and 880vs cm.$^{-1}$ while the soluble product absorbs at 990vs cm.$^{-1}$ with no absorption around 900 cm.$^{-1}$.

In the reactions between pyridine and vanadium(IV) chloride in liquid hydrogen chloride, the pyridine was distilled into a reaction vessel followed by hydrogen chloride and vanadium (IV) chloride. The reaction mixtures were stirred for 2 hr. at −96° prior to removal of all volatile materials and evacuation of the residue at room temperature. Using a VCl_4 : py mole ratio of 0·76, the product had Cl, 50·4; V, 13·8; pyH (by difference) 35·8%, giving a ratio V : Cl : pyH = 1·00 : 5·24 : 1·65, *i.e.*, equivalent to *ca.* 0·83 $(pyH)_2VCl_6$ + 0·17 VCl_3. With a reacting ratio of 0·57 (VCl_4 : py), the dark red *product* had Cl, 49·7; V, 12·7% [$(pyH)_2VCl_6$ requires Cl, 50·1; V, 12·1%].

Infrared Spectra.—These were measured as mulls on a Grubb–Parsons double-beam instrument using sodium chloride optics; the following peaks were obtained (cm.$^{-1}$): $(pyH)_2VCl_6$: 1637m, 1601s, 1529s, 1482s, 1325m, 1270w, 1242w, 1196m, 1164w, 1054m, 1034w, 1028w, 1024w,

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[23] D. Nicholls, Ph.D. Thesis, Southampton, 1959.

1007w, 981vw, 867w, 740vs, 666vs. After being opened to the air for a few minutes, this sample gave an identical spectrum, with an additional very strong sharp peak at 970 cm.$^{-1}$ (ν V=O); (quin H)$_2$VCl$_6$: 1626m, 1590m, 1544m, 1480w, 1294m, 1266w, 1224m, 1204m, 1160w, 1146m, 1131w, 952w, 882w, 839w, 799vs, 771w, 730m; (iso-quin H)$_2$VCl$_6$: 1637s, 1608m, 1584m, 1535m, 1490w, 1394m, 1279m, 1258m, 1238w, 1209w, 1171m, 1158m, 1036m, 1015m, 972vw, 953w, 892m, 864m, 813vs, 789m, 770w, 762w, 743m; [py$_2$VCl$_4$]: 1596s, 1515w, 1475m, 1437s, 1348w, 1263vw, 1236w, 1211s, 1155w, 1090w, 1063s, 1040m, 1012s, 942w, 751w, 861vs, 676vs.

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