THE COORDINATION CHEMISTRY OF VANADIUM

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CONTENTS

A. INTRODUCTION

This review is concerned with the chemistry of vanadium complexes; simple compounds will be described only where they have features of interest in co-ordination chemistry. A suitable source of information up to 1949 can be found in Sidgwick's book[1] and this information will not be repeated here. Excellent and comprehensive reviews on compounds of oxovanadium(IV) have recently appeared[2] and so these too will not be discussed here. There are virtually no previous reviews on the other complexes of vanadium; the magnetic properties of vanadium compounds have been discussed by Figgis and Lewis[3], the reactions of vanadium halides with nitrogen bases surveyed by Fowles[4] and the absorption spectra of vanadium complexes summarised by Ballhausen[5] and by Jørgensen[6].

Vanadium has a particularly interesting chemistry. The ground state electronic configuration is $4s^2 3d^3$ and it exhibits compounds in all oxidation states from $+5$ (d^0) to -1 (d^6). In this review we shall use these oxidation states as a means of classifying the co-ordination compounds*.

B. OXIDATION STATES -1, 0 AND $+1$

These low formal oxidation states of vanadium are found in compounds with the usual ligands capable of stabilising such states, i.e. CN^-, CO, tertiary phosphines, bipyridyl, phenanthroline, and possibly also in some complexes of bidentate sulphur donors.

(i) Cyanide complexes

Only one cyanide complex has been characterised; this is the interesting orange compound $K_5[V(CN)_5NO \cdot H_2O]$ obtained in the reaction of hydroxylamine hydrochloride with potassium vanadate in the presence of an excess of cyanide and hydroxyl ions[7]. It is diamagnetic and the N–O stretching frequency appears at 1575 cm^{-1} indicating that the nitric oxide is present as NO^+ and hence vanadium as V^{1-}. Reduction of a solution of potassium hexacyanovanadate(III) with potassium in liquid ammonia yields a brown precipitate which is pyrophoric in air and contains vanadium in a low-oxidation state[8].

(ii) Carbonyl complexes

Although hexacarbonyl vanadium was first described only some seven years ago[9], its chemistry is now quite extensive. It is a volatile, air sensitive, blue-green substance which decomposes at 60–70°. Being one electron short of the inert-gas configuration the molecule is paramagnetic in the solid state ($\mu_{eff} = 1.73$ BM at 300 °K) and in solution in benzene or toluene[10]. Indeed the ease of formation of the hexacarbonylvanadate(–I) ion which has the inert gas configuration is a

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* Abbreviations: bipy, 2,2′-bipyridyl; phen, 1,10-phenanthroline; py, pyridine; diglyme, diethylene glycol dimethyl ether; THF, tetrahydrofuran; diars, *o*-phenylenebisdimethylarsine.

characteristic feature of its chemistry. The carbonyl is most conveniently prepared from the hexacarbonylvanadate(–I) by acidification:

$$[V(CO)_6]^- + H^+ \rightarrow V(CO)_6 + \tfrac{1}{2}H_2$$

The strong acid $HV(CO)_6$ is almost certainly an intermediate in this reaction[11] Single crystal X-ray data for hexacarbonyl vanadium bear close resemblance to those of the group-VI metal carbonyls and the existence of a dimer in the solid state is thereby excluded[12].

The hexacarbonylvanadate(–I) anion is obtained[13] in the reductive carbonylation of vanadium halides with excess sodium in diglyme at 90–120° and under 3000–5000 lbs/sq.in of carbon monoxide. The bright-yellow $(Na\,diglyme_2)^+[V(CO)_6]^-$ is isolated by precipitation with petroleum ether and can be recrystallised from diethyl ether. It is water soluble, melts with decomposition at 173–176° and yields hexacarbonyl vanadium when treated with 100% phosphoric acid at 25°. The tetramethylammonium salt can be precipitated from aqueous solutions of $(Na\,diglyme_2)^+[V(CO)_6]^-$, and the diglyme-free alkali metal and ammonium salts have also been isolated[14]. The powerful non-metallic reducing agent, tetrakis-(dimethylamino)ethylene reacts[15] with hexacarbonyl vanadium to give the octamethyloxamidinium hexacarbonylvanadate(–I). This amine thus acts as a two-electron reducing agent rather than as a Lewis base (viz. later).

The $[V(CO)_6]^-$ anion is also formed when vanadium hexacarbonyl oxidises dimesitylenevanadium(O) to the dimesitylenevanadium(I) cation, with the formation[16] of $[V(C_6H_3Me_3)_2][V(CO)_6]$. In the reaction of the hexacarbonyl with cycloheptatriene, the hexacarbonylvanadate(–I) of the π-cycloheptatrienyl-π-cycloheptatrienevanadium(O) cation is obtained as red-brown paramagnetic microcrystals[17]. With aromatic hydrocarbons vanadium hexacarbonyl yields the complexes $[V(CO)_4arene]^+[V(CO)_6]^-$; the reactions are accompanied by the formation of water-soluble hexacarbonylvanadates of vanadium(I) and -(II), viz. $V[V(CO)_6]$ and $V[V(CO)_6]_2$ by thermal elimination of the ligands from the $[V(CO)_4arene]^+$ cation. This elimination becomes progressively less-important as the degree of methyl substitution in the benzene ring increases so that higher yields of the arene complexes are obtained with polymethylbenzenes[18].

When vanadium hexacarbonyl is reduced with 1% sodium amalgam in benzene in the presence of triphenylphosphine, and the product triturated in acetone, the monosubstituted hexacarbonylvanadate(–I) ion, $Na[V(CO)_5PPh_3]\cdot 3\,Me_2CO$ is formed[14]. The tetraalkylammonium salts of this anion are obtained as yellow, diamagnetic, air-stable crystals, by the addition of tetraalkylammonium iodides to a solution of $[(Ph_3P)_2V(CO)_4]$ which has been reduced by sodium amalgam in ethanol.

Vanadium hexacarbonyl is extremely reactive with oxygen and nitrogen bases, forming solid hexacarbonylvanadates(–I) of the four- or six-co-ordinated vanadium(II) cation:

$$3\,V(CO)_6 + nB \rightarrow [VB_n][V(CO)_6]_2 + 6\,CO$$

($n = 4$ or 6; B = wide variety of O and N bases)

e.g.[11] red-brown $[V(Me_2CO)_6][V(CO)_6]_2$ and brown $[V(Ph_3P{:}NH)_4][V(CO)_6]_2$. In these reactions vanadium(O) undergoes disproportionation viz.:

$$3\,V^{\circ} \rightarrow V^{2+} + 2\,V^{-}$$

The magnetic susceptibilities of the products all lie in the range 3.66–4.04 BM, in agreement with the formulation as a vanadium(II) cation and spin-paired complex vanadium(–I) anions. Triphenylphosphine and nitric oxide, however, differ from most other donors in that they give substitution products with the carbonyl. In ether, triphenylphosphine and vanadium hexacarbonyl yield $[V(OEt_2)_6][V(CO)_5PPh_3]_2$, which has a magnetic moment of 4.02 BM. In hexane, however, at room temperature, orange paramagnetic $[(PPh_3)_2V(CO)_4]$ is formed, and if nitric oxide is bubbled through this product in hexane, orange diamagnetic crystals of $[Ph_3P(NO)V(CO)_4]$ are formed[19]. Nitric oxide and vanadium hexacarbonyl react in cyclohexane to form[14] violet-red unstable $[V(CO)_5NO]$, which has ν(N–O) at 1700 cm^{-1}.

(iii) Complexes with bidentate nitrogen and phosphorus ligan

2,2'-Bipyridyl forms co-ordination compounds with vanadium in all three oxidation states from[20] –1 to +1. Reduction of the vanadium(II) cation $[V(bipy)_3]^{2+}$ with powdered magnesium in 50% methanol yields $V(bipy)_3$ (μ_{eff} = 1.9 BM); this complex forms deep-blue solutions in several polar and non-polar solvents and sublimes undecomposed *in vacuo* at 250°. In pyridine it reacts with two equivalents of iodine per mole reforming $[V(bipy)_3]^{2+}$. The red-violet solutions, formed in pyridine or methanol by $V(bipy)_3$ and one equivalent of iodine per mole or by $V(bipy)_3$ and $[V(bipy)_3]^{2+}$, contain $[V(bipy)_3]^{+}$ which on addition of water, benzene or ether disproportionates into $[V(bipy)_3]^{2+}$ and $V(bipy)_3$. No solid complexes of bipyridyl with vanadium(I) have been isolated; the substance $[V(bipy)_3]I \cdot \frac{1}{2}py$ is probably a mixed crystal of two similar compounds of vanadium(0) and vanadium(II)[21]. Reduction of $[V(bipy)_3]^{2+}$ with excess lithium aluminium hydride in tetrahydrofuran gives violet-red solutions which, on cooling, deposit black diamagnetic crystals of $Li[V(bipy)_3] \cdot 4\,THF$ containing vanadium in the formal oxidation state (–1). This complex is oxidised by phenyl isocyanide to[22] $V(bipy)_3$.

Using electron paramagnetic resonance measurements, the six nitrogen atoms in $V(bipy)_3$ were shown to be equivalent and a trigonal symmetry was suggested[23] The X-ray structural examination of solid $V(bipy)_3$ shows the nitrogen atoms to be at the corners of a distorted octahedron; the N–M–N angles being 73.6 ± 1.5° and the M–N distances 2.10 ± 0.03 Å. The vanadium(–I) complex also shows a trigonal distortion[23]. The odd electron in $V(bipy)_3$ is probably strongly delocalised on the ligand and the electronic structure of the molecule is analogous[24] to that for $[VS_6C_6Ph_6]$.

Tris(1,10-phenanthroline)vanadium(0) is obtained by reduction of $[V(phen)_3]I_2$ with naphthalene dilithium[25]. It forms dark-green crystals which are soluble in tetrahydrofuran, benzene and pyridine to give red-brown solutions; unlike $V(bipy)_3$ it cannot be sublimed in vacuo and decomposes at 200°.

The ditertiary phosphine, $Me_2PCH_2CH_2PMe_2$, is also capable of stabilising vanadium(0). The black rhombododecahedral $V(Me_2PCH_2CH_2PMe_2)_3$ can be crystallised from benzene after reduction of the green vanadium(III) chloride–diphosphine solution in tetrahydrofuran with sodium naphthenide[26]. It oxidises rapidly in air, melts at 253–254° with decomposition and has $\mu_{eff} = 2.10 \pm 0.25$ BM at room temperature.

(iv) Complexes with bidentate sulphur ligands

Some very interesting compounds of vanadium with bidentate sulphur donors have recently been examined. The oxidation-state formalism cannot always be rigorously applied here so that while these compounds are discussed here under these low-oxidation states, it should be understood that they may be formulated otherwise.

Dimethyldisulphide or methyl mercaptan react with π-cyclopentadienylvanadium tetracarbonyl to give a compound of formula $[\pi\text{-}C_5H_5V(MeS)_2]_2$. The suggested structure (Fig. 1) has a configuration around the vanadium atom similar to that proposed[28] for $[(\pi\text{-}C_5H_5)V(CO)_4]$, i.e. the vanadium atom is at the apex of a square pyramid with the four sulphur atoms at the corners of the base. The electronic structure of the molecule is not clear but one plausible description is to regard each vanadium as formally vanadium(0) and each sulphur atom as a three-electron donor to the pair of metal atoms. The compound is weakly paramagnetic with $\mu_{eff} = 1.04$ BM at 344.5 °K.

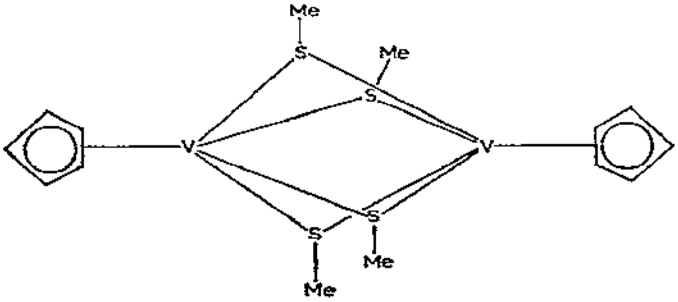
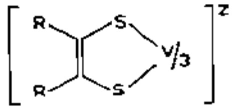


Fig. 1. Suggested structure for $[\pi\text{-}C_5H_5V(SMe)_2]_2$.

Some trigonal complexes in which the vanadium atom is hexa-co-ordinated to six sulphur atoms have recently been investigated. These are of two types[24,29] (Figs. 2 and 3). Electronic structures of these paramagnetic complexes have been discussed using results from electron paramagnetic resonance measurements. In the complex $[VS_6C_6(CN)_6]^{2-}$ ($\mu_{\text{eff}} = 1.82$ BM) the electronic configuration (assuming D_3 symmetry) is believed to contain an electron pair in an antibonding a_1^* orbital which should be mainly localised on the metal, and the unpaired electron in a molecular orbital mainly localised on the ligand. In a purely formal sense this ion may be regarded as containing diamagnetic vanadium(III) bonded to two dinegative (diamagnetic) ligands and a single radical anion. The E.P.R. evidence suggests that in $[VS_6C_6(C_6H_5)_6]$ (for which $\mu_{\text{eff}} = 1.80$ BM) the unpaired electron is even less localised on the metal than in the di-anions. Most recently the crystal and molecular structure of tris(*cis*-1,2-diphenylene-1,2-dithiolato)rhenium, $Re[S_2C_2(C_6H_5)_2]_3$, has been determined[30] and the rhenium atoms found to be surrounded by six equidistant sulphur atoms in a trigonal prismatic co-ordination. Since the vanadium compound may[30] be isomorphous with this rhenium complex, it too may have the trigonal prismatic co-ordination.



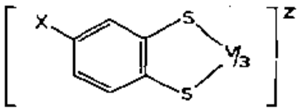


Fig. 2. Dithiolate complexes of vanadium. $R = CF_3$, CN, $z = -2$; $R = CF_3$, CN, C_6H_5; $z = -1$; $R = C_6H_5$, $z = 0$.

Fig. 3. Dithiolate complexes of vanadium. $X = H$, CH_3; $z = -2$.

C. OXIDATION STATE +2 ($3d^3$)

In this oxidation state, vanadium forms cationic, neutral and anionic complexes. As with the simple compounds of vanadium(II), few complexes have been well characterised, and this is in many respects, the least-well studied oxidation state of vanadium. In aqueous solution, oxidation is rapid so that contamination from higher-oxidation states is difficult to avoid; much of the co-ordination chemistry of vanadium(II) has therefore been carried out in non-aqueous solvent systems and particularly in fused salts. The complexes usually have octahedral stereochemistry; the room-temperature magnetic moments of the complexes are expected from theory[3] to be slightly below the "spin-only" value for three unpaired electrons.

(i) Cationic complexes

The violet hexaaquovanadium(II) cation can be obtained by reducing acidic solutions of vanadium(IV) electrolytically, or chemically using zinc. The absorption spectrum of this ion has been studied recently by several workers[31]. With vanadium(II) in M H_2SO_4 two bands are observed, both with very low extinction coefficients, at 11,800 cm^{-1} and 17,500 cm^{-1}.

The quartet terms arising from the $3d^3$ configuration, ^4P and ^4F are split[6] in the octahedral field as shown in Fig. 4. Assigning the first band as the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition, the value of 10 Dq is 11,800 cm^{-1}. The $^4T_{1g} \leftarrow {}^4A_{2g}$ transition is then calculated to occur at 18,100 cm^{-1}. The $^4T_{1g}(P) \leftarrow {}^4A_{2g}$ transition would be expected at 28,500 cm^{-1}. Because of charge-transfer absorption, this transition has not been observed. In the crystal of $VSO_4 \cdot 7\ H_2O$ however, this third transition is observed at 27,800 cm^{-1}.

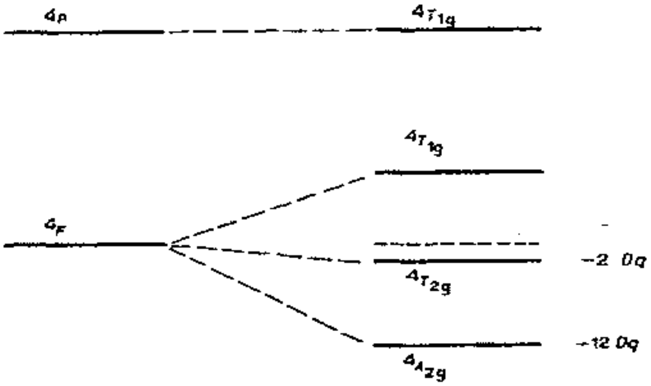


Fig. 4. Spin quartet terms for V^{II} in octahedral field.

Aqueous vanadium(II) sulphate forms dark-green solutions when mixed with methanolic solutions of 2,2'-bipyridyl, and potassium iodide or ammonium perchlorate; these solutions yield the cationic complexes $[V(bipy)_3]I_2$ (dark green) and $[V(bipy)_3](ClO_4)_2$ (violet) respectively. The magnetic moment of the iodide is 3.7 BM. The perchlorate may decompose explosively on thermal drying, but is stable for weeks in air. On standing in its mother liquor it changes (more rapidly with increasing methanol concentration) to a green isomer (also paramagnetic); both isomers give identical green solutions in water, methanol and pyridine. The occurrence of many four- and six-co-ordinate vanadium(II) cations with nitrogen and oxygen ligands in salts with the $[V(CO)_6]^-$ anion have already been mentioned.

The polarographic characteristics of vanadium(II) complexes with a wide range of anions have been studied[32]. In the concentration region $5 \cdot 10^{-3}$ M there is indication that the V^{II} exists predominantly in a dimeric form. Fluoro- and thiocyanato-complexes of V^{II} have lower formation constants than the V^{III} complexes. No indication of complex formation of V^{II} with sulphate, chloride, bromide or iodide ions was found in aqueous solution.

(ii) Neutral complexes

With nitrogen donors vanadium(II) chloride usually forms adducts which, unlike the bipyridyl complexes, are unstable in aqueous solution. There is no reaction with liquid ammonia at −33° but at room temperature an ammoniate is formed with between five and six ammonia molecules bonded to each vanadium[33] The reaction of vanadium(II) chloride with monomethylamine is very slow, but a purple-brown hexaminate, $[VCl_2 \cdot 6\,NH_2Me]$ is formed[34]. This is stable *in vacuo* up to 70° but above this temperature, four mols of amine are evolved readily. Virtually no reaction occurs between vanadium(II) chloride and dimethylamine, mono- or di-ethylamine or n-propylamine at room temperature. In pyridine however a deep-red solution is formed, from which dark-red crystals of VCl_2py_4 can be crystallised; this complex has $\mu_{eff} = 3.87$ BM[35].

Few neutral oxygen-donor complexes are known with vanadium(II); acetylacetone forms mono-, bis- and tris-acetylacetone complexes, the formation constants of which have been measured[36].

(iii) Anionic complexes

The existence of a complex fluoride of vanadium(II) has been indicated[37] from electron-spin resonance spectra on mixtures of K_3VF_6 and $KMgF_3$ at 1150°, but only complex chlorides have been isolated. The phase diagrams for the systems MCl–VCl_2 (M = Na, K or Cs) have been constructed from differential thermal analysis data[38]. Potassium chloride forms green hexagonal needles of $KVCl_3$ melting congruently at 946 ± 8° and K_2VCl_4 is formed by solid-state reaction at 645 ± 5°. Caesium chloride similarly forms $CsVCl_3$ which melts congruently at 1084 ± 10°. Absorption-spectra measurements[39] on vanadium(II) chloride in LiCl–KCl eutectic can be understood if VCl_6^{4-} is formed at temperatures around 400°. Three absorption bands are observed, at 19,050 cm^{-1}, 12,020 cm^{-1} and 7200 cm^{-1}; with $Dq = 700$ cm^{-1} the theoretical energies for the transitions from the $^4A_{2g}$ ground state are 20,000 cm^{-1} ($^4T_{1g}(P)$), 11,600 cm^{-1} ($^4T_{1g}(F)$) and 7000 cm^{-1} ($^4T_{2g}$). Octahedral Dq for the Cl^- ion is thus some 60–65% as large as that found for water in the aqueous solutions. In the VCl_2 solutions in the LiCl–KCl eutectic at higher temperatures (1000°) the spectra undergo changes which can be accounted for in terms of an octahedral–tetrahedral transformation involving the equilibrium

$$VCl_6^{4-} \rightleftharpoons VCl_4^{2-} + 2\,Cl^-$$

In molten aluminium chloride, absorption-spectra measurements again indicate the formation of octahedrally-co-ordinated vanadium(II) chloride species[40].

New complex chlorides and halide hydrates of vanadium(II) have also been prepared from aqueous solutions of vanadium(II). Thus red-violet hexahydrates

$M^IVCl_3 \cdot 6\,H_2O$ (M^I = Rb, Cs or NH_4) have been obtained by the addition of M^ICl and evaporation of the solutions *in vacuo*[41]. They lose water on heating *in vacuo* but decomposition with oxidation occurs at about 120°. Hydrates of the simple halides isolated include $VCl_2 \cdot 4\,H_2O$ (steel-blue crystals), $VBr_2 \cdot 6\,H_2O$ (blue-violet needles, soluble in alcohol and acetone but insoluble in ether) and the red-violet $VI_2 \cdot 6\,H_2O$.

The complex cyanide $K_4V(CN)_6 \cdot 3\,H_2O$ was reported over sixty years ago[42] but has not been confirmed since. It is said to be isomorphous with $K_4Fe(CN)_6 \cdot 3\,H_2O$ and so contains octahedrally-co-ordinated vanadium(II). The heat of complexation of cyanide ion with V^{2+} aq. has been determined calorimetrically[43], a large excess of cyanide ion being used to ensure the formation of the hexacyanocomplex. By neglecting the spherical-field contribution to the heats of complexation and by employing pairing-energy approximations an upper limit has been established for 10 *Dq* of 13,900 cm^{-1}. Unfortunately no magnetic or spectral data are available on this complex.

D. OXIDATION STATE +3 ($3d^2$)

Like vanadium(II), vanadium(III) forms cationic, neutral and anionic complexes. The most-common stereochemistry is octahedral (with a trigonal distortion), five co-ordination is not uncommon but tetrahedral stereochemistry is rare.

(i) Cationic complexes and spectral properties of the hexaaquovanadium(III) cation and related species

In the cationic complexes, vanadium(III) is almost always attached to oxygen. The triplet terms arising from the configuration $3d^2$ are ^3F and ^3P. In a cubic crystal field the energy-level diagram[44] including only the triplet terms is as shown in Fig. 5. It is apparent therefore that there are three possible spin-allowed transitions which might be observed in the visible and ultraviolet spectra of octahedral vanadium(III) complexes. Solutions of the hexaaquo cation $[V(H_2O)_6]^{3+}$, have absorption bands[45] at 17,700 cm^{-1} and 25,000 cm^{-1} which have been assigned[46] to the $^3T_{2g} \leftarrow {}^3T_{1g}$ and the $^3A_{2g} \leftarrow {}^3T_{1g}$ transitions. The third spin-allowed band is not observable because of strong charge-transfer absorption in the ultraviolet part of the spectrum. Using the *Dq* value from the other assignments this band is expected to lie at ~37,000 cm^{-1}. Spectral measurements on vanadium corundum, however, (i.e. V^{3+} substituted in to Al_2O_3) have revealed[47,48] three relatively-strong bands at 17,400 cm^{-1}, 25,200 cm^{-1} and 34,500 cm^{-1} and these are interpreted as the transitions from the $^3T_{1g}$ ground state to the $^3T_{2g}$, $^3T_{1g}(P)$ and $^3A_{2g}$ levels, respectively. In addition, however, several weak bands are observed at 21,000 cm^{-1}, 25,400 cm^{-1}, 29,300 cm^{-1} and 30,150 cm^{-1}, which have been

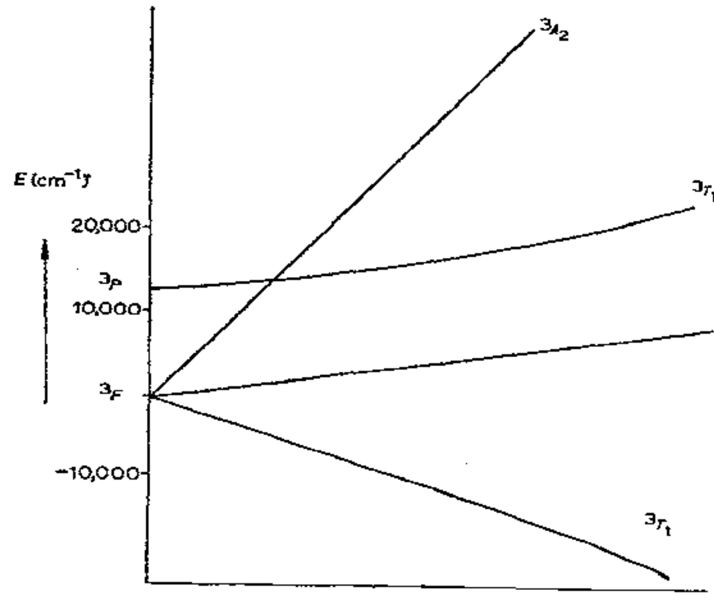


Fig. 5. Spin triplet terms for V^{III} in octahedral field.

assigned to spin-forbidden transitions. A crystal-field calculation of the energy levels including spin–orbit coupling and configuration interaction has been described by Liehr and Ballhausen[49] and quite good agreement found between theory and experiment. Further refinements have been made by including an additional trigonal component[48,50] and the magnetic properties of vanadium corundum satisfactorily explained using values of the optical parameters obtained from the absorption spectra[50].

There are considerable experimental and theoretical reasons[51] to expect that all cubic vanadium(III) compounds are distorted along the trigonal axis to some extent. There is X-ray evidence for the trigonal distortion of the six octahedrally-co-ordinated water molecules surrounding the tervalent metal ion in the alums[52]. In a trigonal field, the octahedral ground state in vanadium(III) will be split (Fig. 6) into $^3A_2$ and ^3E components; spin–orbit coupling then causes further splitting of the $^3A_2$ term. The magnetic properties of $NH_4V(SO_4)_2 \cdot 12\,H_2O$ can be interpreted on the basis of the scheme in Fig. 6; the magnetic data on this and other vanadium(III) complexes have been discussed in some detail by Figgis and Lewis[3,53]

The visible spectrum of tris(acetylacetonato)vanadium(III) has been measured in solution[54] and shoulders on the charge-transfer bands observed at 18,200 cm^{-1} and 21,700 cm^{-1}. The polarised crystal spectra of single crystals of aluminium acetylacetonate, with part of the aluminium isomorphously replaced by V^{3+},

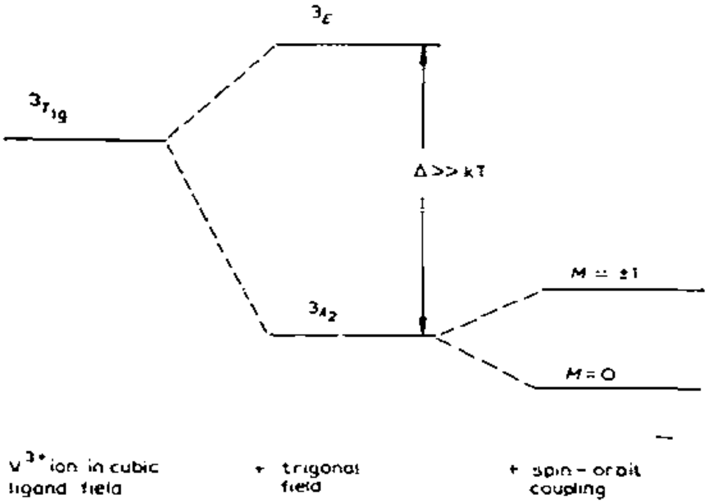


Fig. 6. Splitting of the ground term of the V^{3+} ion.

are similar[55]; at 77 °K the shoulders appear at 17,500 cm^{-1} (∥) and 18,800 cm^{-1} (⊥); these data require a Dq of about 1800 cm^{-1}. The spectral and magnetic data[53] are again consistent only with a $^3A_2$ ground state.

In the trisoxalatovanadate(III) ion, Hartmann and co-workers[56] assign the 16,450 cm^{-1} band to the $^3T_2$ and the shoulder at 23,500 cm^{-1} to the $^3A_2$ level. Trigonal splittings were not observed in the solution spectrum. The polarised visible spectra of single crystals of $NaMgAl(C_2O_4)_3 \cdot 9\,H_2O$ with part of the aluminium replaced by vanadium(III), are suggestive of trigonal splitting of the $^3T_2$ level. The 16,670 cm^{-1} (⊥) band is assigned to the ^3A, and the 17,230 cm^{-1} (∥) band to the ^3E_b level.

In the complete energy-level diagram for octahedral V^{III} (viz. ref. 57) one sees that there are two low-lying singlet states, ^1E_g and $^1T_{2g}$. Whilst they could not be located in tris(acetylacetonato)vanadium(III) these first spin-forbidden bands have been observed[58] in the reflectance spectra of the fluoro-complexes shown in Table 1. The calculated positions of the absorption maxima for a d^2 cubic configuration are those calculated according to the method of Liehr and Ballhausen[49]. In a purely cubic crystalline field the ^1E_g and $^1T_{2g}$ levels are nearly degenerate.

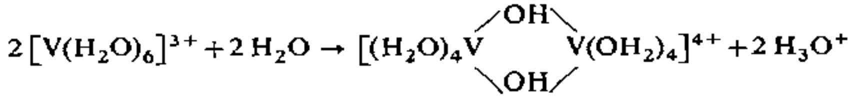
TABLE I

SPECTRA OF FLUORO–AQUO COMPLEXES OF VANADIUM(III)

Transitions from $^3T_{1g}$ *to:*	*Calculated* ($Dq = 1585\ cm^{-1}$, $\lambda = 65\ cm^{-1}$, $F_4 = 70\ cm^{-1}$, $F_2 = 14\ F_4$)	VF_6^{3-}	$VF_5OH_2^{2-}$	$VF_4(OH_2)_2^-$	$VF_3(OH_2)_3$
^1E_g, $^1T_{2g}$	9,200	10,200	10,500	12,000	11,500
$^3T_{2g}$	14,800	14,800	15,500	16,000	16,200
$^3T_{1g}$	23,200	23,000	23,500	23,800	24,500

However if a trigonal component is now added, the ${}^1T_{2g}$ level will be split into ${}^1E_g$ and ${}^1A_{1g}$ levels while ${}^1E_g$ will not be split. The degeneracy of ${}^1E_g$ and ${}^1T_{2g}$ at 9,200 cm^{-1} is thus removed and three levels located at 10,200 cm^{-1}, 9,200 cm^{-1} and 8,700 cm^{-1} are expected. The latter two levels are so far undetected.

The solution spectrum of the $[V(H_2O)_6]^{3+}$ ion can only be obtained in acid solution since hydrolysis occurs at higher pH. The hydrolysis occurring in slightly-acid solution gives $[VOH]^{2+}$ and possibly $[V_2(OH)_3]^{3+}$; olation then occurs in a similar way to that found with other transition metals:



$$2\,[V(H_2O)_6]^{3+} + 2\,H_2O \rightarrow [(H_2O)_4V\overset{OH}{\underset{OH}{\rightleftharpoons}}V(OH_2)_4]^{4+} + 2\,H_3O^+$$

this process is characterised[59] by a strong charge-transfer band at 22,930 cm^{-1}. The same binuclear species is formed as an intermediate in the reaction between V^{II} and V^{IV} in acid perchlorate solutions[60]; the species present was initially formulated as $[VOV]^{4+}$ but magnetochemical evidence[59] favours the presence of -ol rather than oxo-bridges. Polynuclear vanadium(III) complexes are also formed in acetic and chloracetic acid solutions. In acetic acid, spectroscopic and potentiometric techniques have demonstrated the presence of the binuclear $[V_2(OAc)_3(OH)_2]^+$ complex ion[61]. In aqueous solutions containing V^{3+} and chloracetic acid at pH 1.0 to 1.5, Job's method and pH titrations indicate[62] three kinds of complex to be present corresponding to the ratios (V: chloracetic acid) 3 : 7, 3 : 8 and 3 : 9. The first of these is the most stable in solution and can be isolated as $[V_3(ClCH_2COO)_6(OH)_2]OOCCH_2Cl$. The instability constant of this complex is $3.0(\pm 0.3) \cdot 10^{-18}$ at 22.5° and is independent of pH. From a solution containing 6 moles vanadium(III) per litre the complex $[V_2(OH)_2(ClCH_2COO)_4 \cdot 2\,H_2O]$ can be crystallised.

Few cationic complexes of vanadium(III) with ligands other than oxygen are known. The well-quoted[63] hexammine $[V(NH_3)_6]Cl_3$ certainly does not exist (see later). The products obtained from vanadium(III) chloride and the bidentate ligands ethylene- and propylene-diamine may however be best considered as cationic complexes viz. $[Ven_3]Cl_3$ and $[Vpn_3]Cl_3$. These compounds are stable up to 100°.

(ii) Neutral complexes

There is now quite an extensive co-ordination chemistry of vanadium(III) halides and it will be convenient to divide the complexes into groups having similar stereochemistries.

Five-co-ordinate complexes. During the last decade it has been established that the occurrence of five co-ordination in metal complexes is more common than was at one time thought. Vanadium compounds have played an important part in this[65]; Table 2 lists some established five-co-ordinate compounds derived from vanadium(III) halides. The compounds are non-electrolytes in nitrobenzene and monomeric in solvents such as benzene[66]. The visible spectra of the solid complexes are the same as those of solutions in various solvents so that five co-ordination is probably retained in the solid state. Fowles and co-workers[66] have measured the dipole moments of three of the compounds and the data supports their formulation as *trans*-trigonal bipyramidal (rather than square pyramidal). The infrared spectra in the M–Cl stretching region also support this formulation.

TABLE II

FIVE-CO-ORDINATE COMPLEXES DERIVED FROM VANADIUM(III) HALIDES

Complex	*Colour*	μ_{eff} *(BM) (~293 °K)*	*Dipole moment (D)*	*Other properties*	*Ref.*
$VCl_3(NMe_3)_2$	red	2.69	0.4	ν(V–N) at 507 cm^{-1}	65, 66
$VCl_3(SMe_2)_2$		2.54	2.3		66
$VCl_3(SEt_2)_2$		2.50	2.6		66
$VCl_3(OPEt_3)_2$	red-violet			decomp. 118°	67
$VCl_3(OPPr_3)_2$	red-violet			decomp. 126°	67
$VCl_3(OP(C_6H_{11})_3)_2$	blue			m.p. 270–273°	67
$VCl_3(OPPh_3)_2$	blue	2.61		decomp. 265°	67
$VCl_3(PEt_3)_2$	light red	2.83		decomp. 160°	67
$VCl_3(PPr_3)_2$	light red	2.61			67
$VBr_3(NMe_3)_2$				ν(V–N) at 513 cm^{-1}	66

Bis(trimethylamine)vanadium(III) chloride is isomorphous with the corresponding titanium compound; the crystals are orthorhombic. The X-ray powder pattern has been recorded[68] but a full structural study (to establish five co-ordination in the solid state) has not been performed. The magnetic susceptibility obeys the Curie–Weiss law over the range 100–300 °K and a reversible colour change from pink to pale green occurs (without change of crystal form) at about 170 °K.

The ethyl acetate adduct[69] $VCl_3 \cdot 2\,EtOAc$ may also be five co-ordinate although no physical measurements have been made on this compound.

Vanadium(III) chloride only reacts with triphenyl- and tricyclohexyl-phosphine when the reactants are heated together at about 300°. Orange-red products of varying atomic ratios are formed which are believed[67] to contain binuclear complexes $[VCl_3 \cdot PR_3]_2$.

Six-co-ordinate complexes of vanadium(III) halides. The six-co-ordinate adducts formed by vanadium(III) halides with donor molecules are listed in Table 3. Not much information is available concerning these compounds except with the nitriles as ligands. All the adducts in the Table are prepared by direct interaction,

TABLE III

HEXA-CO-ORDINATE ADDUCTS OF VANADIUM(III) HALIDES

Complex	*μ_{eff}(BM) (~293 °K)*	*Colour*	*Ref.*
$VCl_3 \cdot 3$ THF		orange	70
$VCl_3 \cdot 3$ EtOH		green	71
$VCl_3 \cdot 3$ MeCN	2.75	green	72, 73
$VCl_3 \cdot 3$ EtCN	2.59	green	72
$VBr_3 \cdot 3$ MeCN		brown	72
$VBr_3 \cdot 3$ EtCN	2.50	brown	72
$VCl_3 \cdot 3\ CH_2{=}CHCN$		purple-black	74
$VCl_3 \cdot 3$ PrCN		purple-black	74
$VCl_3 \cdot 3$ py		purple	75
$VCl_3 \cdot$ n-$BuNH_2$			4
$VCl_3 \cdot 3$ n-$C_6H_{11}NH_2$			4

usually by refluxing the halide in the solvent. The alkyl cyanide complexes can also be prepared by direct reaction of the nitriles with vanadium(IV) chloride since reduction occurs here[72].

The diffuse reflectance spectra of [$VCl_3 \cdot 3$ MeCN] and the absorption spectrum of a solution of vanadium(III) chloride in acetonitrile are practically identical[72,73] and so the absorbing species is probably the same. Since these compounds are virtually non-electrolytes in the parent nitriles they are clearly formulated as [$VX_3 \cdot 3$ RCN]^0. Two peaks are observed in the visible region by [$VCl_3 \cdot 3$ MeCN]; the band at 14,400 cm^{-1} is assigned to transition $^3T_{2g} \leftarrow {}^3T_{1g}(F)$ and the shoulder around 21,000 cm^{-1} to the $^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$ transition. The bromo complexes show only the first ligand-field band since a strong charge-transfer absorption obscures the second band. These data yield[73] an average Dq value of 1550 cm^{-1} and a ^3P–^3F term separation of 8100 cm^{-1}. The spectrum of $Ph_4As[VCl_4 \cdot 2$ MeCN] has also been recorded; the two bands being at 13,500 cm^{-1} and 20,400 cm^{-1}, giving $Dq = 1460$ cm^{-1} and a ^3P–^3F separation of 8000 cm^{-1}. The reduction in the ^3P–^3F separation from the free-ion value[76] of 12,925 cm^{-1} in these complexes is ascribed to a decreased effective charge on the central metal ion due to increased screening by the donated σ-electrons of the ligands. The [$VX_3 \cdot 3$ RCN] complexes lose alkyl cyanide when heated *in vacuo*, almost all of the ligand being evolved by 180°. The ultra-violet and infrared spectra of these compounds are recorded[72].

Complexes of composition [$VX_3 \cdot 4$ MeCN] (X = Cl, Br) can also be isolated ($VBr_3 \cdot 4$ MeCN has a magnetic moment of 2.56 BM). Since washing [$VCl_3 \cdot 4$ MeCN] with a non-polar solvent leaves [$VCl_3 \cdot 3$ MeCN], the extra nitrile molecule is probably weakly held in the crystal lattice[72]. With alcohols too, adducts with four molecules of alcohol are sometimes formed[71] e.g. [$VCl_3 \cdot 4$ MeOH] and [$VCl_3 \cdot 4$ iso-PrOH], but their thermal stability has not been reported.

Solvolytic reactions of the vanadium(III) halides. The hydrolysis of the hexaaquovanadium(III) cation under alkaline conditions has already been mentioned. The solvolytic products from other protonic solvents are listed in Table 4.

While vanadium(III) chloride is not solvolysed in alcohols, the addition of lithium alkoxides brings about precipitation of the green vanadium(III) alkoxides. Attempts at preparing the tri-isopropoxide and the tri-tert-butoxide have failed, oxidation of the vanadium occurring despite the use of inert atmospheres[71]. A similar oxidation appears to occur with vanadium(III) chloride in propionic acid where a green propionate slowly turns to a brown vanadium(IV) compound when refluxed in excess of the acid under nitrogen[8].

TABLE IV

SOLVOLYTIC REACTIONS OF VANADIUM(III) HALIDES

Halide	*Reagent*	*Product*	*Ref.*
VCl_3	LiOMe in MeOH	$V(OMe)_3$	71
VCl_3	LiOEt in EtOH	$V(OEt)_3$	71
VCl_3	HCOOH	$V(OOCH)_3 \cdot HCOOH$	77
VCl_3	NH_3 (−33°)	$VCl_2(NH_2) \cdot 4\ NH_3$	33, 79
VBr_3	NH_3 (−33°)	$VBr_2(NH_2) \cdot {}^{9}/_{2}\ NH_3$	78, 79
VCl_3	NH_2Me	$VCl_2(NHMe) \cdot 5\ NH_2Me$	34
VCl_3	NH_2Et	$VCl_2(NHEt) \cdot 3\ NH_2Et$	34
VCl_3	n-$PrNH_2$	VCl_2(n-PrNH) · 5 n-$PrNH_2$	34
VCl_3	n-$BuNH_2$	VCl_2(n-BuNH) · 5 n-$BuNH_2$	34
VCl_3	$NHMe_2$	$VCl_2(NMe_2) \cdot NHMe_2$	34
VCl_3	$NHEt_2$	$VCl_2(NEt_2) \cdot NHEt_2$	34
VCl_3	n-Pr_2NH	VCl_2(n-Pr_2N) · n-Pr_2NH	34
$VCl_3 \cdot 3\ THF$	$(C_6H_{11})_2PLi$ in C_6H_6	$[(C_6H_{11})_2P]_3V$	80

Even at −37° the "ammoniates" formed by the vanadium(III) halides contain one mol of ammonium halide per vanadium so that ammonolysis of one V–X bond occurs. No further ammonolysis occurs if the reaction is carried out in a Carius tube at room temperature. The complexes "$VX_3 \cdot nNH_3$" have an ammonia content which is very dependent upon the temperature. At 20°, $n = 5$–6; on heating to 200°, ammonia is rapidly evolved, ammonium halide sublimes and some nitride formation occurs. The amidohalides are insoluble in all solvents with which they do not react chemically and are presumably polymeric. Gaseous ammonia reacts with vanadium(III) chloride at 325° to give a product with a V : Cl ratio of 1 : 1 so that two V–Cl bonds are broken under these conditions. Complete removal of the halogen can be achieved by treatment of the halides with potassium in liquid ammonia; thus the ammonobasic vanadium(III) bromide yields black, pyrophoric and ammonia-insoluble $KV(NH)_2$. The same imide is obtained by treating $K_3[V(SCN)_6]$ with potassium amide in liquid ammonia. By reaction of the imide with ammonium nitrate in ammonia, a white compound believed to be $[(NH)V(NH_2)]$ is obtained[81].

The solvolytic products obtained with the primary aliphatic amines are similar to the ammonia derivatives. With n-propylamine and n-butylamine, purple anionic complexes (in addition to those compounds listed in Table 4) can be isolated of composition $[NH_3R][VCl_3(NHR)(NH_2R)_2]$. The products obtained with secondary amines, $[VCl_2NR_2 \cdot NHR_2]$ are largely monomeric in benzene solution. Completely-substituted amides have not yet been obtained (except with ammonia), but these could presumably be prepared by reaction of the lithium alkylamide with the vanadium(III) halide in a fashion similar to that used for the preparation of the cyclohexylphosphide. This latter product $V(PR_2)_3$ undergoes an interesting reaction with iodine in tetrahydrofuran to produce $VI(PR_2)_3$—a derivative of the as yet unknown vanadium(IV) iodide.

A stable oxinate, $V(C_9H_6OH)_3$ formed by 8-hydroxyquinoline can be crystallised in brown tablets from organic solvents; it has a magnetic moment of 2.83 BM at room temperature[82].

Vanadium(III) carboxylates. It is perhaps remarkable that these compounds have received so little study especially in view of the recent interest in bidentate carboxylate groups and the magnetic properties of the binuclear carboxylates such as those of copper(II).

A hydrated acetate $V(OCOCH_3)_3 \cdot H_2O$ was described some thirty years ago[83] but it is only very recently that the anhydrous carboxylates have been prepared. The simplest route to these carboxylates is by refluxing vanadium(III) chloride in the carboxylic acid. In this way Seifert[77] obtained the green formate $V(OOCH)_3 \cdot HCOOH$, a substance previously described[84] as $V(OOCH)_4$. The effective magnetic moment of 2.7 BM and oxidation-state titration confirms Seifert's formulation. The formic acid molecule can be removed at 180° *in vacuo* leaving green $V(OOCH)_3$ which also has $\mu_{eff} = 2.7$ BM. Vanadium(III) acetate can be similarly prepared as a green solid[8]. Its reflectance spectrum shows two bands at 25,450 cm^{-1} and 16,340 cm^{-1}.

Whilst vanadium metal does not react with acetic acid, vanadium diboride reacts with both acetic and benzoic acids to give dimeric vanadium(III) carboxylates[85]

$$2\ VB_2 + 6\ RCO_2H \rightarrow V_2(O_2CR)_6 + 3\ H_2 + 4\ B$$

The infrared and nuclear mangetic-resonance spectra on these compounds show two types of carboxyl group to be present and the molecular weight of the acetate in freezing acetic acid confirms a dimeric formula. The structure (Fig. 7) has been proposed for these compounds. Their magnetic properties are complicated and not yet understood; μ_{eff} at room temperature is 0.77 BM. These carboxylates are rapidly hydrolysed in moist air and turn brown in solution in donor solvents.

Aqueous quinaldinic acid (HQ) forms a blue-violet complex $[V(OH)Q_2 \cdot 3\ H_2O]$ ($\mu_{eff} = 3.02$ BM) with aqueous vanadium(III) solutions[86]. In the absence of water, tris(acetylacetonato)vanadium(III) reacts with HQ in chloroform to give the soluble red-brown VQ_3 ($\mu_{eff} = 2.66$ BM) which has visible absorption bands at 26,300 cm^{-1} and 20,800–21,700 cm^{-1}.

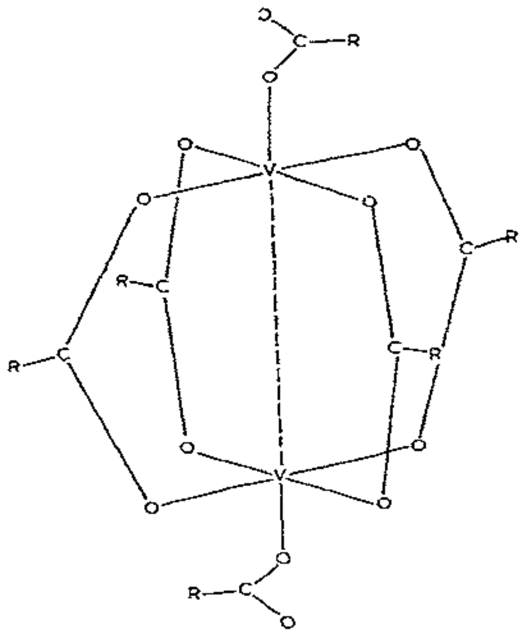


Fig. 7. Dimeric vanadium(III) carboxylates.

(iii) Anionic complexes

Complex Halides. Octahedral fluorides of the types $M^I_3VF_6$, $M^I_2VF_5(H_2O)]$ and $[M^IVF_4(H_2O)_2]$, are long known and well established[1]; they have magnetic moments in the range 2.74–2.79 BM[87]. Their spectra have already been discussed. The preparation of green K_3VF_6 from powdered vanadium and potassium hydrogen fluoride at 800° has recently been reported[37] and the thermal decomposition of $(NH_4)_3VF_6$ to VN has been studied[88].

Complex chlorides previously formulated[89] as $K_2VCl_5 \cdot n\,H_2O$ have been shown to be mixtures of $KVCl_4 \cdot n\,H_2O$ and KCl[90]. Two complexes can be isolated from vanadium(III) chloride and potassium chloride in aqueous hydrogen chloride; a green 6-hydrate $KVCl_4 \cdot 6\,H_2O$ and a red $\frac{3}{2}$-hydrate $KVCl_4 \cdot \frac{3}{2}\,H_2O$. These can be interconverted using simple hydration or dehydration procedures. The hexahydrate has absorption bands at 16,050 cm^{-1} and 22,990 cm^{-1} and the $\frac{3}{2}$-hydrate absorbs at 12,580 cm^{-1} and 19,300 cm^{-1}. The compound $VCl_3 \cdot 4\,H_2O$ has been prepared by dehydration of $VCl_3 \cdot 6\,H_2O$; both these compounds exhibit absorption spectra identical to that of $KVCl_4 \cdot 6\,H_2O$. It is most likely that in $KVCl_4 \cdot 6\,H_2O$, $VCl_3 \cdot 6\,H_2O$ and $VCl_3 \cdot 4\,H_2O$ the vanadium is octahedrally surrounded by four water and two chloride ions as nearest neighbours; the band in the 19,000–22,000 cm^{-1} region being assigned to the $^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$ transition. The anhydrous Cs_2VCl_5 ($\mu_{eff} = 2.56$ BM) is obtained[91] when Cs_2VCl_6 is thermally decomposed at 284°; its reflectance spectrum shows a sharp peak at 17,700 cm^{-1} and a weaker broader band at 11,200 cm^{-1}. This spectrum is similar to that of the VCl_6^{3-} anion (see below) so that the co-ordination around the vanadium atom in the pentachlorovanadate(III) appears to be octahedral. No X-ray studies have been made on this compound and there is the possibility that Cs_2VCl_5 is a mixture of Cs_3VCl_6 and $Cs_3V_2Cl_9$.

The chemistry of vanadium(III) chloride in molten alkali-metal chlorides and their eutectic mixtures has been extensively studied during the last few years. Equilibrium-phase diagrams and X-ray studies in the systems VCl_3 with NaCl, KCl and RbCl indicate[92] the presence of the compounds $M^I_3VCl_6$ (M = Na, K, Rb), $K_3V_2Cl_9$, $Rb_3V_2Cl_9$ and $RbVCl_4$. A spectrophotometric study of VCl_3 in the KCl–LiCl eutectic at 400° reveals[39] two bands at 18,020 cm^{-1} ($^3T_{1g}(P) \leftarrow {}^3T_{1g}(F)$) and 11,000 cm^{-1} ($^3T_{2g} \leftarrow {}^3T_{1g}$); a similar spectrum is found in molten pyridinium chloride at 160°. The spectra fit Liehr and Ballhausen's scheme[49] for a d^2 ion in an octahedral field using $Dq = 1200\ \text{cm}^{-1}$. At 1000°, the spectra change markedly due to the octahedral–tetrahedral transformation:

$$VCl_6^{3-} \rightleftharpoons VCl_4^{-} + 2\,Cl^{-}$$

The tetrahedral VCl_4^- spectrum has also been observed in the $CsAlCl_4$ lattice[93].

The binuclear complex ion $[V_2Cl_9]^{2-}$ has been prepared also in thionyl chloride and isolated as the tetraethylammonium salt[94]. The far-infrared spectrum has been recorded. The caesium salt is isomorphous with $Cs_3Ti_2Cl_9$ and $Cs_3Cr_2Cl_9$; in these compounds, two octahedrals are joined by a face containing three bridging chlorine atoms[95].

Using methyl cyanide as solvent, compounds $M^IVX_4 \cdot 2\,MeCN$ ($M^I = Et_4N$ or Ph_3MeAs; X = Cl, Br or I) can be isolated from M^ICl and VX_3. On heating to 80°, these complexes lose the solvent molecules and M^IVCl_4 and M^IVBr_4 are obtained. The iodide complex, however, undergoes some decomposition on heating[96]. The formation of the VCl_4^- ion in methyl cyanide has recently been shown also by spectrophotometric, potentiometric and conductometric techniques[97]. With azide ions however in this solvent, the hexaazidovanadium(III) species $[V(N_3)_6]^{3-}$ are formed.

Complex cyanides and thiocyanates. The complex cyanide $K_3V(CN)_6$ was reported over half a century ago[98] and the $[V(CN)_6]^{3-}$ ion shown to be unhydrated in solution[99], but solid hexacyano complexes do not seem to have been isolated since. A wine-coloured solution claimed to contain $[V(CN)_6]^{3-}$ has been obtained[100] by the addition of cyanide ion to a vanadium(III) solution obtained by reducing the oxovanadium(IV) ion with sodium amalgam. Its visible spectrum has been measured and the bands tentatively assigned[101]; however, the authors admit to preparative difficulty with this ion. Other workers[8] have found that the wine-coloured solution is obtained only after standing the solution at room temperature and that in the presence of excess cyanide ions at 0 to −10°, vanadium(III) forms an intensely-blue complex cyanide of formula $[V(CN)_6]^{3-}$; the potassium salt can be isolated.

The application of Job's continuous variation method to the formation of vanadium(III) thiocyanate complexes has established that in aqueous solutions $VNCS^{2+}$ and $[V(NCS)_6]^{3-}$ are formed[102,103]. The latter has maximum absorption at 26,300 cm^{-1}; addition of pyridine shifts the absorption maximum to 18,870 cm^{-1} and $[V(NCS)_3 \cdot py]$ is formed. The colour developed by vanadium(III) and thiocyanate ions in aqueous acetone has been used for the spectrophotometric determination of vanadium[104]. The infrared spectrum of $(NH_4)_3V(NCS)_6 \cdot 4\ H_2O$ shows a C–S stretching frequency at 830 cm^{-1}, characteristic of thiocyanates with nitrogen bonded to the metal; these complexes are therefore isothiocyanates[105].

E. OXIDATION STATE +4 ($3d^1$)

This is by far the most-widely studied oxidation state. In aqueous solutions the blue oxovanadium(IV) cation, $[VO(H_2O)_5]^{2+}$ is characteristic of this oxidation state and there are a very large number of complexes derived from this ion. In recent years the bonding in these compounds has attracted widespread interest and molecular-orbital schemes for these complexes are currently being debated. In view however of the recent comprehensive reviews on oxovanadium(IV) complexes[2] this subject will not be discussed here. In the oxidation state +4 then we are left with the non-aqueous chemistry and as the only Lewis acids here are the halides we are consequently dealing with the co-ordination chemistry of the vanadium(IV) halides. Only complexes of the fluoride and chloride are known; vanadium(IV) bromide has been prepared recently[106] but is unstable at room temperature, the iodide is unknown. No cationic complexes of V^{4+} are known with the possible exception of $[Ven_3]F_4$. The stereochemistries of the neutral and anionic complexes are largely octahedral (with tetragonal distortion) but some five- and eight-coordinate complexes are known.

(i) The co-ordination chemistry of the vanadium(IV) halides

With the ground state electronic configuration $3d^1$, this oxidation state is of great interest from a spectroscopic point of view. Before examining the co-ordination complexes it would perhaps be not inappropriate to briefly examine the properties of the vanadium(IV) halides themselves.

The tetrahedral vanadium(IV) chloride molecule itself undergoes a Jahn–Teller distortion[107] and three bands are found in its absorption spectrum. The spectrum in carbon tetrachloride solution[108] and in the vapour[109] are very similar, bands being observed at 9010, 7880 and 6600 cm^{-1} for the solution and at 9250, 7850 and 6600 cm^{-1} for the vapour. This similarity between the spectra suggests that the molecule consists of non-interacting monomeric species in solution as well as in the vapour[110]. Assigning the 7880 cm^{-1} band to the $^2T \leftarrow {}^2E$ transition we get $Dq = \sim 790$ cm^{-1} which is somewhat high when compared with the Dq of ~ 1520 cm^{-1} found for vanadium(IV) octahedrally co-ordinated by chloride ions[91].

The magnetic moment of vanadium(IV) chloride is independent of temperature down to its freezing point; vanadium(IV) fluoride, however, has a magnetic moment which falls to 1.18 BM at 80 °K[111,112]. This indicates that this molecule cannot consist (like the chloride) of magnetically dilute tetrahedrals since it would then have a moment of 1.73 BM at all temperatures as a consequence of a ^2E ground term. It may be octahedrally co-ordinated in the solid state or tetrahedral with antiferromagnetic interactions responsible for the lowering of the moment from the free-ion value. Its spectral properties are not yet recorded.

Let us now consider the formation of octahedral complexes from these halides. In an octahedral field the free-ion term ^2D will be split (Fig.8) into E_g and T_{2g} terms with a separation equal to 10 Dq. In a complex $VCl_4 \cdot 2$ L the non-equivalence of the six ligands introduces a tetragonal distortion into the molecule which has the effect of splitting the ^2E_g and $^2T_{2g}$ terms further. Yet a further splitting of the ^2E_g term derived from $^2T_{2g}$ can occur in fields of lower symmetry than D_{4h}. In the visible region of the spectrum then, for tetragonally-distorted complexes two bands are expected corresponding to the transitions $^2B_{1g} \leftarrow {}^2B_{2g}$ and $^2A_{1g} \leftarrow {}^2B_{2g}$. The separation between the bands will give an estimate of the magnitude of the tetragonal component. It should be noted however that even in the case of six identical ligands surrounding V^{4+} (e.g. as in $VCl_6{}^{2-}$) some tetragonal distortion will occur[113] as a result of the Jahn–Teller effect.

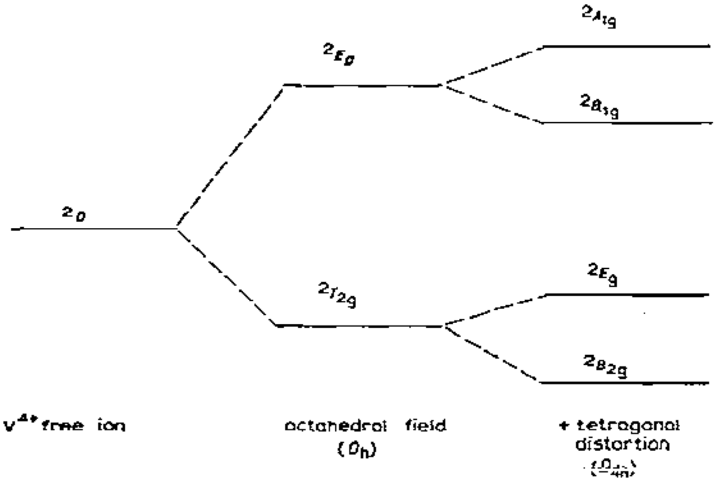


Fig. 8. Splitting of free ion term for V^{4+} in octahedral and tetragonal fields.

TABLE V

MAGNETIC AND SPECTRAL PROPERTIES OF SOME VANADIUM(IV) CHLORIDE COMPLEXES

Complex	μ_{eff}*(BM)* (~293 °K)	$^2B_{1g} \leftarrow {}^2B_{2g}$ (cm^{-1})	$^2A_{1g} \leftarrow {}^2B_{2g}$ (cm^{-1})	*Ref.*
$VCl_4 \cdot C_4H_8O_2$	1.80	17,400	22,200	114
$VCl_4 \cdot 2\ C_4H_8O$	1.77	13,600	18,180 (br)	114
$VCl_4 \cdot 2\ C_5H_{10}O$	1.81	15,500	19,230	114
$VCl_4 \cdot C_4H_{10}O_2$	1.76	14,300	18,500	114
$VCl_4 \cdot 2$ PhCOPh	1.70	14,300	20,400 (br)	114
$VCl_4 \cdot 2\ C_6H_8N_2$		15,000 (sh)	19,600	114
$VCl_4 \cdot 2\ C_4H_4N_2$	1.80	16,700 (sh)	21,300	114
$VCl_4 \cdot 2$ MeCN	1.77	20,000	22,000	72
$VCl_4 \cdot 2$ py	1.80	15,750	obscured	91
$VCl_4 \cdot$ bipy	1.77	17,400	21,300	112*
$VCl_4 \cdot$ phen	1.76	18,000	21,700	112*
$VCl_4 \cdot C_6H_4(AsEt_2)_2$	1.76	14,700	obscured	115

* As it is not known which of the two terms, $^2B_{1g}$ and $^2A_{1g}$ is the higher the authors original assignments for these complexes have been reversed so as to conform with the other assignments in the Table.

The spectral properties of some complexes of vanadium(IV) chloride are recorded in Table 5. If we assume the validity of Jørgensen's rule of average environment, this data together with the data for VCl_6^{2-} can be used to provide a spectrochemical series of ligands complexed with vanadium(IV) chloride:

$$\text{MeCN} > \text{phen} \sim C_4H_8O_2 > \text{bipy} > C_4H_4N_2 >$$
$$C_5H_{10}O \sim \text{PhCOPh} \sim C_6H_8N_2 > C_4H_{10}O_2 > C_4H_8O > Cl^-$$

The magnetic properties of [$VCl_4 \cdot$ bipy] and [$VCl_4 \cdot$ phen] have been studied over a temperature range; the moments drop to 1.60 BM at 80 °K. The separation (δ) between the ^2E_g and $^2B_{2g}$ terms is found to be 1100 cm^{-1} for [$VCl_4 \cdot$ bipy] and 750 cm^{-1} for [$VCl_4 \cdot$ phen][112].

The reactions of vanadium(IV) chloride with Lewis bases are conveniently listed under three headings: addition reactions, reduction reactions, and solvolytic reactions.

Addition reactions of the vanadium(IV) halides. Vanadium (IV) fluoride[111] is a brilliant lime-green powder which hydrolyses in moist air and disproportionates above 100°. It forms 1 : 1 complexes with ammonia, pyridine and selenium tetrafluoride (Table 6). The ammonia and pyridine adducts are also formed in the reactions of vanadium(V) fluoride with these ligands[116]. The adducts are probably fluorine-bridged polymers. It is difficult to formulate the SeF_4 adduct as a donor acceptor complex however in view of the evidence[117] that SeF_4 is not a good electron donor; it may have an ionic structure e.g. $SeF_3{}^+VF_5{}^-$. Sulphur tetrafluoride does not form a complex with vanadium(IV) fluoride.

Vanadium(IV) chloride forms stable adducts only with those donor mole-

TABLE VI

COORDINATION COMPOUNDS OF VANADIUM(IV) FLUORIDE

Reactant	*Product*	*Comments*	*Ref.*
NH_3	$VF_4 \cdot NH_3$	$\mu_{eff} = 1.83$ BM (293 °K)	111
py	$VF_4 \cdot py$	$\mu_{eff} = 1.79$ BM (293 °K)	111
KF	K_2VF_6	SeF_4 as solvent	111
NO_2F	NO_2VF_5	IF_5 as solvent	111
SeF_4	$VF_4 \cdot SeF_4$		111

cules which do not contain protonic hydrogen; with tertiary bases reduction often follows after co-ordination, stable adducts can usually be isolated however by using low donor concentrations and/or low temperatures or by gas-phase reaction. Adducts formed in these ways are listed in Table 7. As can be seen from this Table, complexes are formed by oxygen-, sulphur-, selenium-, nitrogen-, phosphorus- and arsenic-donor molecules. In some cases further reaction, i.e. reduction

TABLE VII

CO-ORDINATION COMPOUNDS OF VANADIUM(IV) CHLORIDE

Reactant	*Stoichiometry of product, VCl_4 : Base*	*Comments*	*Ref.*
Et_2O	1 : 2	m.p. 25°	118
1,4-dioxane	1 : 1	red-brown	114, 119
tetrahydropyran	1 : 2	red-brown	114
tetrahydrofuran	1 : 2	red-brown	114
diglyme	1 : 1	red-brown	114
EtCHO	1 : 2	vapour phase reaction	119
CH_2 : CHCHO	1 : 2	vapour phase reaction	119
PhCHO	1 : 2	CCl_4 solution	119
PhCOPh	1 : 2		114
$POCl_3$	1 : 2	m. p. 45°	120
NO	1 : 1	CCl_4 solution	121
MeCN	1 : 2	benzene solution	72, 122
$PhCH_2CN$	1 : 2	blue	122
EtCN	1 : 2	purple-black	72
S_4N_4	1 : 1		123
Me_3N	1 : 1		65
pyridine	1 : 2	toluene solution, −20°	91
pyrrole	1 : 2	vapour phase reaction	119
pyrazine	1 : 2		114
2,6-dimethylpyrazine	1 : 2		114
bipy	1 : 1		112
$EtNH_2$	1 : 2	vapour phase reaction	119
phen	1 : 1		112
PhN=NPh	1 : 1	brown-black	124
thiophen	1 : 1	vapour phase reaction	119
$MeSe(CH_2)_3SeMe$	1 : 1	purple-grey, decomp 114°	125
$MeSe(CH_2)_2SeMe$	1 : 1	purple-grey, decomp 130°	125
diars	1 : 2	orange, $\mu_{eff} = 1.75$	126
o-$C_6H_4(AsEt_2)_2$	1 : 1	brown-black	115

or solvolysis occurs in the presence of an excess of the ligand. All the complexes listed in Table 7 are of course extremely susceptible to hydrolysis and their preparations must be performed under rigorously-anhydrous conditions to prevent the formation of oxovanadium(IV) species.

With unidentate ligands 1 : 2 complexes are normally formed. In general these adducts are insoluble in organic solvents so that physical measurements on solutions are not possible. The $[VCl_4 \cdot 2\,RCN]$ complexes however give brown solutions in benzene; molecular-weight measurements on these solutions indicate extensive dissociation presumably of the type:

$$VCl_4 \cdot 2\,RCN \rightleftharpoons VCl_4 \cdot RCN + RCN$$

There is infrared evidence to support the belief that the 1 : 2 complexes have a *trans* configuration. As vanadium(IV) chloride gives vanadium(III) chloride on heating, it is not surprising to find that thermal decomposition of these complexes often results in the production of vanadium(III) compounds. The bis(pyridine) adduct sublimes *in vacuo* at 132°, but if heated rapidly to a slightly-higher temperature it yields a residue of violet $VCl_3 \cdot py$. The diethyl ether complex decomposes at 60° liberating ethyl chloride and a residue containing vanadium(III).

The most interesting of these adducts is that of *o*-phenylenebisdimethylarsine, $[VCl_4 \cdot 2\,\text{diars}]$. It is isostructural with the titanium complex whose structure has been studied by single-crystal X-ray diffraction methods. The structure of $[VCl_4 \cdot 2\,\text{diars}]$ is thus known to be dodecahedral with bidentate diarsine ligands. This is the only established example so far of eight-co-ordinate vanadium. It is remarkable that while a six-co-ordinate derivative of diars, $VCl_4 \cdot \text{diars}$ can also be prepared, the diethylarsine gives only the 1 : 1 complex. This would appear to indicate that the methyl arsine forms stronger complexes with vanadium than does the ethyl arsine.

Ligands which are not normally bidentate sometimes form 1 : 1 complexes with vanadium(IV) chloride, e.g. trimethylamine and thiophen. These complexes may be five co-ordinate. The reaction of vanadium(IV) chloride with nitric oxide leads to various products depending upon the conditions employed. Even under similar conditions, i.e. passage of nitric oxide through solutions of the halide in carbon tetrachloride, different authors have obtained a brown diamagnetic[127] $[V(NO)_3Cl_2]$ and a paramagnetic[121] $[VCl_4 \cdot NO]$. In the vapour-phase reaction, paramagnetic $[V_2Cl_8(NO)_5]$ and VCl_3 are the major products while passage of nitric oxide through liquid vanadium(IV) chloride results in precipitation of paramagnetic $[V_2Cl_7NO]$. All these compounds are insoluble in common organic solvents; in water they liberate nitric oxide and form the oxovanadium(IV) cation.

With bidentate ligands 1 : 1 complexes are the rule. Two structural types are possible here; those in which both donor atoms of the ligand are co-ordinated to the same metal atom and those in which the bidentate donor acts as a bridge between two different metal atoms. Infrared and solubility data have been used to decide that e.g. [VCl_4 · bipy], [VCl_4 · phen] and [VCl_4 · o-$C_6H_4(AsEt_2)_2$] belong to the first mentioned group and [VCl_4 · dioxane] to the second group. The tetrasulphur tetranitride adduct is believed to contain the ligand bidentate through nitrogen to the one vanadium atom.

Reduction reactions of vanadium(IV) chloride. The reaction of vanadium(IV) chloride with a large number of tertiary bases results in oxidation of the base and reduction to vanadium(III). This reduction occurs usually in the direct reaction (no solvent) between vanadium(IV) chloride and excess of the ligand at room temperature. Often, when using the reactants in dilute solution in a solvent, reduction slowly occurs and frequently the preparative problem here is that of isolating a complex with vanadium in an integral oxidation state (and not some value between +3 and +4). Thus whilst reduction has been observed with many ligands, the products, apart from those listed in Table 8, have not been isolated in a pure state. Amongst the ligands known to bring about reduction are azomethane and azobenzene[124], triphenylarsine, $Ph_2PCH_2CH_2PPh_2$, tetrahydrothiophen, 1,4-dithian and 1,4-thioxane[114].

TABLE VIII

REDUCTION OF VANADIUM(IV) CHLORIDE BY DONOR MOLECULES

Donor	*Product*	*Ref.*
Me_3N	$VCl_3(NMe_3)_2$	65
C_6H_5N	$VCl_3(py)_3$	75
MeCN	$VCl_3(MeCN)_3$	72
PPh_3	$[Ph_3PH]\,[VCl_4(PPh_3)]$	114
Me_2S	$VCl_3(Me_2S)_2$	66
pentamethylenesulphide	$VCl_3(PMS)_2$	114

The oxidation products of the organic ligands still remain something of a mystery, despite the fact that similar redox reactions occur with many other transition metals. In the reduction by alkyl cyanides, the chlorine is lost from vanadium as hydrogen chloride and in the trimethylamine reaction the chlorine is recovered as trimethylamine hydrochloride. In the reduction of tungsten(VI) chloride and tungsten(V) bromide with pyridine, the oxidation product of pyridine is believed to be the 1-(4-pyridyl)pyridinium ion[128]. It seems likely in these reactions that after co-ordination by the ligand, the initial step is that of electron transfer to the vanadium to give a radical cation e.g. $C_5H_5N\cdot^+$ and a radical anion $VCl_4\cdot$

Solvolytic reactions of vanadium(IV) chloride. Whilst in water vanadium(IV) chloride is hydrolysed violently, an incomplete solvolysis occurs in most other protonic solvents (Table 9). In liquid ammonia at −37°, tensimetric studies[129] indicate that between two and three chlorine atoms in vanadium(IV) chloride are

TABLE IX

SOLVOLYTIC REACTIONS OF VANADIUM(IV) CHLORIDE

Reagent	*Product*	*Ref.*
NH_3	$VCl_2(NH_2)_2 + VCl(NH_2)_3$	129
NH_2R (R = Me, Et, n-Pr, n-Bu)	$VCl_2(NHR)_2 \cdot 4\,NH_2R$	65, 130
NHR_2 (R = Me, Et, n-Pr)	$VCl_2(NR_2)_2$	130
ROH (R = Me, Et, n-Pr, i-Pr, n-Bu)	$VCl_2(OR)_2 \cdot ROH$	131
o- or *p*-HOC_6H_4CHO	$VCl_2(OC_6H_4CHO)_2$	119
m- or *p*-ClC_6H_4OH	$VCl_2(OC_6H_4Cl)_2$	122
o- or *p*-$O_2NC_6H_4OH$	$VCl_2(OC_6H_4NO_2)_2$	122
$(MeCO)_2CH_2$	$VCl_2(C_5H_7O_2)_2$	122
$PhCOCH_2COMe$	$VCl_2(C_{10}H_9O_2)_2$	122

replaced by amide groups. The ammonia-insoluble amide chloride, $V(NH_2)_2Cl_2$, dissolves in a solution of ammonium chloride in liquid ammonia and complex anions of vanadium are believed to be formed, e.g. $(NH_4)_2[V(NH_2)_2Cl_4]$. The khaki-coloured amide chloride is insoluble in non-polar solvents and is presumably polymeric. With primary and secondary amines at room temperature aminolysis definitely stops at the formation of the dichlorodiamides. The green primary-amine products are insoluble in benzene and in the parent amines and are thought to be polymeric. They release two molecules of primary amine on heating to 60° leaving the purple $[VCl_2(NHR)_2 \cdot 2\,NH_2R]$. The products obtained with secondary amines are more soluble; molecular-weight measurements on $VCl_2(NMe_2)_2$ in benzene indicate it to be present in solution as a mixture of monomer and dimer.

Alcohols and phenols similarly cause cleavage of two V–Cl bonds, forming the dichloroalkoxides. The alkoxides formed by the aliphatic alcohols are dark-green solids, dimeric in boiling benzene. These dimers probably contain hexa-co-ordinated vanadium with a structure consisting of two octahedrals sharing a common edge through alkoxide bridges. They cannot be sublimed, but on heating at 150°/0.1 mm they yield the oxychloride alkoxides, $[V_2OCl_3(OR)_3]$. The tert-butyl and tert-amyl alkoxide chlorides are most conveniently prepared by alcohol exchange on the iso-propoxides. The alkoxides $[VCl_2(OR)_2 \cdot ROH]$, where R = n-Bu or tert-Bu, give well resolved electron-spin resonance spectra with *g* values[132] equal to 1.95.

Complete replacement of the halogen atoms in vanadium(IV) chloride can be achieved using lithium dialkylamides. The reaction of vanadium(IV) chloride with $LiNEt_2$ gives[133] the dark-green liquid $V(NEt_2)_4$. This and the dimethylamide[134] react vigorously with alcohols to give the moisture-sensitive tetraalkoxides $V(OR)_4$, a whole range of which (having primary, secondary and tertiary alcoholic groups) have been characterised. They are benzene-soluble so that molecular-weight measurements have been used to determine their degree of polymerisation. The tertiary alkoxides are all monomeric liquids, the secondary alkoxides are predominantly monomeric liquids but the primary alkoxides are associated. Tetra-

(methoxy)vanadium(IV) approximates to a trimer which is the limiting degree of polymerisation for an octahedrally-co-ordinated metal alkoxide. Little magnetic or spectral data are available on these compounds but an electron-spin resonance spectrum of the tetrahedral tetrakis(tert-butoxy)-vanadium(IV) shows a g value of 1.964 (at 30°)[135].

Whilst alkali-metal alkoxides do not usually effect complete cleavage of V–Cl bonds, the pale-blue solid, tetrakis(triphenylsiloxy)-vanadium(IV) is obtained[136] in the reaction of vanadium(IV) chloride with sodium triphenylsilanolate. The liquid ethyl analogue $V(OSiEt_3)_4$, is prepared from the vanadium(IV) diethylamide and triethylsilanol in benzene[134].

(ii) Anionic complexes

Hexafluorovanadates(IV). The hexahalogenovanadates(IV) are interesting d^1 complexes because they have six identical ligands surrounding the metal ion. Tetragonal distortion can arise here only as a consequence of the Jahn–Teller effect. They have only very recently been isolated in the solid state.

The hexafluorovanadates(IV) can be prepared from vanadium(IV) fluoride and potassium fluoride in selenium tetrafluoride(III) or by fluorination[137] of e.g. K_2VF_5. The magnetic susceptibilities of the potassium, rubidium and caesium salts have been measured over a temperature range; they obey the Curie–Weiss law and have large values of θ.

The one-electron molecular-orbital energy levels for the VF_6^{2-} and VF_6^{3-} ions have been calculated using the Wolfsberg–Helmholtz approximation[138]. The spectrum of K_2VF_6 in a potassium chloride pellet shows a band at 20,120 cm^{-1}; by comparison, the calculated position for the $^2E_g \leftarrow {}^2T_{2g}$ transition is at 20,750 cm^{-1}. The agreement between the observed and calculated band positions for VF_6^{3-} using this scheme is not good, however.

Hexachlorovanadates(IV). The VCl_6^{2-} species cannot be prepared by the conventional routes to hexachloro compounds. Even from saturated ethanolic hydrogen chloride solutions of vanadium(IV), salts of the blue oxotetrachlorovanadate(IV) ion are precipitated upon addition of a suitable basic chloride. With some cations salts of a presumably tetrahedral species $VOCl_3^-$ can be isolated[139]. High-temperature routes to VCl_6^{2-} are also impracticable in view of the ready decomposition of vanadium(IV) chloride. It is apparent therefore that hexachlorovanadates(IV) must be prepared at relatively low temperatures in solvents which are incapable of solvolysing the VCl_6^{2-} ion. Such solvents have been intensively explored by Gutmann[140–144]. The first identification of a hexachlorovanadate(IV) was in the conductimetric titration of potassium chloride with vanadium(IV) chloride in iodine monochloride. Using the solvent system of acids and bases this reaction may be written:

$$2\,KICl_2 + (I)_2VCl_6 \rightarrow K_2VCl_6 + 4\,ICl$$

Subsequently conductimetric titrations of vanadium(IV) chloride with various bases have shown the formation of hexachlorovanadates(IV) in a range of chlorine-containing solvents (Table 10). There is conductimetric evidence in several solvents for the ions VCl_5^-, VCl_7^{3-} and VCl_8^{4-}.

TABLE X

THE FORMATION OF CHLOROVANADIUM(IV) SPECIES IN NON-AQUEOUS SOLVENTS

Solvent	*Base*	*Product*	*Ref.*
ICl	KCl	K_2VCl_6	140
HCl	py	$(pyH)_2VCl_6$*	91
$SOCL_2$	Me_4NCl	$(Me_4N)_2VCl_6$	141
	py	$(pySOCl)_2VCl_6$	91
SO_2Cl_2	Me_4NCl	$(Me_4N)_2VCl_6$	141
		$(Me_4N)_3VCl_7$	141
		$(Me_4N)_4VCl_8$	141
	py	$(pySO_2Cl)VCl_5$	142
		$(pySO_2Cl)_2VCl_6$	142
	$TeCl_4$	$(TeCl_3)_2VCl_6$	142
$POCl_3$	py	$(pyPOCl_2)_2VCl_6$	143
	PCl_5	$(PCl_4)_2VCl_6$*	141
		$(PCl_4)_3VCl_7$	141
	MCl_2 (M = Hg, Zn)	$MVCl_6$	141
		$(MCl)_2VCl_6$	141
	$AlCl_3$	$(AlCl_2)VCl_5$	141
$AsCl_3$	Me_4NCl	$(Me_4N)PVCl_5$*	144, 141
		$(Me_4N)_2VCl_6$	141
		$(Me_4N)_3VCl_7$	141
		$(Me_4N)_4VCl_8$	141

* Only these compounds have been isolated and analysed.

Only very recently have the dark-red hexachlorovanadates(IV) been fully characterised. The diethyl- and triethyl-ammonium salts were prepared[145] by reaction of vanadium(IV) chloride or the ethyl cyanide adduct with the alkylammonium chlorides in chloroform. The other salts (Table 11) were prepared by

TABLE XI

HEXACHLOROVANADATES(IV)

Compound	μ_{eff} *(BM) (~293 °K)*	*Absorption maxima (ε_{max} in parentheses)*	*Λ ($\Omega^{-1}cm^2$) (~10^{-3} M in MeCN at 25°)*	*Ref.*
$(Et_2NH_2)_2VCl_6$	1.74			145
$(Et_3NH)_2VCl_6$	1.75	14,900 (65); 21,300 (310)	195	145
$(pyH)_2VCl_6$	1.74	15,400 (89); 21,050 (1040)	180	91
$(quinH)_2VCl_6$	1.74			91
$(isoquinH)_2VCl_6$	1.73		206	91
Cs_2VCl_6	1.75			91

the reaction of thionyl chloride with the corresponding oxotetrachlorovanadate(IV) at room temperature[91]:

$$M_2VOCl_4 + SOCl_2 \rightarrow M_2VCl_6 + SO_2$$

When the $[VOCl_4]^{2-}$ salt is insoluble in thionyl chloride the hexachlorovanadate(IV) can be obtained by using a solution of thionyl chloride in nitromethane (in which the $[VOCl_4]^{2-}$ complexes are slightly soluble).

The hexachlorovanadates(IV) of organic cations dissolve in methyl cyanide to give red solutions and the solution spectra in this solvent are recorded in Table 11. The reflectance spectra of the complexes are very similar to the solution spectra; the molar conductivities of these salts are in the region expected for 1 : 2 electrolytes in methyl cyanide. The band around 15,000 cm^{-1} is assigned to the $^2T_{2g} \leftarrow {}^2E_g$ transition and a Dq value of 1520 cm^{-1} thus obtained. The band is somewhat broad and asymmetric and similar to that observed for the d^1 hexaaquotitanium(III) cation. Jahn–Teller distortion is detectable then in these complexes. The more intense band around 21,000 cm^{-1} is responsible for the dark-red colour of these compounds and is almost certainly due to charge transfer.

The thermal decomposition of two of these compounds has been studied[91]. The pyridinium salt decomposes above 130° mainly according to:

$$(pyH)_2VCl_6 \rightarrow py_2VCl_4 + 2\,HCl$$

The caesium salt is stable up to 210°; at 284° chlorine is evolved and violet Cs_2VCl_5 is left as residue. No further decomposition occurs up to 350°.

F. OXIDATION STATE $+5$ $(3d^0)$

This, the highest oxidation of vanadium is achieved largely in compounds with the electronegative ligands oxygen and fluorine. It represents a d^0 ground state electronic configuration and so the complexes are coloured only through their charge-transfer absorption, and are diamagnetic. They nearly always contain at least one oxygen atom bonded solely to vanadium. Cationic complexes containing V^{5+} are unknown; in acidic aqueous solutions of vanadium(V), the "pervanadyl" ion VO_2^+ is the major species present. The exact nature of this ion and of other species present in solutions of vanadium(V) oxide in sulphuric acid has been discussed[146]. It is not intended in this review to discuss the hydrolysis of vanadium(V) through all the various forms of vanadate; this has been discussed in detail elsewhere[147,148] as has the chemistry of peroxyvanadates[148]. Many analytical methods for the quantitative estimation of vanadium have used the addition of complex organic ligands to vanadate solutions to produce coloured complexes suitable for colorimetric determination, but the exact nature of the absorbing species has seldom been determined.

The co-ordination compounds formed by vanadium(V) under non-aqueous conditions are limited largely to those formed by VF_5, VOF_3 and $VOCl_3$. Some nitrates of vanadium(V) have also been studied.

(i) Co-ordination compounds of vanadium(V) halides and oxyhalides

The only pentahalide known is the fluoride. In its reactions with ammonia and pyridine, reduction occurs and the vanadium(IV) fluoride adducts $VF_4 \cdot NH_3$ and $VF_4 \cdot py$, are formed[116]. With fluoride ions however, hexafluorovanadates(V) can be obtained. Thus vanadium(V) fluoride reacts with potassium[149], nitrosyl, nitryl and chloryl fluorides[150] to yield KVF_6, $NOVF_6$, NO_2VF_6 and ClO_2VF_6 (which is stable at low temperatures only). The hexafluorovanadates(V) can also be prepared as e.g. the caesium, silver and barium salts, in solvents such as bromine trifluoride[149] and anhydrous hydrogen fluoride[151]. Potassium hexafluorovanadate(V) decomposes into KF and VF_5 on heating *in vacuo* to 330°; it is hydrolysed in moist air. The potassium, thallium, rubidium and caesium salts have the rhombohedral $KOsF_6$ structure, the silver salt has the tetragonal $KNbF_6$ structure and the lithium and sodium salts the rhombohedral $LiSbF_6$ structure[152]

Complex oxofluorides can be prepared in aqueous hydrogen fluoride and are well established[1]. Selenium tetrafluoride dissolves vanadium(V) oxide to give a colourless solution from which white plates of $[VOF_3 \cdot 2\,SeF_4]$ separate on cooling; it is suggested[153] that this compound is best formulated as $[(SeF_3)_2VOF_5]$. No complex chlorides, bromides or iodides of vanadium(V) are known but some oxochlorides with the $[VOCl_4]^-$ anion are briefly reported[1,154].

Vanadium(V) oxytrichloride undergoes reactions of addition and solvolysis; reduction by Lewis bases occurs also but this has not been studied to any extent. The donor power of $VOCl_3$ is negligible[155]. The co-ordination compounds formed by $VOCl_3$ as an acceptor, with oxygen and nitrogen donors, are listed in Table 12. By the addition of the donor dissolved in an inert organic solvent, dark-red, or black solids are formed by $VOCl_3$ with ketones, ethers, tertiary amines and nitriles. These complexes are sensitive to hydrolysis and are often soluble in organic solvents such as nitrobenzene. Bidentate ligands form 1:1 complexes only, unidentate ligands usually form hexa-co-ordinate complexes with two molecules of the donor. An interesting reduction occurs when the $VOCl_3$–pyridine adduct is dissolved in excess pyridine; the blue-green crystals of $[VOCl_2 \cdot 3\,py]$ can be isolated. This complex cannot, however, be obtained from vanadium(IV) oxydichloride which is insoluble in pyridine[154].

In addition to the solid complexes isolated, the yellow $VOCl_3$ gives, in aromatic solvents, highly-coloured solutions which have concentration-dependent extinction coefficients[156]. The charge transfer spectra of $VOCl_3$ in benzene, toluene, *p*-xylene, mesitylene and other aromatic solvents show an additional band at 19,000–23,000 cm^{-1} over that found[156] at 29.000 cm^{-1} for pure $VOCl_3$. The

TABLE XII

CO-ORDINATION COMPOUNDS OF VANADIUM(V) OXYTRICHLORIDE

Reactant	*Product*	*Ref.*
camphor	$VOCl_3(C_{10}H_{16}O)_2$	156
benzophenone	$VOCl_3(PhCOPh)_2$	156
fluorenone	$VOCl_3(C_{12}H_8CO)_2$	156
phenanthraquinone	$VOCl_3(C_{14}H_8O_2)$	156
dioxane	$VOCl_3[O(CH_2CH_2)_2O]$	119
acetonitrile	$VOCl_3(MeCN)_2$	154
benzonitrile	$VOCl_3(PhCN)_2$	154
triethylamine	$VOCl_3(NEt_3)_2$	154
pyridine	$VOCl_3py_2$	154
quinoline	$VOCl_3(C_9H_7N)$	156
isoquinoline	$VOCl_3(C_9H_7N)$	156
acridine	$VOCl_3(C_{13}H_9N)$	156
azobenzene	$VOCl_3(C_{12}H_{10}N_2)$	156
2,2′-bipyridyl	$VOCl_3 \cdot bipy$	154
1,10-phenathroline	$VOCl_3 \cdot phen$	156

stoichiometry of these solution complexes with π-electron donors has been established[157] as 1 : 1. The E.S.R. spectra of solutions of $VOCl_3$ in arenes at −196° show a split up signal of V^{4+} and C^+ at about $g = 2$. The spin concentration (which is about 0.1–1.0% of the vanadium concentration by comparison with the E.S.R. spectrum of $[VO(MeCOCHCOMe)_2]$) is inversely proportional to the ionisation energy of the arene. While the solid complexes (Table 13) show an E.S.R. signal at room temperature, the arene complexes do so only at low temperatures.

TABLE XIII

SOLVOLYTIC REACTIONS OF VANADIUM(V) OXYTRICHLORIDE

Reagent	*Product*	*Ref.*
MeOH	$VOCl_2OMe$	154
	$[MeOH_2]^+ [VOCl_2(OMe)_2]^-$	154
	$VO(OMe)_3$	154
EtOH	$VOCl_2OEt$	154, 160
	$VOCl(OEt)_2$	154, 160
i-PrOH	$VO(i\text{-}PrO)_3$	162
Ph_3SiOH	$VO(OSiPh_3)_3$	136
$CHF_2CF_2CH_2OH$	$VOCl(OR)_2$	163
	$VO(OR)_3$	163
resorcinol	$VOCl(C_6H_4O_2)$	161
	$VO_2(C_6H_4O_2)_3$	161
PhOH	$VOCl(OPh)_2$	154
o- or *p*-HOC_6H_4CHO	$VOCl_2(OC_6H_4CHO) \cdot HOC_6H_4CHO$	119
o- or *p*-ClC_6H_4OH	$VOCl(OC_6H_4Cl)_2$	154
$(MeCO)_2CH_2$	$VOCl_2(C_5H_7O_2)$	154
	$VOCl(C_5H_7O_2)_2$	154
$(MeCNOH)_2$	$VOCl(C_4H_6O_2N_2)$	154
CH_3CO_2H	$VO_2(OAc)$	164
$PhCO_2H$	$VO(OCOPh)_3$	165

(ii) Solvolytic reactions of vanadium(V) oxytrichloride

Studies of solvolytic reactions of $VOCl_3$ are largely limited to those with alcohols, phenols and carboxylic acids. Reactions with nitrogen and sulphur ligands are virtually unreported, cursory studies only have been made of the reactions of $VOCl_3$ with aniline[158] and liquid hydrogen sulphide[159].

In most of the solvolytic reactions (Table 13) the product depends to a large extent upon the nature of the reaction conditions. Thus, for example, the reaction of the halide with excess ethanol in benzene is highly exothermic and some reduction to vanadium(IV) is observed along with the formation of mixed chloride alkoxides of vanadium(V)[160]. Using $VOCl_3$: EtOH ratios of 1 : 1 and 1 : 2 in carbon tetrachloride however, reduction is negligible and the compounds [$VOCl_2$(OEt)] and [VOCl$(OEt)_2$] are formed, respectively[154]. With phenols, the reaction takes place in two quite well-defined stages. At room temperature and using an excess of phenol in carbon tetrachloride solution, two chlorine atoms are replaced by one molecule of a dihydroxyphenol or two molecules of a monohydroxyphenol. On refluxing, three molecules of a monohydroxyphenol react with one of $VOCl_3$ and three molecules of a dihydroxyphenol react with two of $VOCl_3$, forming [$VO(OPh)_3$] and [$(VO)_2(OPh)_3$], respectively[161].

When the alcoholysis reaction stops at an intermediate stage, the chlorine-free alkoxides can often be obtained using ammonia gas to base catalyse the solvolysis. Thus, triphenylsilanol reacts with $VOCl_3$ in the presence of ammonia forming [$VO(OSiPh_3)_3$]. The sulphur analogue of this compound [$VS(OSiPh_3)_3$], has been prepared from vanadium(IV) chloride, sulphur and sodium triphenylsilanolate in benzene[136].

The conversion of oxovanadium(V) alkoxides into oxovanadium(V) chloride alkoxides can be effected[160,162] either by reaction with $VOCl_3$:

$$2\,VO(t\text{-}BuO)_3 + VOCl_3 \rightarrow 3\,VOCl(t\text{-}BuO)_2$$

or with acetyl chloride:

$$VO(OR)_3 + 2\,CH_3COCl \rightarrow VOCl_2(OR) + 2\,CH_3COOR \quad (R = Et \text{ or } i\text{-}Pr)$$

Solutions of vanadium(V) oxytrichloride in aliphatic carboxylic acids are brown and quite stable at room temperature. Reaction occurs on heating however, and with acetic acid, yellow VO_2OAc (but not $VO(OAc)_3$) can be isolated. With other acids however e.g. formic, propionic, n- and iso-butyric and mono-, di- and tri-chloracetic acids, reduction of the vanadium occurs and oxovanadium(IV) carboxylates can be isolated:

$$2\,VOCl_3 + 7\,HCOOH \rightarrow 2[VO(HCOO)_2 \cdot H_2O] + 6\,HCl + 2\,CO + CO_2$$

Upon heating long-chain and aromatic carboxylic acids with $VOCl_3$ in carbon tetrachloride to a temperature some 10° higher than the melting point of the acid, complete solvolysis occurs without reduction:

$$\mathrm{VOCl_3+3\,PhCO_2H \rightarrow [VO(OCOPh)_3]+3\,HCl}$$

The reaction is more vigorous with dibasic acids and the carboxylates are formed, e.g. phthalic acid gives $[C_6H_4(COO)_2]_3(VO)_2$. These carboxylates are coloured crystalline compounds insoluble in ether and benzene and hydrolysed in water.

Some well-characterised silylamino-substituted vanadium(V) compounds have been synthesised[162] by reaction of sodium bis(silyl)amides $NaN(SiR_3)_2$ (R = Me or i-PrO) with oxovanadium(V) compounds. The oxytrichloride thus reacts with one or three moles of $NaN(SiMe_3)_2$ giving $Cl_2OVN(SiMe_3)_2$ and $OV[N(SiMe_3)_2]_3$; on the basis of nuclear magnetic resonance and infrared spectra the latter is best formulated as $[(Me_3Si)_2N]_2V(OSiMe)(:NSiMe)$. Similar compounds with alkoxide groups in place of chlorine can be prepared starting from, e.g. $(RO)_2VOCl$.

(iii) Azide and nitride chlorides of vanadium(V)

Very recently a novel vanadium(V) nitrilochloride has been described[166]. The reaction between vanadium(IV) chloride and chlorine azide yields a dark-brown explosive azide chloride of vanadium(V):

$$\mathrm{VCl_4+ClN_3 \rightarrow VCl_4N_3+\tfrac{1}{2}\,Cl_2}$$

On warming in carbon tetrachloride solution this azide loses nitrogen:

$$\mathrm{VCl_4N_3 \rightarrow Cl_3V{:}NCl+N_2}$$

and forms the hygroscopic, crystalline nitrilochloride. This compound is monomeric in benzene, it melts at 136° and decomposes on heating to 150°:

$$\mathrm{2\,VNCl_4 \rightarrow 2\,VCl_3+N_2+Cl_2}$$

In its reactions with donor and acceptor molecules, $VNCl_4$ is Lewis amphoteric. It reacts with pyridine and with antimony pentachloride to form $[VNCl_4\cdot 2\,py]$ and $[VNCl_4\cdot SbCl_5]$, respectively. In the solid state these compounds are ionic, viz. $[VNCl_3]^+[Cl(py)_2]^-$ and $[VNCl_3]^+[SbCl_6]^-$.

(iv) Nitrates of vanadium(V)

Dinitrogen pentoxide reacts with vanadium(V) oxide or $VOCl_3$ to give $VO(NO_3)_2$ as a yellow liquid[167]. The reaction of vanadium metal with dinitrogen tetroxide in acetonitrile at 0° gives the mononitratodioxovanadium(V)[168]:

$$\mathrm{V+2\,N_2O_4 \rightarrow VO_2NO_3+3\,NO}$$

This is an amorphous brick-red diamagnetic powder which on heating decomposes into V_2O_5 and N_2O_5; it is insoluble in common organic solvents but readily soluble (with hydrolysis) in water. No structural studies have been made on these compounds nor any co-ordination compounds prepared from them.

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