Coordination Chemistry Reviews, 81 (1987) 173–226
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

4 VANADIUM

E.M. PAGE

CONTENTS

INTRODUCTION

The following review contains reports of studies carried out on the inorganic coordination chemistry of vanadium. The material is arranged in descending order of oxidation state, hence vanadium(V) and its complexes are dealt with in the first sections. Within each section, subdivisions of the content have been made depending upon the element bonding to the vanadium atom and commencing with elements at the right hand side of the periodic table. In the final section are reports on the chemistry of various vanadate ions and species that formally contain oxo-anions of vanadium. Such species have the vanadium atom arranged in a range of oxidation states and so material is divided according to the nature of the type of chemistry involved, rather than specifically adhering to individual oxidation states.

Studies on the use of vanadium and its compounds as catalysts have not been included, except in cases where the behaviour of the vanadium species is of particular interest. Nor have reports on the wide organometallic chemistry of vanadium been covered, as these are reviewed elsewhere.

4.1 VANADIUM(V)

4.1.1 Species containing vanadium-halogen bonds

The molecular structure of $[VF_5]$ in the gas phase at 30 °C has been investigated by electron diffraction with the aim of detecting any distortion of the molecule from its trigonal bipyramidal (D_{3h}) symmetry [1]. Accurate interatomic distances and amplitudes were obtained which agree well with those found in earlier investigations. However the results regarding the molecular symmetry of $[VF_5]$ were inconclusive and any deviations from D_{3h} symmetry assumed slight.

The $[VF_5]/[XeF_6]$ system has been studied and two new components, namely $XeF_6.VF_5$ and $XeF_6.2VF_5$, were prepared along with $2XeF_6.VF_5$. The Raman spectra of the products indicated that ionic character decreases in the series $2XeF_6.VF_5 > XeF_6.VF_5 > XeF_6.2VF_5$ [2].

The reactions of V_2O_5 with alkali metal fluorides AF (A = $[NH_4]$, Na or K) and hydrogen peroxide in a highly alkaline medium yielded blue microcrystalline salts containing the $[V(O_2)_3F]^{2-}$ ion [3]. The compounds were characterised by elemental analysis, magnetic measurements and infrared spectroscopy. The vanadium atom was shown to be in the +5 oxidation state by redox titrations and by the diamagnetic nature of the compounds. Infrared spectra in the region 850-855 cm^{-1} showed a single strong absorption for all three salts which was inferred to imply that all three peroxy groups are bonded in a triangular bidentate manner to the vanadium atom. A single absorption in the region 470-475 cm^{-1} for each compound was attributed to ν(VF) modes suggesting that the compounds contain heptacoordinated vanadium(V) although the possibility of a polymeric structure with bridging {V-F-V} units was not totally discounted. Using less alkaline media, the same workers have prepared yellow alkali oxodiperoxofluorovanadates(V), $A_2[VO(O_2)_2F]$ (A = $[NH_4]$, Na or K), in high yields from the reaction of V_2O_5, AF and H_2O_2(9%) [4]. Infrared spectral studies indicated the presence of triangularly coordinated peroxo ligands, a terminal V=O bond and a V-F bond in the ions. Another group obtained a dark yellow fluoroperoxovanadate from the reaction between V_2O_5 in HF with H_2O_2 and aqueous KOH [5]. Analytical results (elemental analysis, IR, Raman spectroscopy and X-ray diffraction) showed the salts to be tetrameric in structure.

Salts containing the oxotetrafluorovanadate(V) ion, $[VOF_4]^-$, have been prepared from V_2O_5, HF (40%), and $A[HF_2]$ (A = $[NH_4]$, K, Rb or Cs) [6]. In the solid state, infrared studies showed $[VOF_4]^-$ to have the expected square-pyramidal structure. However, ^{19}F NMR spectra in solution indicated rapid fluorine rearrangement occurs, the ion fluctuating between C_{4v} and trigonal bipyramidal geometry.

A new method of synthesising graphite-VOF_3 ($C_{40}VOF_3$), which involves the action between a saturated solution of VOF_3 in HF on pyrographite for several weeks, has been reported [7]. From a radiocrystallographic determination VOF_3 molecules were found to be organised, without correlation, between the layers.

An electron impact mass spectrometric investigation on a mixture of $VOCl_3$(g) and VCl_3(g) has been carried out [8]. However, the values of appearance potentials of fragment ions and their mass spectra were found to be at variance with those previously reported. The ^{51}V NMR spectra of frozen $VOCl_3$, $VO(OCHMe_2)_3$ and $VOCl(OCHMe_2)_2$ have been measured and the coupling constants e^2qQ/h evaluated from quadrupolar pertubations. The magnitude of the coupling constants was found to decrease in the order expected ($VOCl_3$ > $VOCl(OCHMe_2)_2$ > $VOCl(OCHMe_2)_3$), *i.e.* with increasing shielding of the vanadium nucleus [9,10].

Adducts of $VOCl_3$ continue to be made. Reaction of the oxochloride with 1,5-disubstituted 2,4-dithiobiurets and 1,5-disubstituted-2-thiobiurets (L) in CCl_4 solution yields $VOCl_3$.L [11]. Coordination to the vanadium atom is proposed to occur *via* the sulfur atoms in the former and the sulfur and oxygen atoms in the latter ligand. Other complexes of the type $VOCl_3$.L have been prepared from $VOCl_3$ and *N*-pyridyl-*N'*-alkyl thioureas, L {$RC_5H_4NNC(S)NC_6H_4R'$ (R = H, 4-Me, 6-Me or 5-NO_2; R' = H, 2-Me or 4-Me) or $RC_5H_4NNC(S)NCH_2CH=CH_2$}. Analytical results showed the complexes to contain six-coordinated vanadium(V) with bidentate ligands coordinating through the pyridyl nitrogen and thioketo sulfur atoms [12]. The reactions of both $VOCl_3$ and VCl_3 with PCl_3 and $PPhCl_2$ in the presence of various alkylating agents such as tertiary butyl chloride and triphenylchloromethane have been studied and structures proposed for the complexes formed [13].

4.1.2 Species containing vanadium-oxygen bonds

Kinetic studies have been carried out on the formation of oxoperoxo vanadium(V) complexes (VO_3^+) by oxidation of vanadium(IV) species with hydrogen peroxide [14]. The reactions between the aqua(nitrilotriethanoato)-oxovanadate(IV) ion, $[VO(nta)(H_2O)]^-$, or diaqua(pyridine-2,6-dicarboxylato)-oxovanadium(IV), $[VO(pda)(H_2O)_2]$, and H_2O_2 were carried out at ionic strengths of 1.0 mol l^{-1} $Na[ClO_4]$ in acidic aqueous solution (equations (1) and (2)). The rates of formation of the oxoperoxo vanadium(V) complexes were found to be

$$[VO(nta)(H_2O)]^- + 3/2H_2O_2 \longrightarrow [VO(O_2)(nta)]^{2-} + H_3O^+ + H_2O \qquad (1)$$

$$[VO(pda)(H_2O)_2] + 3/2H_2O_2 \longrightarrow [VO(O_2)(pda)(H_2O)]^- + H_3O^+ + H_2O \qquad (2)$$

first order with respect to the formation of the vanadium(IV) complexes and H_2O_2 and independent of excess ligand concentration and acidity. It was proposed that the rate determining step involved insertion of a H_2O_2 molecule into the first coordination sphere of the vanadium(IV) complex followed by rapid electron transfer and peroxo coordination. The kinetics of two reactions involving the $(VO_3)^+$ ion have been studied spectrophotometrically [15]. In the first reaction (equation 3) $(VO_3)^+$ is oxidised by $[HSO_5]^-$ in acidic solution and in the presence of low concentrations of $(VO)^{2+}$. The rate law was found to be expressed by equation (4). The value of k_1 and the

$$HSO_5^- + VO_3^+ \longrightarrow VO_2^+ + HSO_4^- + O_2 \qquad (3)$$

$$-d[VO_3^+]/dt = k_1[HSO_5^-][VO^{2+}] \qquad (4)$$

reaction scheme proposed are the same as those found in previous studies on the $[HSO_5]^-/(VO_3)^+$ reaction. The second reaction studied involved the oxidation of $(VO_3)^+$ by Co^{3+}. The results from both reactions were thought to suggest the formation of $(VO_3)^{2+}$ followed by its subsequent decomposition to

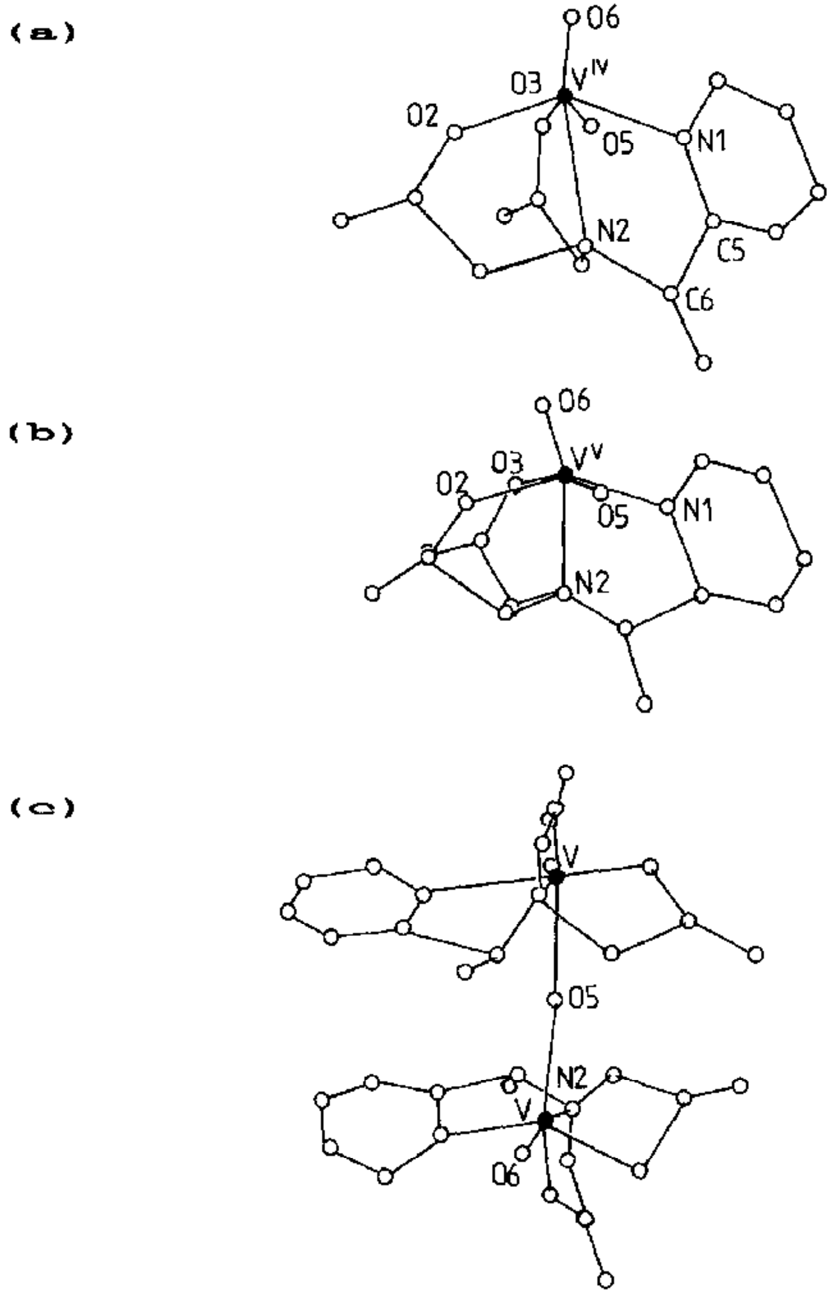


Figure 1: The structures of the complexes (a) $[V^{IV}O(S\text{-peida})(H_2O)]$, (b) $[V^{V}O_2(S\text{-peida})]^-$, and (c) $[V^{IV}V^{V}O_3(S\text{-peida})_2]^-$. In (a), O5 is the oxygen atom of H_2O [16].

$\{VO\}^{2+}$ and O_2. In both cases the primary mode of oxidation of $\{VO_3\}^+$ appeared to be a one electron process.

A series of optically active vanadium(V) and vanadium(IV) complexes containing the (S)-*N*-[1-(2-pyridyl)ethyl]imino ethanoate ion, $[S\text{-peida}]^{2-}$, has been prepared [16]. The structures of three of the complexes, namely $[V^{IV}O(S\text{-peida})(H_2O)]$, $Li\{V^{V}(O)_2(S\text{-peida})\}$ and $Na[V^{IV}V^{V}O_3(S\text{-peida})_2]$, and have been determined by X-ray crystallography, and are illustrated in Figure 1. In each structure the tertiary amine is in the *trans* position to the oxo ligand and the methyl group on the asymmetric carbon atom has an equatorial orientation in the puckered five-membered chelate ring. The structure of the fourth compound $Na[V^{V}O(O_2)(S\text{-peida})]$ was not determined crystallographically but estimated using NMR spectral results. The proposed structure is shown in Figure 2.

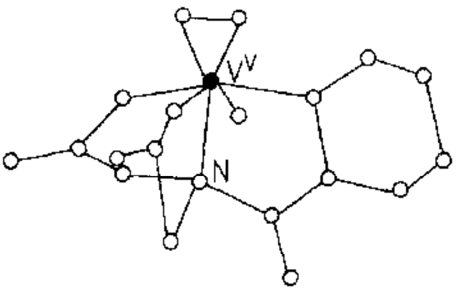


Figure 2: Proposed structure of $[V^{V}O(O_2)(S\text{-peida})]^-$ [16]

The complex ammonium dioxo(2-hydroxynaphthaldehyde semicarbazonato) vanadate(V), $[NH_4][VO_2L]$, has been prepared by reaction of H_2L and $VOSO_4.3H_2O$ in MeOH and its X-ray crystal structure determined [17]. The structure as depicted in Figure 3, was found to contain pentavalent vanadium with *cis*-V=O bonds, $\{O(3)\text{-}\hat{V}\text{-}O(4) = 107.9\,^\circ\}$. The coordination sphere holds one long $(r\{V{=}O(3)\} = 1.654$ Å) and one short $(r\{V{=}O(4)\} = 1.609$ Å) terminal oxygen to vanadium bond. The discrepancy between the bond lengths was thought, almost certainly, to be due to the different sites occupied by the oxygen atoms in the coordination sphere. Atom O(3) is *trans* to the coordinated ligand nitrogen atom and fairly close to a hydrogen atom of the cation. Both factors give rise to a slightly long V=O(terminal) bond length. Atom O(4) is situated on the equatorial axis of the bipyramid and has no ligand *trans* to itself.

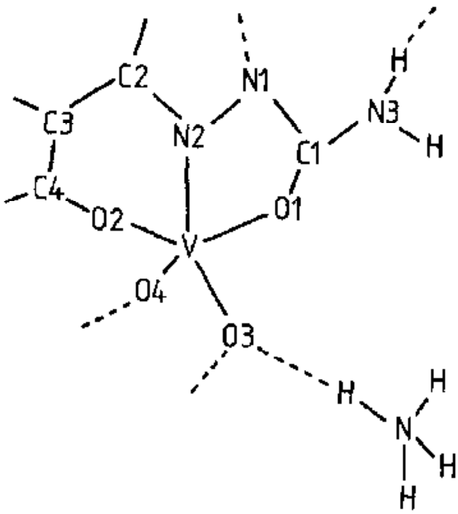


Figure 3: Bonding around the vanadium atom in ammonium dioxo(2-hydroxynaphthaldehyde semicarbazonato)vanadate(V) [17]

By treating $VOCl_3$, $VOCl_2$ and VCl_3 with trifluoroethanoic acid the complexes $VO_2(O_2CCF_3)$, $VO(O_2CCF_3)_2$and $V(O_2CCF_3)_3$ respectively have been obtained [18].

The interaction between $(VO_2)^+$ and 2,4-dithiobiuret in the presence of Cu^{2+} ions has been studied by amperometric titration [19]. The reaction involves reduction of $[CuCl_4]^{2-}$ by 2,4-dithiobiuret to $[CuCl_2]^-$ which then reduces $(VO_2)^+$ to $(VO)^{2+}$.

A number of methods have been described for the determination of the equilibrium concentration of $(VO_2)^+$ in aqueous solutions of phosphomolybdovanadic heteropolyacids [20]. The equilibrium involved is given by equation (5). Each of the methods which include Raman spectroscopy, elemental analysis and spectrophotometry, gave results which agreed well with each other.

$$10(VO_2)^+ + 8H_2O \rightleftharpoons [H_2V_{10}O_{28}]^{4-} + 14H^+ \qquad (5)$$

A technique has been developed in which vanadium(V) and vanadium(IV) can be extracted synergistically by forming a primary dithizonate. The extraction is carried out in benzene and is represented by equations (6) and (7), where

$$\{VO_2\}^+ + H_2dz + tbpo \rightleftharpoons [VO_2(Hdz)(tbpo)] + H^+ \qquad (6)$$

$$\{V(O)OH\}^+ + H_2dz + topo \rightleftharpoons \{V(O)OH(Hdz)(topo)] + H^+ \qquad (7)$$

H_2dz = dithizone, tbpo = tributyl phosphine oxide, and topo = trioctyl phosphine oxide [21].

The kinetics of ligand substitution reactions of $[edta]^{4-}$ (ethylenediaminetetracetate) and $[edda]^{2-}$ (ethylenediaminediacetate) by $[nta]^-$ (nitrilotriacetate) ions in vanadium(V) complexes has been carried out in order to determine a general mechanism [22]. It was concluded that the reaction can proceed by H^+ induced dissociation of $[VO_2(edta)]^{3-}$ and $[VO_2(edda)]^-$ followed by formation of the nta complex or by direct attack of the nta species with the fast formation of outer sphere complexes followed by aminocarboxylate ligand exchange. The kinetics of complex formation between $\{VO_2\}^+$ and various phosphorus containing complexones, nitrilomethylphosphoric acid (ntp), ethylenediaminetetramethylphosphoric acid (edtp), aminodimethylphosphoric monoethanoic acid (adpa), and diethylenetriaminepentamethylphosphoric acid (dtpp) have been studied spectrophotometrically [23].

Electrochemical studies by cyclic voltammetry and controlled potential coulometry on the reduction of $[VO_2(acac)(phen)]$ and $[V_2O_4(acac)_2]$ have been carried out [24]. The reduction potentials were calculated for one electron reductions and $[VO(acac)_2]$ found to be the major product in both cases. In the presence of excess ligand, three-electron reductions occurred with the formation of $[V(acac)_3]^-$ as the final product.

An analogy has been drawn between the $\{VO_2\}^-$ unit ,studied by X-ray crystallography in the salts $[\{VO_2(O\text{-}8\text{-}quin)_2\}_2Na_2(H_2O)_4(\mu\text{-}dmf)]$, (1), and $[NBu_4][VO_2(O\text{-}8\text{-}quin)_2].H_2O$, (2) and the carboxylato group, $[RCO_2]^-$ [25]. The salts were prepared by the basic hydrolysis of (μ-oxo)bis[bis(8-quinolinato)-oxovanadium(V)], $[\{(quin\text{-}8\text{-}O)_2VO\}_2O]$, whose chemistry has previously been compared to that of organic anhydrides. Several structural features concerning the $\{VO_2\}^+$ unit found in the salts (1) and (2) are considered to justify comparison with the $[RCO_2]^-$ group. Complex (1) is a dimer, shown in Figure 4, in which two $\{VO_2\}^+$ units are bridged by two Na^+ ions sharing the oxygen atom of a dmf molecule. Complex (2), Figure 5, contains the free anion, but structural data for the $\{VO_2\}^+$ units in both salts are very similar. On acidifying an aqueous solution of $[VO_2(8\text{-}O\text{-}quin)_2]^-$ the inorganic analogue of a carboxylic acid was formed, namely $[(quin\text{-}8\text{-}O)_2V(O)(OH)]$, which is a weak acid, $pK_a = 6.3$.

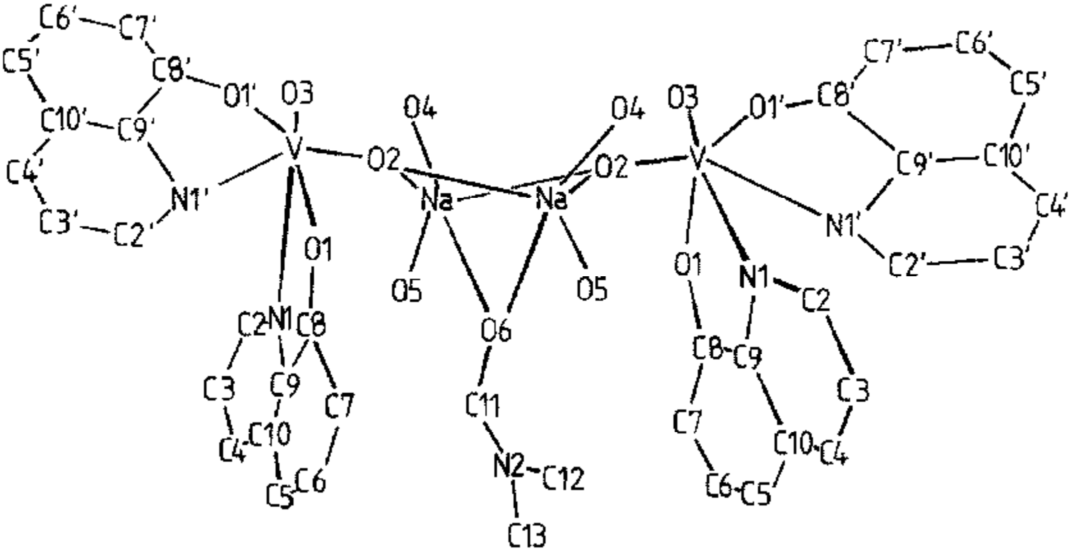


Figure 4: View of complex (1), $[\{VO_2(O\text{-}8\text{-}quin)_2\}_2\{Na(H_2O)_2\}_2(\mu\text{-}dmf)]$ [25]

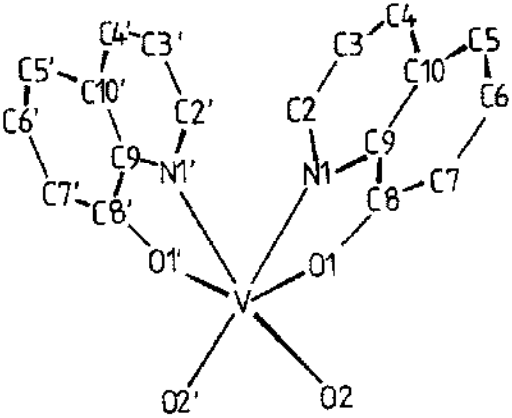


Figure 5: Structure of the anion from (2), $[(quin\text{-}8\text{-}O)_2VO_2]^-$ [25]

The ^{51}V NMR spectra of some dinuclear complexes $[\{VO(ONR_2)_2\}\text{-}\mu\text{-}O]$ and some mononuclear complexes $[VXYZ]$ $\{X = O^{2-}$ or NO^-; $Y = O^{2-}$, $[O_2]^{2-}$ or R_2NO^-; Z = picolinate, dipicolinate, nitrilotri(2-propanolate) or phen$\}$ have been recorded in order to study the effect of the various ligands upon the shielding of the nucleus. The trends found are based upon the variations of molecular parameters correlated to electronic and steric effects associated with the ligands [26].

Two mixed-valence divanadium complexes have been identified. The first is a 1:1 cation/cation complex, $[V_2O_3]^{3+}$, formed between $[VO_2]^+$ and $[VO]^{2+}$ in $HClO_4$, H_2SO_4 or HCl [27]. The formation of the complex, according to equation (8), was studied by spectrometry, the ion being characterised by intense

$$[VO]^{2+} + [VO_2]^+ \longrightarrow [V_2O_3]^{3+} \tag{8}$$

absorption over the whole of the visible range. The oxidation of a mixed-valence ion, $[\{V^{IV}O(O\text{-}8\text{-}quin)_2\}\text{-}O\text{-}\{V^{V}O(O\text{-}8\text{-}quin)_2\}]^-$, whose synthesis was reported last year has been studied [28]. The complex was found to undergo a reversible one-electron-per-dimer oxidation in CH_3CN to give a stable divanadium product (equation 9):

$$[\{VO(O\text{-}8\text{-}quin)_2\}\text{-}O\text{-}\{VO(O\text{-}8\text{-}quin)_2\}]^- \longrightarrow [\{VO(O\text{-}8\text{-}quin)_2\}\text{-}O\text{-}\{VO(O\text{-}8\text{-}quin)_2\}] + e^-; \qquad E = 0.025\ V \tag{9}$$

The cyclic voltammogram of the solution was found to be similar to that of $[VO(OH)(O\text{-}8\text{-}quin)_2]$, from which the dimer can be formed by heating (equation 10):

$$2[VO(OH)(O\text{-}8\text{-}quin)_2] \longrightarrow [\{VO(O\text{-}8\text{-}quin)_2\}\text{-}O\text{-}\{VO(O\text{-}8\text{-}quin)_2\}] + H_2O \tag{10}$$

Stable complexes of vanadium(V), vanadium(IV) and vanadium(III) with 3,5-di-*tert*-butylcatechol ($dtbcH_2$) in aprotic media have been synthesised and their redox chemistry investigated [29]. The complexes $Na[V^{V}O(dtbc)_2]$, $Na_2[V^{IV}O(dtbc)_2]$, $Na_2[V^{IV}Cl_2(dtbc)_2]$ and $Na_3[V^{III}(dtbc)_3]$ can be prepared in non-redox reactions but the vanadium(III) and vanadium(IV) species are oxidised to vanadium(V) by protons from MeOH or H_2O. From a comparison of the electrochemistry of the two vanadium(IV) species the terminal oxygen group seemed to inhibit reversible electron transfer.

Mixed ligand complexes of vanadium(V) with pyrocatechol violet (PCV) and cetylpyridinium bromide (CP) in aqueous and organic media have been prepared and studied spectrophotometrically [30]. The effect of different vanadium-PCV ratios upon the absorption spectra was investigated to establish the composition of the resulting compounds. The results were used to ascertain stability constants.

A series of dimeric and monomeric complexes of vanadium(V) with β-diketones ($[VO(OH)L_2]$, $[VOCl_2L]$, $[VOCl_2L']$, $[V_2O_4L_2]$, $[V_2O_4L'_2]$, *etc.*) (LH = dibenzoylmethane and L'H = pentane-2,4-dione) have been prepared and characterised by standard techniques [31,32].

Intercalation reactions of the layered oxides of vanadium(V), $VOPO_4$ and $VOAsO_4$, with pyridine and 4-substituted pyridines have been carried out by two different methods [33]. The first involves heating $VOPO_4.2H_2O$ under reflux with pyridine for several days and the second direct heating of pyridine with anhydrous $VOPO_4$ or $VOAsO_4$ in sealed evacuated tubes at elevated temperatures. Both methods lead to formation of intercalation compounds $VOPO_4(py)$ or $VOAsO_4(py)$ in which the pyridine molecule is directly coordinated to the vanadium atom in the vanadium oxide layer. Intercalation of pyridine in $VOPO_4$ and $VOAsO_4$ was found to expand the layer separation by 5.5 Å. With 4-substituted pyridines, the reactions are slower and the products less crystalline than with free pyridine.

The complex $Na_4[V_4O_8(C_4H_2O_6)_2].6H_2O$, whose preparation was reported last year, has been studied by IR and NMR spectroscopy, and a tetranuclear structure in which four $\{VO\}^{3+}$ groups are cyclically bridged by oxygen atoms has been proposed [34]. The tartrato(4-) ligands are thought to bridge two vanadium atoms on the basic $\{V_4O_4\}$ skeleton. The same author has also reported the exact conditions for the reproducible synthesis of the relatively unstable tartrato complex $(K_3[V_2O_4OH(C_4H_2O_6)].H_2O$ [35]. The structure of dioxane-bis-{μ-oxobis(oxovanadium(V) 2-(2'-hydroxyphenyl)iminomethylphenato}, $[\{(VOL)_2O\}_2.\text{dioxane}]$ has been investigated [36]. The complex was prepared in an attempt to obtain crystals of the vanadium(IV) dimer $(VO)_2L_2$ from a dioxane solution. In the structure two five-coordinate vanadium atoms are oxygen bridged to form a binuclear asymmetric unit. Two such units are bridged by a dioxane molecule, which bonds weakly to two symmetrically related vanadium atoms, forming a tetrameric complex as shown in Figure 6. The terminal V=O distances are characteristic of double bonds. The V-O distances to the ligand oxygen atoms average 1.85 Å, whereas those to the bridging oxygen atom are slightly shorter (1.76 and 1.81 Å). All V-O distances are shorter than the V-N distances (2.17 and 2.16 Å), which is thought to reflect the low affinity of the $\{VO_2\}^+$ ion for the imino nitrogen.

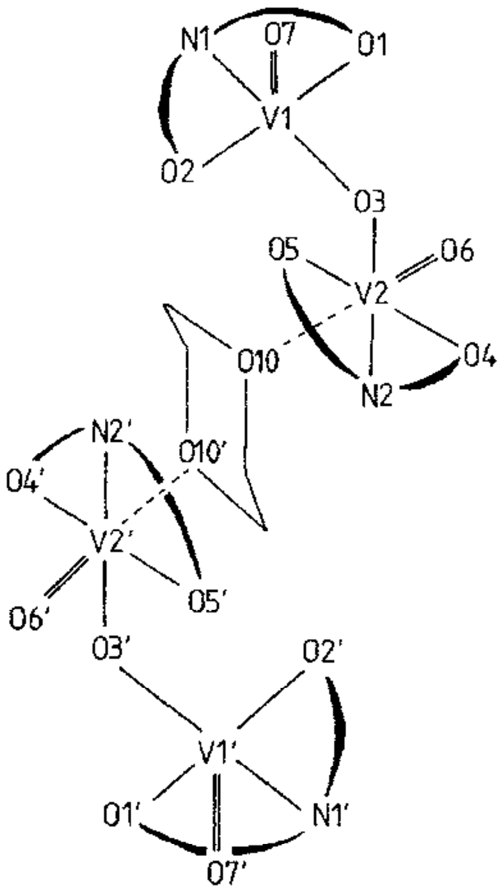


Figure 6: The structure of dioxane-bis-(μ-oxobis{oxovanadium(V) 2-(2'-hydroxyphenyl)iminomethylphenato}, [{(VOL)$_2$O}$_2$.dioxane] [36].

Formation constants between vanadium(V) ions and chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) have been determined by measuring the bathochromatic shift of the UV absorbtion maximum at 360 nm which occurs on complexation [37].

4.1.3 Species containing vanadium-sulfur bonds

A series of complexes of 3-(4-pyridyl)triazoline-5-thione (HL) with early transition metals has been prepared, and the species characterised by standard techniques. The complex formed with vanadium(V), [V(HL)$_4$(H$_2$O)$_2$]Cl$_4$ was thought to have a *trans*-octahedral structure in which the ligand is monodentate, coordinating through the sulfur atom [38].

4.2 VANADIUM(IV)

4.2.1 *Reactions of vanadium(IV) ions*

The extraction of V^{4+} ions from mixed sulfate/phosphate media, buffered with ethanoate, has been achieved successfully using bis(2-ethylhexyl) phosphoric acid (Hdehp) in kerosene. Uptake of vanadium was measured as a function of concentration of Hdehp, V^{4+}, $[SO_4]^{2-}$, $[PO_4]^{3-}$ and $[O_2CMe]^-$, and also at various pH values and temperatures [39].

4.2.2 *Species containing vanadium-halogen bonds*

The structure of liquid VCl_4 has been studied by neutron diffraction, assuming the separation of the intermolecular scattering function into radial and angular parts, an assumption which is approximate for this molecule [40].

The reaction of $VOCl_3$ in methyl cyanide with an excess of hexamethylphosphoramide, $[OP(NMe_2)_3]$, led to the formation of a vanadium(IV) complex $[VOCl_2\{OP(NMe_2)_3\}_2]$ whose structure is depicted in Figure 7 [41]. The

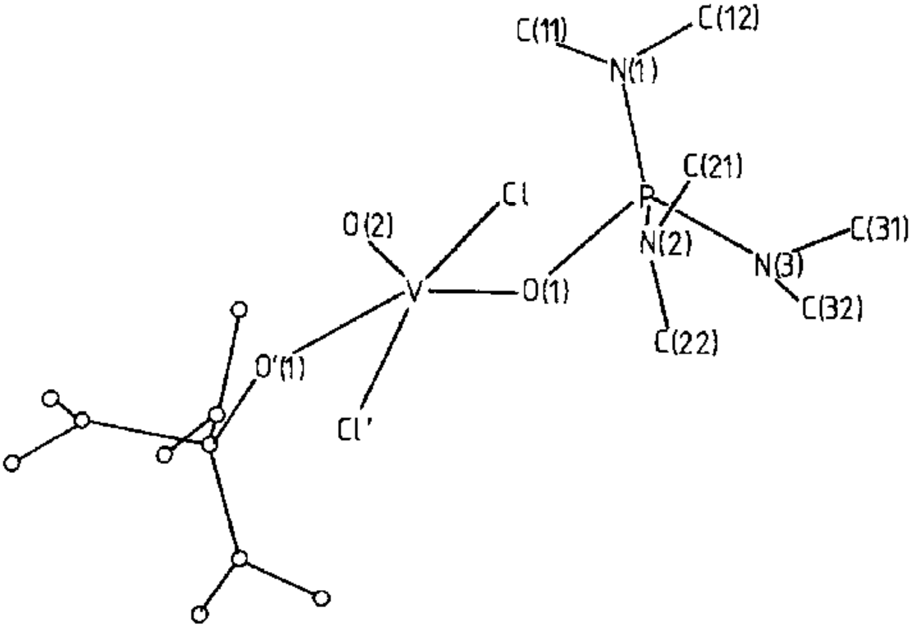


Figure 7: Structure of the complex $[VOCl_2\{OP(NMe_2)_3\}_2]$ [41]

vanadium atom has a tetragonal pyramidal coordination with two chlorine atoms and two ligand oxygen atoms in the equatorial plane. The chlorine atoms are situated *trans* to each other. The vanadium to terminal oxygen bond length, $r\{V{=}O(2)\}$, is 1.566(11) Å and the vanadium to ligand oxygen atoms, $r\{V{-}O(1)\}$ and $r\{V{-}O'(1)\}$, are 2.011(5) and 1.984(5) Å, respectively. Vanadium(IV) species of the type $VOCl_2.R_2P(S)P(S)R_2$ (R = Me or Et) are obtained by reduction from the reaction of $VOCl_3$ with the ligands $R_2P(S)P(S)R_2$ [42]. Reaction with VCl_4 leads to hexacoordinate complexes, $[VCl_4\{R_2P(S)P(S)R_2\}]$. The conformation of the ligand in each type of complex was predicted using infrared, electronic and EPR spectral results.

Replacement of the vanadyl oxygen atom in a series of vanadium(IV) porphyrins, by halogen atoms, has been achieved by reaction of the oxovanadium porphyrin with SOX_2 or $(COX)_2$ (X = Br, Cl) under mild conditions [43]. This parallels a reaction reported in last year's review in which anhydrous HCl was used as the deoxygenating agent. The porphyrins prepared are depicted in Figure 8 and reaction proceeds according to equation (11).

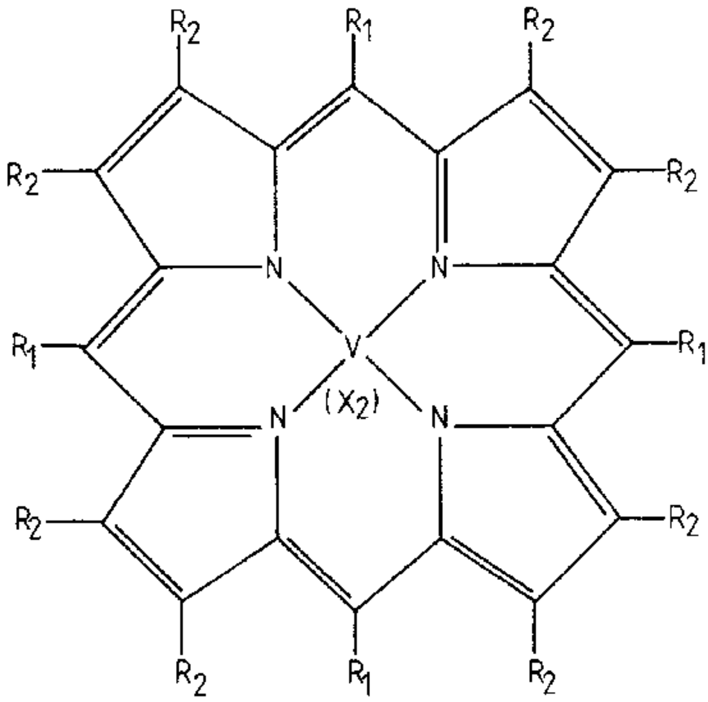


Figure 8: Series of porphyrin complexes prepared in [43], where R_1 = H, Ph, Ph-3-Me or Ph-4-Me; R_2 = C_2H_5 or H.

$$[V^{IV}L(O)] \xrightarrow[CH_2Cl_2 \text{ or } PhCl]{SOX_2 \text{ or } (COX)_2} [V^{IV}LX_2] \qquad (11)$$

The complexes formed are highly reactive and readily reduced to lower valent vanadium porphyrins.

An EXAFS study on the Br-*K* edge on $[V^{IV}(OEP)Br_2]$ confirmed the *trans* configuration of halogen atoms. Deoxygenation of metal porphyrins [VOL] (H_2L = etioporphyrin or tetraphenylporphyrin) has also been accomplished by reaction with metal halides [44]. This is thought to proceed *via* a bimetallic complex in which the metal halide is coordinated to the oxygen atom. In this study, the reaction products were investigated by EPR spectroscopy, whereas in the previous work no EPR signal could be observed in the products when investigated at 77 K in toluene.

Complexes of VOX_2 (X = Cl, Br, NO_3, ClO_4 or ½$[SO_4]$) with propanone, semicarbazone and propanone thiosemicarbazone (L) have been prepared by reaction of VOX_2 with the ligand in hot EtOH [45]. The products, VOX_2L_2, were found to be six-coordinate octahedral complexes and 1:1 electrolytes in the case of all but $VO(SO_4)L_2$.

4.2.3 Species containing vanadium-oxygen bonds

Once again, the preparation of oxovanadium(IV) complexes and investigation of their properties comprises the largest area of research involving the coordination chemistry of vanadium. In some cases interesting structural and spectroscopic studies have been carried out and the results of these will be discussed in more detail.

A series of mononuclear oxovanadium(IV) complexes with various β,δ-triketones and β-diketophenols have been isolated and characterised [46]. The adducts $VO(Hdba)_2$ {H_2dba = 1,5-diphenyl-1,3,5-pentanetrione, $VO(Hdmba)_2$ {H_2dmba = 1,5-bis(4-methoxyphenyl)-1,3,5-pentanetrione}, $VO(Hbap)_2OH$ {H_2bap = 2-benzoyl-acetylphenol} and $VO(Haap)_2$ {H_2aap = 2-acetoacetylphenol} may all act as ligands towards a second $(VO)^{2+}$ group forming dinuclear complexes, such as $[(VO)_2(dba)_2]$, $[(VO)_2(dmba)_2]$, $[(VO)_2(bap)_2]$, and $[(VO)_2(aap)_2]$. Such dinuclear vanadium(IV) complexes have received little attention in the literature, although the preparation of $[(VO)_2(dana)_2]$ {H_2dana = 1,5-bis(4-methoxyphenyl)-1,3,5-pentanetrione} was reported in 1981 [47]. Both the mononuclear and dinuclear adducts were tested for use as ethylene-propylene copolymerization catalysts. The same group have prepared a series of complexes of alkoxyoxovanadium(IV) with β-diketones {$VO(OMe)(acac)$, $VO(OC_2H_5)(acac)$, $VO(OMe)(tmh)$ [Htmh = 2,2,6,6-tetramethylheptanedione], $VO(OMe)(ach)$ [Hach = 2-acetylcyclohexanone] and $VO(OMe)(thtfac)$ [48]. The possible use of all these complexes as soluble Zeigla-Natta catalysts was also tested. Crystals of one of the products [$\{VO(OMe)(acac)\}_2$] were obtained and the structure reported. The structure was found to consist of dimeric {$VO(OMe)(acac)$} units as shown in Figure 9. The vanadium atoms are bridged by the oxygen atoms of the methoxy group leading to a 'chair-like' conformation in the molecule. The five-coordinate vanadium atoms have approximate tetragonal bipyramidal coordination spheres, with the vanadyl oxygen occupying the apical position. The V=O bond length (1.587(3) Å) is typical of a V^{IV}-oxygen double bond.

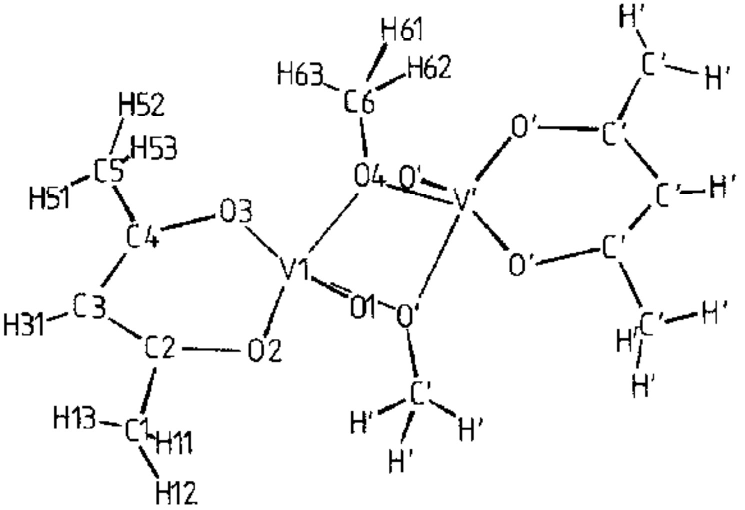


Figure 9: Numbering scheme and structure for [$\{VO(OMe)(acac)\}_2$] [48]

In a study of the reactions of transition metals with ligands of the catechol (1,2-dihydroxybenzene; $catH_2$) type, three complexes of vanadium with catechol itself have been prepared and their X-ray structures determined (see Figure 10) [49]. Two of the structures contain vanadium(IV), $[Et_3NH]_2[V(cat)_3].MeCN$ and $K_2[VO(cat)_2].EtOH.H_2O$, and the third vanadium(III), $K_3[V(cat)_3].1\frac{1}{2}H_2O$. The complex $K_2[VO(cat)_2].EtOH.H_2O$ is a typical square

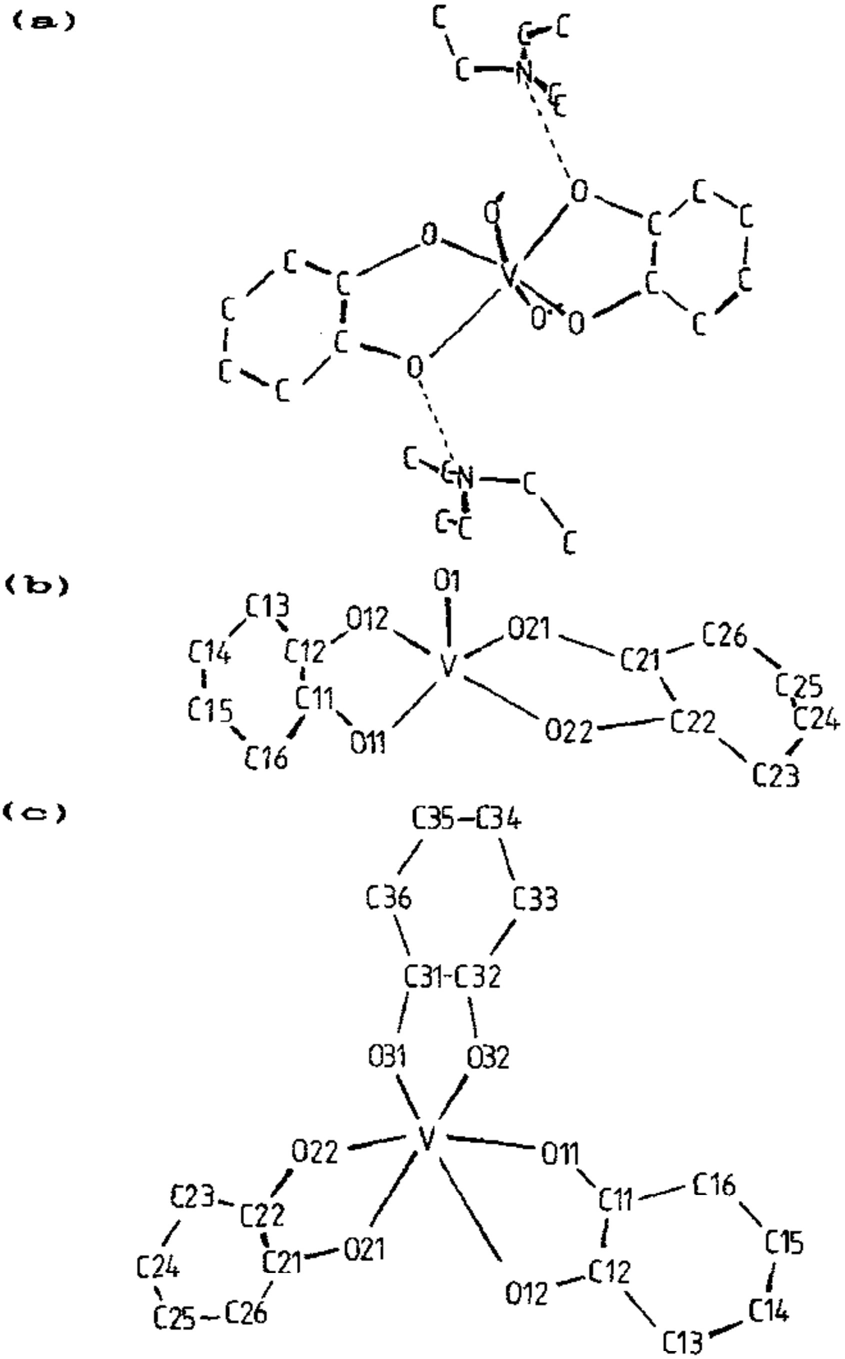


Figure 10: The molecular structures of the complex anions in (a) $[Et_3NH]_2[V(cat)_3].MeCN$, (b) $K_2[VO(cat)_2].EtOH.H_2O$, and (c) $K_3[V(cat)_3].1\frac{1}{2}H_2O$ [49]. In (a), the hydrogen bonding between the anion and cation is illustrated, and the carbon atoms of the third catechol ring have been omitted for clarity.

pyramidal vanadium(IV) structure (r(V=O) = 1.616 Å, r(V–O(cat)) = 1.956 Å). However, in $[Et_3NH]_2[V(cat)_3].MeCN$, a catechol molecule has displaced the oxygen atom producing an octahedral vanadium(IV) complex, although the geometry is far from being rigorously octahedral due to hydrogen bonding of the triethylammonium to two of the catechol oxygen atoms. The V–O(cat) bond lengths average 1.930 Å and the O–$\hat{V}$–O angles are 88.8 °. The vanadium(III) complex, $K_3[V(cat)_3].1\frac{1}{2}H_2O$, closely approximates to octahedral symmetry about the metal and is isostructural with its chromium and iron analogues. Besides the crystal and molecular structures of these three species, IR, UV-VIS and EPR spectra and electrochemical and magnetic data were reported for the complexes VOL, VOL_2 and VL_3 (L = catechol, 3,5-di-*tert*-butylcatechol or 4,5-dihydroxybenzene-1,3-disulfonate).

In the continuation of studies on the magnetic properties of heterobimetallic complexes, the X-ray crystal structure of the complex $[CuVO\{(fsa)_2en\}(MeOH)]$ $\{(fsa)_2en^{4-}$ is a binucleating ligand derived from the Schiff base *N,N'*-(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane} has been determined [50]. In the structure both metal atoms are five-coordinate, having square-pyramidal geometry with the methanolic oxygen and the vanadyl oxygen forming the apices of the pyramids, as shown in Figure 11. Both

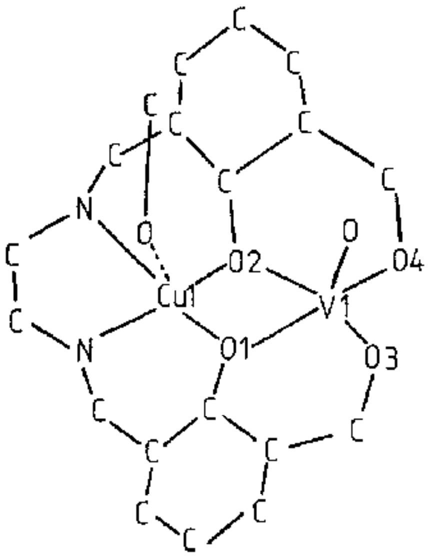


Figure 11: The structure of $[CuVO\{(fsa)_2en\}(MeOH)]$ [50]

pyramids point in the same direction. Two other structures were found during attempts to grow suitable crystals of $[CuVO\{(fsa)_2en\}(MeOH)]$. In one, disorder existed in the orientation of the $\{CuN_2O_3\}$ and $\{VO_5\}$ pyramids and, in the other structure, molecules of $[Cu_2\{(fsa)_2en\}(MeOH)]$ replace the heteronuclear complex about 15% of the time. The magnetic behaviour of $[CuVO\{(fsa)_2en\}]$ was studied in the temperature range 4-300 K, which showed that the exchange interaction between Cu^{2+} and VO^{2+} is purely ferromagnetic due to the orthogonality of the magnetic orbitals centred on the metal ions.

The syntheses of the sodium salts of a series of binuclear oxovanadium(IV) complexes containing methyl substituted tartrate(4-) bridges have been reported (see Figure 12), along with results from spectral studies

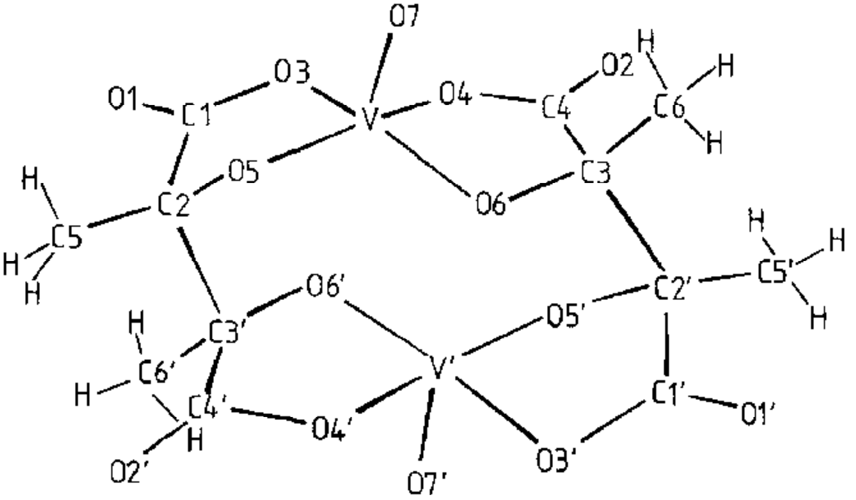


Figure 12: View of the $Na_4[(VO)_2\{(+)\text{-dmt}\}\{(-)\text{-dmt}\}]^{4-}$ anionic complex. Primed ions are generated by $1-x,-y,-z$ [51]

(EPR, IR and electronic spectroscopy) on the various isomers in the solid state and in solution [51]. The salt $Na_4[(VO)_2\{(+)\text{-dmt}\}\{(-)\text{-dmt}\}]$ was found to exist as a blue dodecahydrate and a pink hexahydrate and the X-ray crystal structure of the dodecahydrate was investigated. As expected from studies on the unsubstituted binuclear oxovanadium(IV) tartrate salts, the two $\{VO\}^{2+}$ groups are bridged by dimethyltartrate(4-) ions, the vanadium atoms having approximately square-pyramidal geometry. However, in this dimethyltartrate complex, there is an additional hydroxyl oxygen atom weakly coordinated (2.377 Å) opposite the vanadyl oxygen atom. There is a significant shortening of the V-V distance in this dimethyl substituted tartrate(4-) complex relative to the unsubstituted ones and reasons were given to explain this based on changes in coordination geometry. The aqueous solution ligand exchange reaction between the DD and LL complexes of $Na_4[(VO)_2(C_6H_6O_6)_2].14H_2O$, to give the more stable DL isomer, was studied and found to be extremely slow. As EPR studies on such binuclear oxovanadium(IV) tartrates have been found to indicate decreasing intramolecular V-V distances with increasing methyl substitution of the tartrate(4-) ion, the X-ray crystal structure of a monomethyltartrate complex has been determined by the same group of workers (Figure 13) [52]. Certain geometrical parameters (*i.e.* vanadium to basal least squares plane distance and V-V distance) in tetrasodium [μ-(+)-*threo*-monomethyltartrate(4-)]-[μ-(-)-*threo*monomethyltartrate(4-)]-bis{oxovanadate(IV)} tetradecahydrate, $Na_4[(VO)_2(C_6H_6O_6)_2].14H_2O$, were found to resemble those reported for the oxovanadium(IV) (±)-tartrate(4-) anions more closely than those of the totally substituted binuclear (±)-dimethyltartrate(4-) complex. The shortening of the V-V distance which was predicted by the EPR measurements was not observed in the complex *r*(V...least squares plane) = 0.548 Å, *r*(V-V) = 4.047 Å.

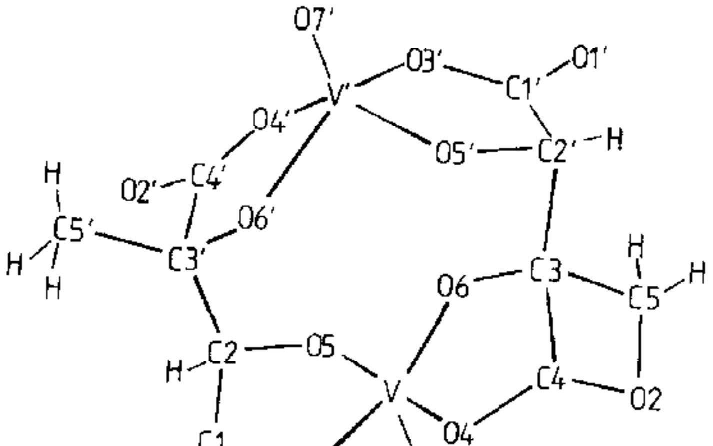


Figure 13: View of the $[(VO)_2\{(+)\text{-mmt}\}\{(-)\text{-mmt}\}]^{4-}$ anionic complex. Primed atoms are generated by $-x$, $1-y$, $-z$ [52]

An unusual trinuclear vanadate carboxylate, $[V_3O_3(thf)(PhCO_2)_6]$, has been obtained from the reaction between $VCl_3.3thf$ and sodium benzoate in CH_2Cl_2 [53]. The single crystal X-ray diffration study of the complex showed it to contain a planar $\{V_3O\}$ trimetal moiety with two different types of vanadium coordination spheres, each having the vanadium atom in the formal oxidation state of (+4). The structure, as shown in Figure 14, consists of a central oxygen atom equivalently bonded to each of the three vanadium atoms, but closer to one of the vanadium atoms, V(1), at 1.626 Å, than the other two, at 2.344(7) and 2.452(6) Å. This grouping with V(1) is regarded as an oxovanadium moiety. The other two vanadium atoms, V(2) and V(3), are each closely bonded to an oxygen atom (at 1.582 and 1.568 Å, respectively). Atom V(1) has a thf oxygen in the position of the terminal oxygen atom. Thus the geometry deviates grossly from that normally found in trinuclear, basic oxo-centred carboxylates (which are ideally D_{3h}). The structure was therefore also analysed in terms of an oxo-vanadium trimer, having the unusual feature of a bridging oxovanadium(IV) group.

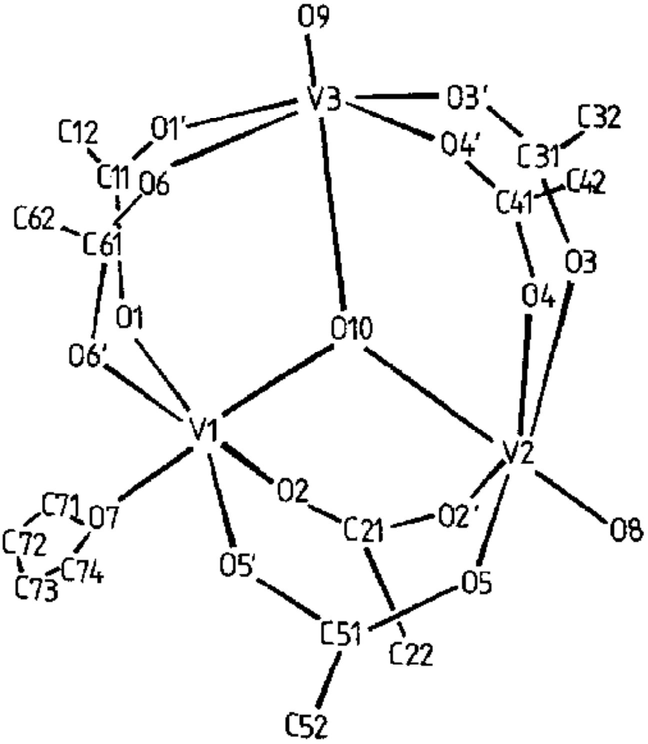
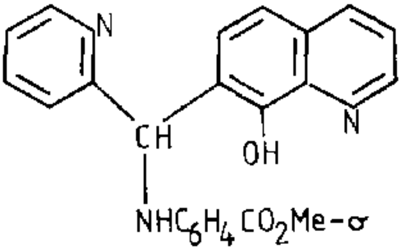


Figure 14: The structure of the $[V_3O_3(thf)(PhCOO)_6]$ molecule. Phenyl groups are omitted for clarity [53]

The compositions of the complexes of $\{VO\}^{2+}$ with 1,5-dimethyl and 1,5-diphenyl-1,3,5-pentanetriones have been determined potentiometrically at 30 °C in the presence of NaCl [54]. The former ligand was found to act monobasically and the latter dibasically. The preparation of VOL_2 (H_2L = bis(2-ethylhexyl)phosphoric acid) has been reported, along with results of various physical measurements including IR spectroscopy, magnetic moments and molecular weight determination.

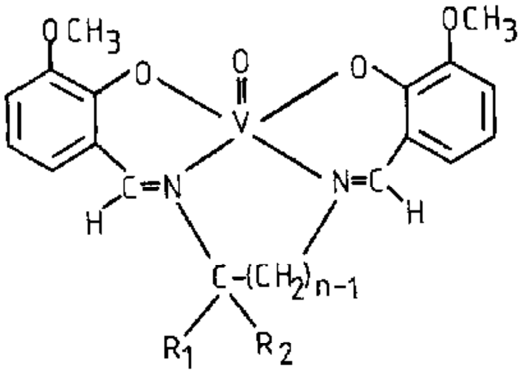
There is considerable interest in the interaction between the oxovanadium ion, $\{VO\}^{2+}$, and nucleotides for several reasons, one of which involves the use of a vanadium complex formed from such a reaction in the separation of RNA. In an investigation carried out over a wide pH range, two types of complexes were observed to be formed between $\{VO\}^{2+}$ and ATP [56]. In acidic and neutral solutions, a blue 1:1 complex was reported, whereas at pH>11 a relatively stronger green 2:1 complex was formed. Two different types of coordination environments were proposed for the complexes on the basis of potentiometric titrations and optical and ESR spectra. The interaction of a range of metal ions, including $\{VO\}^{2+}$, with AMP (adenosine- 5'-monophosphoric acid disodium salt) and ATP (adenosine- 5'-triphosphoric acid disodium salt) has been investigated and the IR, UV-VIS and fluorescence spectra of the complexes formed measured. The $\{VO\}^{2+}$ ion was reported to have formed a light blue 1:1 complex with AMP of fomula $VO(AMP).3H_2O$ but no mention was made of complexation between $\{VO\}^{2+}$ and ATP. As in the previous paper, shifts in ν(P–O) and ν(C–O–P) to higher frequencies in the IR spectrum were observed, which indicated coordination with phosphate. However the $VO(AMP).3H_2O$ complex was found to show fluorescence at nearly neutral pH, which is reported to be an indication of metal-adenine interaction [57]. The complexes $Na_2[VO(ATP)].2H_2O$ and $VOL.xH_2O$ (H_2L = adenosine, inosine, guanosine, cytidene or uridine 5'-monophosphates) have been prepared and studied by IR spectroscopy and magnetic measurements [58]; results suggested that the compounds are polymeric.

Several synthetic and structural studies on mixed ligand complexes of $\{VO\}^{2+}$ of the type VOLL' have been undertaken. In one, the complex[VO(O-8-quin)(acac).H_2O] was prepared as a greenish-black solid, and physical measurements carried out on the complex (UV-VIS, IR, magnetic moments) indicated octahedral geometry for the vanadium atom [59]. The same group have prepared and characterised complexes of the type $[VO(sa)Cl_2]$, [VO(saH)(acac)] and $[VO(acac)_2L]$ (saH = salicylamide, L = 2,3,4-pyridinecarboxamide) [60,61]. In a furthur study the formation of 1:1:1 complexes between $\{VO\}^{2+}$ and phen or bipy as primary ligands, L, and salicylic acid, 5-sulfosalicylic acid or 8-hydroxoquinoline-5-sulfonic acid as secondary ligands, L', was studied potentiometrically [62]. Complexes of $\{VO\}^{2+}$ with hydrazine and substituted hydrazines, VOL_4X_2 (L = N_2H_4, $PhNHNH_2$ or Me_2NNH_2; X = Cl or Br) have been synthesized and characterised. The complexes were thought to be polymeric, and have relatively low magnetic moments (1.26-1.36 μ_B) which was attributed to exchange interaction between vanadium atoms [63]. Various complexes containing $VOSO_4$ and the ligands 4-aminopyridine, 2,3-aminopyridine, 2-aminopyridine or $PhNH_2$ have been prepared and their electronic spectra studied [64]. A series of complexes of $\{VO\}^{2+}$ with various 4-oximo-2-pyrazolin-5-ones has been prepared and characterised [65]. EPR and magnetic measurements have been carried out on the complex VOL_2 {L = (3)} and the results compared with those for $[VO(O\text{-}8\text{-}quin)_2]$ [66].

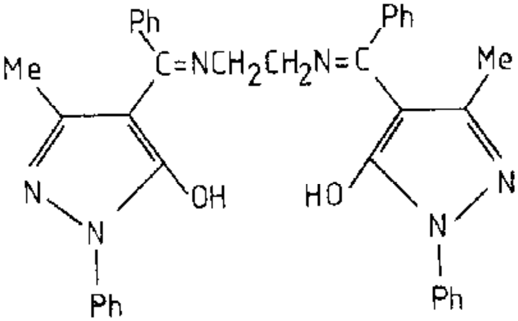


(3)

Once again, numerous Schiff base complexes of $\{VO\}^{2+}$ have been prepared and studied by direct spectroscopic techniques. Furthur studies have been made on the spectroscopic and magnetic properties of various Schiff base complexes of oxovanadium(IV) derived from substituted salicylaldehyde and aliphatic diamines [67]. The complexes described by the general formula $VO\{OC_6H_3(OMe)CH{=}N{-}CR^1R^2{-}(CH_2)_{n-1}{-}N{=}CH(OMe)C_6H_3O\}$, (4), have been prepared to

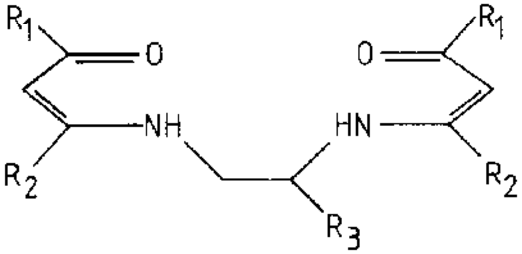


(4; n = 2, R^1 = R^2 = H or Me; n = 3-10, R^1 = R^2 = H) examine the effect of 3-methoxy substitution on the bonding and stereochemistry in the compounds. A distorted square-pyramidal structure was suggested for the complex formed between $\{VO\}^{2+}$ and *N,N'*-ethylenebis(2-hydroxy-4-methylpropiophenone imine) [68]. Polymeric oxovanadium complexes of the type $(VO)_2L(H_2O)_2$, also having square-pyramidal arrangements around the vanadium atoms, are thought to be formed between $\{VO\}^{2+}$ and Schiff bases derived from various dihydrazones and salicylaldehyde (H_4L = $2\text{-}HOC_6H_4CH{=}NNHC(O)(CH_2)_nC(O)NHN{=}CHC_6H_4OH\text{-}2$; n = 1, 2 or 4) [69]. The new Schiff base H_2L, (5) has been used to form the complex VOL in which the



(5)

ligand coordinates through the two oxygen atoms and the azomethine nitrogen atoms [70]. A furthur *O,O,N,N* donor, $MeC(=NNHPh)CH_2C(=NNHPhMe)$, H_2L, has been allowed to react with $\{VO\}^{2+}$ salts to give the complex VOL [71]. Volatility studies have been carried out on a range of transition metal chelates with the tetradentate Schiff bases, (6). The order of stability and volatility of the



(6; R^1 = Me, $CHMe_2$, CMe_3, Ph or CF_3; R^2 = Me, Et, $CHMe_2$ or CF_3; R^3 = H or Me) oxovanadium complexes was investigated and rationalised in terms of the effect of the substituents on the polarity and on Lewis acid-base interactions [72]. A series of tridentate Schiff bases derived from pyrrole-2-carboxaldehyde and taurine, orthranilic acid β-alanine, has been prepared and used to form complexes of the type $VOL(H_2O)_2$ (H_2L represents Schiff base) [73].

A series of oxovanadium(IV) porphyrins appended with the crown ether (benzo-15-crown-5) at different positions 5 (mono), 5 and 10 or 15 (*cis* or *trans*) (bis), 5, 10 and 15 (tris) and 5, 10, 15 and 20 (tetrakis; illustrated in Figure 15) have been synthesised [74]. The cavities in the crown ethers in

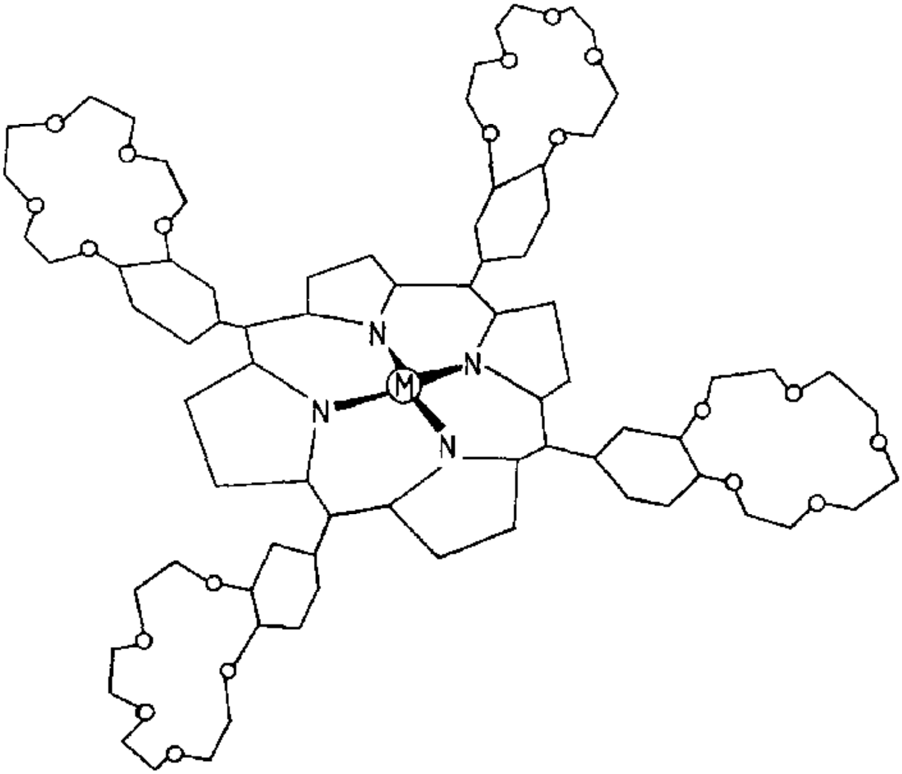


Figure 15: Chemical structure of oxovanadium(IV) tetrakis(benzo-crown-5)-porphyrin. The partially substituted porphyrins are shown [74]

these systems allow complexation of various cations, some of which (namely K^+, Cs^+, $[NH_4]^+$ and Ba^{2+}) induce dimerization of the porphyrins. The tendency to promote dimerization was found to depend on the cation used ($K^+ > Ba^{2+} > Cs^+ > [NH_4]^+$) and the stability of the dimer formed depended on the degree of substitution in the original porphyrin

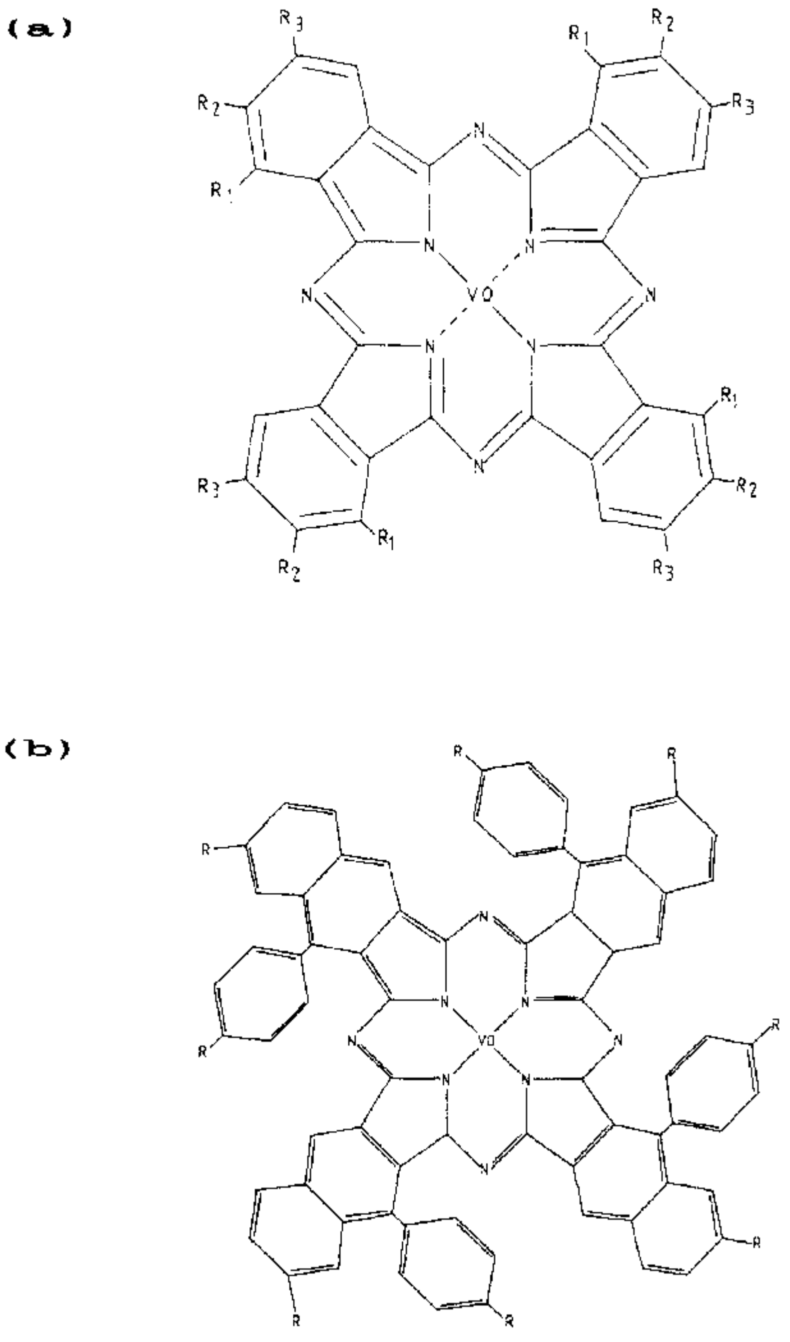


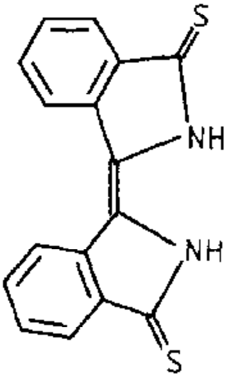
Figure 16: Phthalocyanine complexes of $(VO)^{2+}$ [75,76]. (a) $R_1 = R_3 = H$, $R_2 =$ Br, NMe_2, $C_5H_{10}N$, OC_4H_8N, NO_2 or NH_2; $R_2 = R_3 = H$, $R_1 = NO_2$, NMe_2 or NH_2; $R_2 = H$, $R_3 = CMe_3$, $R_1 =$ Br, NMe_2, NO_2, or NH_2; $R_1 = H$, $R_2 = NO_2$, $R_3 = NH_2$; $R_2 = R_3 = NMe_2$.

(tetrakis > tris > *cis* > bis). Results from EPR spectroscopy were used to propose a V-V distance of 4.70 Å in the dimer.

The syntheses of a vast number of substituted phthalocyanine complexes of oxovanadium(IV) has been described. The various complexes formed are detailed in Figure 16 [75,76].

A study by IR has been made upon the reactions between certain metal phthalocyanine complexes [M(Pc)], including [VO(Pc)], with HCl and HBr to give protonated metal phthalocyanines [77]. There is continuing interest in the possibility of using oxovanadium phthalocyanine complexes for storage of high density optical information. Some success in this area has been reported by the use of [VO(Pc)] in combination with a thin tellurium film [78].

A variety of oxovanadium complexes with sulfur donor ligands has been prepared and characterised.



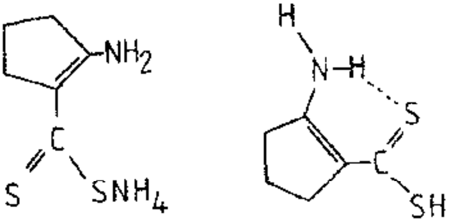
(7)

The ligand dithio-β-isoindigo (7;H_2L), which can exist in three different isomeric forms, has been used to prepare the complex $\{VOH_2L_2.7H_2O\}_n$ (where $n > 1$). Magnetic measurements showed the complex to be diamagnetic but the authors were uncertain as to whether the structure took the form of a dimer or a higher polymer [79].

A study by low frequency IR spectroscopy has been made of the stability of the metal sulfur bond in a series of transition metal complexes of 8-mercaptoquinoline,H_2L, which included the oxovanadium complex VOL_2 [80].

A series of oxovanadium complexes with the thio ligands thiocarbohydrazide (tcH_2; $H_2NNHCSSH$) 1-carbamylthiocarbohydrazide (ctcH; $H_2NNHCSNHNHCONH_2$), 1-thiocarbamylthiocarbohydrazide (tctcH; $H_2NNHCSNHNHCSNH_2$)

and ammonium (2-amino-1-cyclopentene)dithiocarboxylate (8; $[NH_4][aacd]$), has been prepared from VOX_2 (X = Cl or O_2CMe_2). The complexes $[VO(tch)_2].H_2O$, $[VO(ctch)(H_2O)]Cl_2$, (9), $[VO(tctcH)(H_2O)]Cl_2$ and $[VO(aacd)_2]$, (10) were



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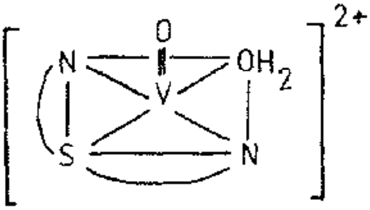

(9)

(10)

readily formed in methanolic solution and were studied by various spectroscopic techniques [81]. Infrared spectral results suggested the ligands exist as monobasic, bidentate donors bonding through the nitrogen and sulfur atoms.

The xanthate complexes $[VO(S_2COR)_2]$ (R = Et, Me_2CH, Me_2CHCH_2, $Me_2CHCH_2CH_2$ or $PhCH_2$) have been prepared and characterised. The complex $[VO(S_2COCHMe_2)_2]$ was found to react with the ligands pyridine and piperidine (L) to give diamagnetic $[VO(S_2COCHMe_2)L_2].5H_2O$ [82]. A series of transition metal chelates with 2-hydroxyacetophenone thiosemicarbazone and its 3-, 4- and 5-methyl substituents has been prepared. The oxovanadium, $\{VO\}^{2+}$, derivative was proposed to have an octahedral structure from spectral results [83]. A bimetallic compound containing both the oxovanadium ion and cadmium complexed with dithiocarbamate, $VOCd(dtc)_4$ (H_2dtc = piperidine dithiocarbamic acid or diethyl dithiocarbamic acid), has been prepared and characterised [84].

Once again a whole range of studies has been carried out on the stability constants of various oxovanadium complexes. In most cases the formation constants were measured potentiometrically at different temperatures and ionic strengths. Stability constants have been measured in this way for the reactions of $\{VO\}^{2+}$ with the ions chloroethanoate (CH_2ClCOO^-), 3-chloropropanoate ($CH_2ClCH_2COO^-$) and hydroxyethanoate (CH_2OHCOO^-) [85], and with ethyldithiodiethanoic acid [86], with L-lysine hydrochloride [87], with DL-tryptophan [88], and with (α-benzoylmethylbenzylideneimino)propanoic, benzoic and benzene sulfonic acids [89].

Vanadyl complexes continue to be the subject of many EPR spectral studies. The ^{51}V hyperfine coupling in $[VO(acac)_2]$ has been measured in mixtures of EtOH and CCl_4 as a function of solvent composition. Data were found to fit the assumption that that hyperfine splitting arises from interaction of the oxovanadium complex with two solvent molecules, as shown in equation (12), rather than simply one [90].

$$[VO(acac)_2E_2] + 2C \overset{k_1}{\rightleftharpoons} [VO(acac)_2EC] + C + E \overset{k_2}{\rightleftharpoons} [VO(acac)_2C_2] + 2E \quad (12)$$

(where $E = EtOH$ and $C = CCl_4$)

The EPR spectrum of $[VO(acac)_2]$ in various alkanes has been studied as a function of temperature in order to obtain information on the rotation correlation spectrum $J(\omega)$ [91]. Electron spin delocalisation studies have been carried out on a series of spin-labelled pyridines coordinated to $[VO(tfacac)_2]$ and $[VO(hfacac)_2]$ [92]. Results show that the spin-spin coupling constant, J, is greater when the spin label is attached to the 4-position of the pyridine ring than when it is attached to the 3-position of the ring. When the linkage between the pyridine ring and the nitroxyl ring was varied, the value of J was found to increase in the order; ester < amide < Schiff base linkages. The type of nitroxyl ring also affects the value of J such that J was found to increase in the order; piperidine < pyrrolidine < pyrroline < tetrahydropyridine. A study by EPR spectroscopy has been made on the interaction of NO_x (x = 1 or 2) with a series of metal chelate complexes which included $[VO(S_2CNEt_2)_2]$ [93]. The EPR parameters of the free radicals formed on passing NO_2 through $[VO(S_2CNEt_2)_2]$ in toluene are reported.

The formation of mixed ligand complexes of $\{VO\}^{2+}$ has been monitored by EPR spectroscopy. The complex [VO(dtp)(dtas)] (dtp = dibutyldithiophosphate, $[(C_4H_9O)_2PS_2]^-$; dtas = dimethyldithioarsinate, $[Me_2AsS_2]^-$) was prepared by ligand exchange reactions from $[VO(dtp)_2]$ and $[VO(dtas)_2]$. As the complex was formed, the ^{75}As hyperfine splitting was seen to increase at the expense of the ^{31}P splitting, which was attributed to electron delocalisation in the stronger bonding ligand [94]. Vanadium(IV) has been extracted from aqueous solutions containing HCl or a HCl/LiCl mixture by bis(2-ethylhexyl)hydrogen phosphate, $[R_3MeN]Cl$ (R = octyl; Aliquat® 336), R_3N, R_3PO and $(BuO)_3PO$. The complexes formed in the organic phases have been examined by electronic and EPR spectroscopy and the nature of the vanadium species formed investigated [95]

The complexes formed between $\{VO\}^{2+}$ and the ligands imidazole, carnosine and histidine have been studied by ENDOR in frozen aqueous solution to obtain information on the proton and nitrogen hyperfine coupling constants as well as the ^{14}N quadrupolar splittings [96]. Results indicated that the complexes $[VO(imid)_4]^{2+}$ and VO-Car have a similar structure, which is different from that of VO-His.

Redox studies using cyclic voltammetry and controlled potential coulometry have been carried out on the complexation reaction between $VO(ClO_4)_2$, VCl_3 or VOF_3 and singly reduced riboflavin ($[Rib]^-$) [97]. The complex $[VO(Rib)_2]$, formed from vanadium(IV), is reduced to $[VO(Rib)_2]^{2-}$ and oxidised at −0.15 V to free $\{VO\}^{2+}$ and neutral riboflavin. Reaction between VOF_3 and $[Rib]^-$ resulted in spontaneous reduction of the metal and oxidation of the riboflavin anion to the neutral compound. With VCl_3, a complex was formed which has an oxidation potential of −0.12 V, similar to that of $[VO(Rib)_2]$.

The oxalatovanadium(IV) anion, $[VO(C_2O_4)_2]^{2-}$, was found to undergo photoreduction at 254 nm to vanadium(III), according to equation (13) [98].

$$[VO(C_2O_4)_2]^{2-} + 2H^+ + ½[C_2O_4]^{2-} \xrightarrow{h\nu} [V(C_2O_4)_2]^- + CO_2 + H_2O \qquad (13)$$

The quantum yield for the reaction was found to be almost independent of H^+ ion concentration or $[VO(C_2O_4)_2]^{2-}$ concentration. A reaction scheme was propsed based upon the stoicheiometry measured for the photoreduction.

^{19}F and ^{13}C NMR spectroscopy have been used to study the kinetics of ligand exchange reactions in oxovanadium(IV) complexes [99]. When flouride ions were added to $[VO(gly)_2]$, reaction occurred according to equation (14). Flouride

$$[VO(gly)_2] + F^- \rightleftharpoons [VO(gly)glyF]^- \qquad (14)$$

ion exchange was studied by ^{19}F NMR spectroscopy and is represented by equation (15). The rate of oxalate exchange on $[VO(ox)_2]^{2-}$ was studied

$$[VO(gly)glyF]^- + {}^*F^- \rightleftharpoons [VO(gly)gly^*F]^- + F^- \qquad (15)$$

by ^{13}C NMR spectroscopy and the reaction is expressed by equation (16) or (17). For both flouride and oxalate ion exchange, the rate was found to be

$$[VO(ox)_2]^{2-} + [ox^*]^{2-} \rightleftharpoons [VO(ox)(ox^*)]^{2-} + [ox]^{2-} \qquad (16)$$

$$[VO(ox)_2]^{2-} + [Hox^*] \rightleftharpoons [VO(ox)(ox^*)]^{2-} + [Hox]^- \qquad (17)$$

first order in the entering ligand and the $(VO)^{2+}$ complex concentration.

4.2.4 Species containing vanadium-sulfur or selenium bonds.

A single crystal and powder EPR study on the eight-coordinate complexes tetrakis(*N,N*-diethyldithiocarbamato)vanadium(IV), $[V(S_2CNEt_2)_4]$, and tetrakis(*N,N*-diethyldiselenocarbamato)vanadium(IV), $[V(Se_2CNEt_2)_4]$, substitutionally diluted in the diamagnetic titanium(IV) analogues, has been reported, along with results for the niobium complex $[Nb(S_2CNEt_2)_4]$ [100]. In the isomorphous host compounds are two chemically inequivalent crystallographic sites, which are populated to different extents by the vanadium(IV) ions, the most asymetric site (A) holding approximately 75% of the total vanadium atoms. The EPR signals were consistent with the eight-coordinate V^{4+} ion experiencing a strong D_{2d} ligand field perturbation with a superimposed small low symmetry field which reduces the overall symmetry to D_2 for the less asymmetric (B) sites or lower for the (A) sites. In the spectrum of $[(V/Ti)(Se_2CNEt_2)_4]$, low intensity satellite lines were observed which were attributed to hyperfine coupling of the unpaired electron with four different selenium nuclei.

A series of mixed lanthanide and vanadium sulfides $LnVS_3$ (Ln = La, Nd or Gd) has been prepared by reaction of $LnVO_x$ with dry H_2S or CS_2 in a furnace at 1000-1200 °C [101]. Reaction of H_2S with the compounds MV_2O_6 (M = Mg, Fe, Co or Ni) yielded MV_2S_4; with MV_4O_{11} (M = Mg, Fe, Co, Ni or Zn), $M_{0.25}VS_2$. The dependence of magnetic properties and specific heats upon stoicheiometry has been investigated for $BaVS_3$. Sulfur deficient $BaVS_3$ was found to have Curie-Weiss paramagnetic behaviour and ordered ferromagnetically at temperatures below 16 K. Stoicheiometric $BaVS_3$ showed a maximum in its magnetic susceptibility at 70 K associated with a semimetal-semiconductor transition [102]. Previous magnetic studies on the layered compounds $Li_xV_{1-y}Fe_yS_2$ (for $0.1 < y < 0.5$) have been extended to lower concentrations ($0.1 > y > 0.01$) of intercalated iron, as well as cobalt and nickel [103].

The cathodic behaviour of the layered mixed metal sulfide $Cr_{0.5}V_{0.5}S_2$ has been studied in a rechargeable cell having the configuration;

liquid		Na^+ containing	
	β″-alumina		$Cr_{0.5}V_{0.5}S_2$
Na		electrolyte	

The cell was operated at 130 °C and the electrolyte used was 1*M* NaI in 1,2-bis(2-methoxyethoxy)ethane [104]. The rechargeable capacity was found to be limited to 70% of the first discharge. The same group have studied the efficacy of VS_2 itself in molten $Na[AlCl_4]$ as a rechargeable cathode in the cell [105].

liquid		liquid
	β″-alumina	VS_2
Na		$Na[AlCl_4]$

The layered diselenide $V_{1+x}Se_2$ does not suffer from non-stoicheiometry to any great extent ($x < 0.1$) and crystals studied for X-ray diffraction studies have been obtained from the vapour phase and a single crystal X-ray structure determination carried out [106]. The structure was found to be close to the CdI_2 type, containing layers of selenium atoms stacked above each other and perpendicular to the *c*-axis. Such an arrangement leads to two types of octahedral sites (000, 00½) of which the former (000) are occupied by the V(1) vanadium atoms and the latter (00½) are partially occupied by the small amount, *x*, of vanadium atoms V(2). Thus the stacking sequence along the *c*-axis is represented by -Se-V(1)-Se-V(2)-Se-V(1)-.

4.2.5 Other vanadium(IV) species

Vanadium(IV) and vanadium(III) halides have been allowed to react with ammonium cyanide in liquid ammonia in an attempt to prepare simple cyanides of vanadium(IV) and vanadium(III) [107]. The reaction with $[VCl_4]$ led to formation of a brown solid in which the cyanide complex thought to be formed (equation (18)) could not be separated from $[NH_4]Cl$. Similarly, with VCl_3

$$[VCl_4] + 3[NH_4]CN + 2NH_3 \longrightarrow V(CN)_3(NH_2) + 4[NH_4]Cl \qquad (18)$$

and VBr_3, the product formed, $V(CN)_3(NH_2)$, could not be separated from $[NH_4]X$. VBr_3 can be reduced with an excess of $K[CN]$ and potassium in liqiud ammonia to give the complex $K_2V(CN)_2.\frac{1}{2}NH_3$ which, when heated, loses ammonia leaving $K_2V(CN)_2$. When the complex having solvated ammonia was treated with $[NH_4][CN]$ in ammonia, a purple solution was obtained which yielded the pale purple

$$K_2V(CN).\frac{1}{2}NH_3 + 2[NH_4][CN] \longrightarrow K_2V(CN)_4 + H_2 + 2\frac{1}{2}NH_3 \qquad (19)$$

$K_2V(CN)_4$ (equation (19)).

4.3 VANADIUM(III)

4.3.1 Species containing vanadium-halogen bonds

The mixed-valence compounds Rb_xVF_3 and Cs_xVF_3 exist over the range $0.52 > x > 0.45$ and two different type of crystal structures, cubic and orthorhombic, are found within each system [108]. A study has been made of the dependence of the structure and magnetic properties in the compounds upon the composition. For small values of x both structures were found to exist, whereas at large values of x only the orthorhombic structure was identified. Unit cell dimensions for $x = \frac{1}{2}$ were calculated for orthorhombic Rb_xVF_3 and Cs_xVF_3 and cubic Cs_xVF_3. The magnetic data were found to support the conclusion that the orthorhombic phase is an electronically ordered structure consisting of linear chains of V^{2+} ions orthogonal to linear chains of V^{3+} ions. Values of T_N, Curie constants (C_M) and Curie-Weiss constants (θ) were reported for different phases of Rb_xVF_3 and Cs_xVF_3. Preparations of a new ternary fluoride of vanadium, $RbCuVF_6$, have been reported [109]. Three different procedures were given, all of which involve the use of high temperatures. Lattice parameters were determined for $RbCuVF_6$, which was found to be orthorhombic.

A new crystal form of VCl_3 has been obtained, starting from α-VCl_3 in a transport reaction represented by equation (20) [110]. New unit cell

$$VCl_3(s_1) + \frac{1}{2}I_2(g) \longrightarrow VCl_3I(g) \longrightarrow VCl_3(s_2) + \frac{1}{2}I_2(g) \qquad (20)$$

parameters were calculated from the X-ray powder diffraction pattern. A procedure has been reported for the preparation of $[VCl_3(OC_4H_8)_3]$, which

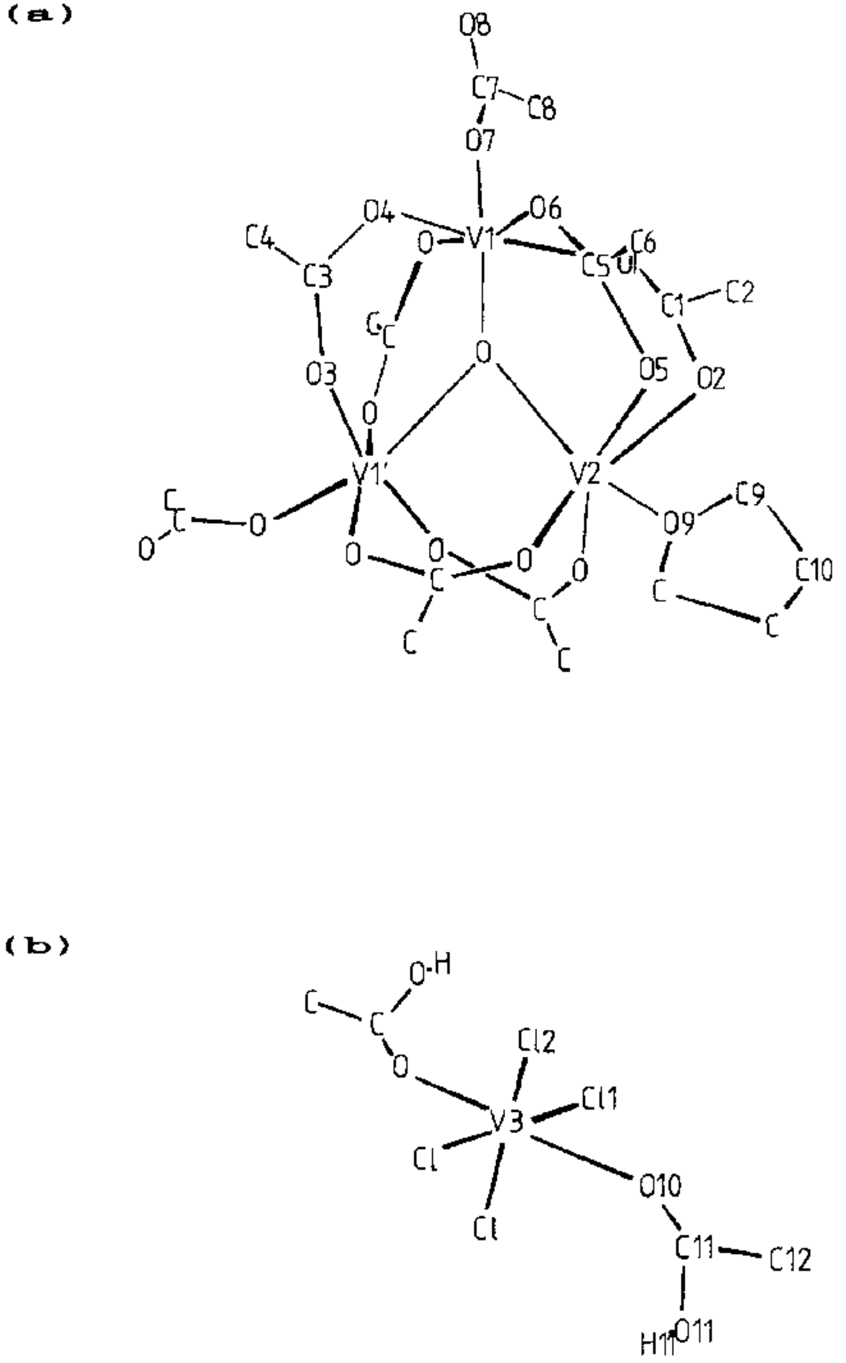

Figure 17: The structure of (a) the cation and (b) the anion in $[V_3(\mu\text{-}O)(MeCO_2)_6(MeCOOH)_2(thf)]^+$ $[VCl_4(MeCOOH)_2]^-$ [113]

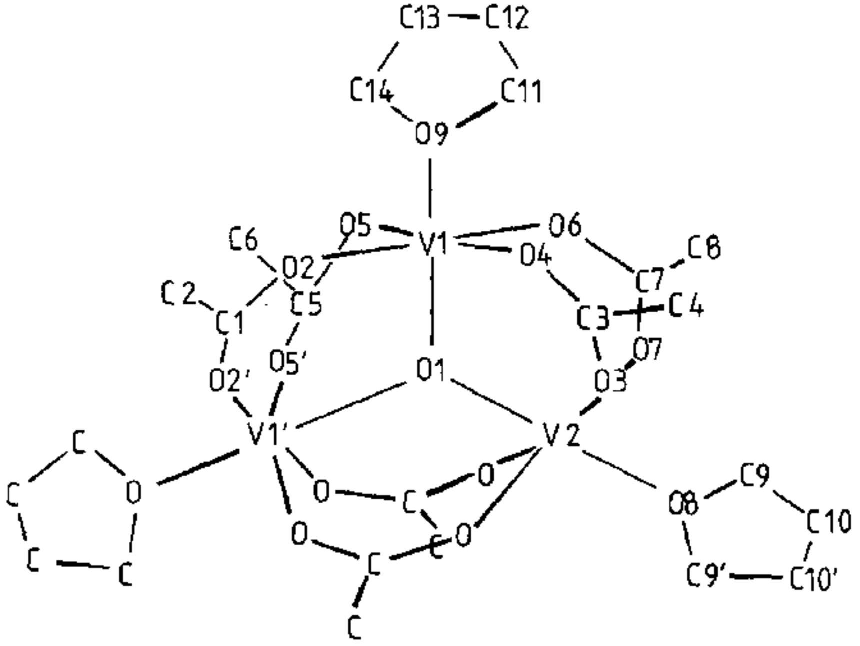

Figure 18: The molecular structure of $[V_3O(CF_3CO_2)_6(thf)_3]$. Fluorine atoms have been omitted for clarity [113]

involves treating VCl_3 with anhydrous thf under reflux for 22 h [111]. The method is claimed to give high yields of pink, crystalline $[VCl_3(thf)_3]$.

The X-ray photoelectron spectra of the 3p electrons in VCl_3 have been measured and the results compared with the theoretical spectra based on ligand field theory [112].

4.3.2 Species containing vanadium-oxygen bonds

The preparations and X-ray structures of two new oxo-centred basic carboxylate complexes of vanadium, namely $[V_3(\mu\text{-}O)(MeCO_2)_6(MeCOOH)_2(thf)]^+$ $[VCl_4(MeCOOH)_2]^-$ and $[V_3(\mu\text{-}O)(CF_3CO_2)_6(thf)]$ [113]. The former was prepared from VCl_3-thf and ethanoic acid and was found to be monoclinic, C_2/c. The structure consists of trinuclear cations situated on crytallographic two-fold symmetry axes and monoclinic anions on crystallographic inversion centres. The way in which the compound is formulated implies all the vanadium atoms to be in oxidation state 3+, although the authors admit they have no conclusive evidence for this formulation and suggest it is the most likely based upon the method of formulation. In the cation (see Figure 17a), the $\{V_3O\}$ unit is planar and has essentially three-fold symmetry with a V–V distance of 3.307(2) Å. The crystallographically non-equivalent V–(μ-O) distances differ only by 0.11(7) Å and therefore are assumed alike at 1.910(6) Å. The anion, $[VCl_4(MeCOOH)_2]^-$, (Figure 17b), has regular *trans* octahedral geometry, with the MeCOOH molecules situated at the vertices, $r(VO) = 2.089(8)$ Å. The second structure, Figure 18, consists of $[V_3O(CF_3CO_2)_6(thf)_3]$ having vanadium atoms in the +2 and +3 oxidation states. It was obtained as an oxidation product in the reaction between $VCl_2.2thf$ and sodium trifluoroethanoate. The structure is monoclinic, space group $P2_1/m$ and the molecule has approximately D_{3h} symmetry. The V–V distances differ by 0.023(2) Å (average 3.357(11) Å) and the crystallographically inequivalent V–(μ-O) distances differ by 0.053(5) Å (at 1.90(2) and 1.953(8) Å). The small distortions of both molecules from perfect D_{3h} symmetry are attributed to unsymmetrical packing forces.

The kinetics of vanadium(III)-monomalonate complex formation in aqueous solution have been studied by stopped-flow techniques and a generalised rate law proposed [114]. Steps in the reaction are depicted in equations (21) to (24) and the rate law expressed in equation (25). The same group has investigated the kinetics of ligand substitution reactions of $[V(mal)_3]^{3-}$

$$[V(H_2O)_6]^{3+} + [Hmal]^- \rightleftharpoons [V(H_2O)_6(Hmal)]^{2+} \qquad (21)$$

$$[V(H_2O)_6(Hmal)]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [V(H_2O)_4(mal)]^+ + H_2O + [H_3O]^+ \qquad (22)$$

$$[V(H_2O)_5OH]^{2+} + H_2mal \rightleftharpoons [V(H_2O)_5(OH).H_2mal]^{2+} \qquad (23)$$

$$[V(H_2O)_5(OH).H_2mal]^{2+} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [V(H_2O)_4(mal)]^+ + H_2O + [H_3O]^+ \qquad (24)$$

$$k_{obs} = (k_{-1} + k_{-4})[H^+] + \frac{k_1}{k_2[H]^+} + k_4.K^{OH}\frac{[H_2mal]}{[H]^+}\,T \qquad (25)$$

with various multi-dentate ligands, including $[edta]^{4-}$ and $[nta]^{3-}$ [115]. The formation of vanadium(III) complexes with citric, malic and tartric acids has been studied by nuclear magnetic relaxation techniques [116,117]: the compositions of the complexes formed were determined and the reaction schemes proposed.

4.3.3 Other vanadium(III) species

Study on the thermal stability of the cyano complexes $K_4[V(CN)_7].2H_2O$ and $K_4[V(CN)_6].3H_2O$ showed the vanadium(III) complex to be less stable than the vanadium(II) complex [118].

4.4 VANADIUM(II)

4.4.1 Reactions of V^{2+}_{aq} ions

The kinetics of reductions of some *trans*-bis(dimethylglyoximato) cobalt(III) complexes by vanadium(II) ions have been studied [119]. The V^{2+}_{aq} ions were obtained from the reduction of vanadium(V) perchlorate by zinc. The reduction rate constants were found to be independent of the hydrgen ion concentration in the range $0.003 \leqslant [H^+] \leqslant 0.1$ mol dm^{-3}.

4.4.2 Species having vanadium-halogen bonds

An X-ray analysis has been carried out on rutile-type VF_2, which showed the V^{2+} ion to be octahedrally coordinated with the axial V-F distances slightly shorter, by 0.019 Å, than the octahedral ones [120]. This difference in magnitude is of the same order as in other rutile-type fluorides where the cations have no degeneracies in their electron configurations. These experimental studies on VF_2, along with data for MgF_2, were used to form the basis of a computer simulation of the structure of VF_2 doped (1%) into magnesium fluoride. The interest in this material lies in its high efficiency as a fusion driver.

The magnetic and structural properties of the series of mixed metal fluorides, $CsVMF_6$ (M = Sc, Ti, Cr, V or Fe), have been studied [121]. The pseudohexagonal phases $Cs_{0.4}V^{II}_{0.4}M^{III}_{1.6}F_6$ (M^{III} = Sc, Ti, or Cr) with tungsten bronze-like structures have been prepared and their lattice constants determined.

The electronic spectra of a series of transition metal cations (Ti^{2+}, V^{2+} and Cr^{2+}) in anhydrous hydrogen fluoride have been recorded [122].

The solutions were prepared by treating the metal, previously cleaned of surface oxide, with anhydrous HF containing a Lewis acid (*e.g.* BF_3, AsF_5 or SbF_5). Crystal field parameters, D_q and B, were calculated for V^{2+} in different environments and compared with those already reported for aqueous V^{2+}. The comparison supported the interpretation of the spectra in anhydrous HF as being due to octahedrally coordinated vanadium(II). Details of the synthesis of VCl_2 in aqueous solution have been reported [123]. The method involves the reduction of V_2O_5, by zinc in the presence of HCl, according to the equation (26):

$$V_2O_5 + 3Zn + 10HCl \longrightarrow 2VCl_2 + 3ZnCl_2 + 5H_2O \qquad (26)$$

The polarised crystal absorption spectra of $CsVX_3$ (X = Cl, Br or I) have been measured between 5000 and 30000 cm^{-1} at temperatures between 6 and 273 K, and the mechanisms of spin-allowed and spin-forbidden transitions investigated [124].

4.4.3 Species containing vanadium-oxygen bonds

^{51}V NMR spectra have been recorded for certain refractory binary compounds of vanadium, namely VX_x (X = O, C or N) [125]. Calculations were made of quadrupolar coupling constants which were found to agree well with theoretical values.

The reduction of dinitrogen in $V(OH)_2/Mg(OH)_2$ and $V(OH)_2/ZrO_2.H_2O$ systems has been directed to yield either hydrazine or ammonia by selecting the appropriate reaction conditions [126]. When the reduction was carried out at high dilution with high N_2 pressures and low $V(OH)_2/Mg(OH)_2$ ratios and high NaOH concentrations, N_2H_4 was formed preferentially. Under these conditions any secondary reduction of N_2H_4 to NH_3 was effectively supressed and so only traces of NH_3 were produced. Conversely the formation of NH_3 from N_2 was found to be favoured by small reaction solution volumes with high $V(OH)_2/Mg(OH)_2$ ratios and low Na concentrations. The $V(OH)_2/ZrO_2.H_2O$ system generally produced lower yields of both reduction products.

4.4.4 *Species containing vanadium-sulfur bonds*

The mixed-valence sulfide Cu_3VS_4 has been formed during the reaction of CuS with VS, or Cu_2S with V_2S_5, at 115±10 K [127].

4.4.5 *Species containing vanadium-nitrogen bonds*

The series of low valent vanadium porphyrins $[V(PPhMe_2)_2(por)]$ {por = octaethylporphinato (OEP) or *meso*-tetra-4-tolylporphinato (TTP)} has been prepared by reduction of $[VCl_2(por)]$ with a zinc amalgam in O_2-free thf containing an excess of dimethylphenylphosphine [128]. The crystal structure of one of the complexes $[V(PPhMe_2)_2(OEP)]$ has been determined. The structure, Figure 19, was found to contain vanadium atoms *pseudo*-octahedrally coordinated

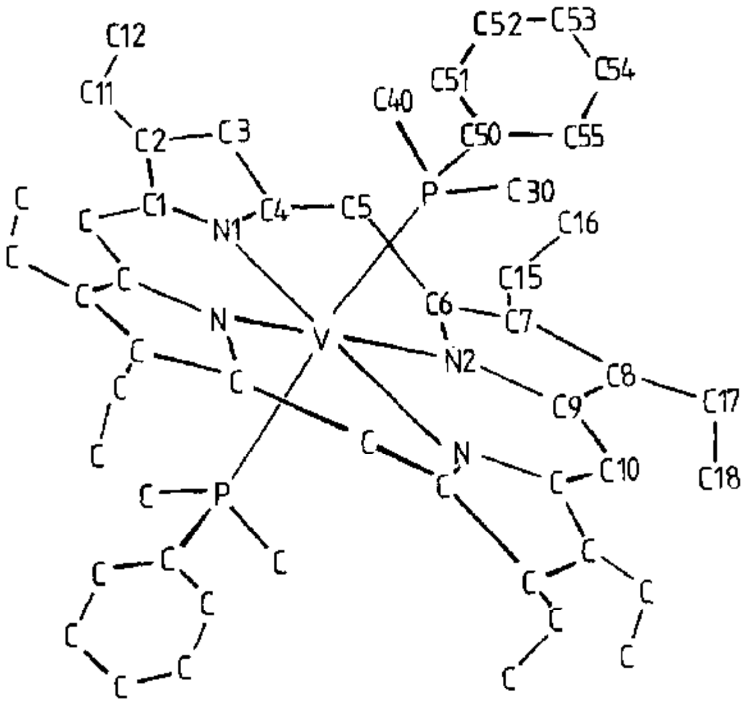

Figure 19: The molecular structure of $[V(PPhMe_2)_2(OEP)]$ [128].

by four nitrogen atoms of the porphyrin ring in the equatorial plane and two phosphorus atoms of $PPhMe_2$ *trans* to each other in the axial positions. The reactions between such low-valent porphyrins and molecular dioxygen were studied and, although the tendency is for rapid oxidation to oxovanadium, $\{V^{IV}{=}O\}$, complexes, the use of ^{18}O provided evidence for the formation of a complex having dioxygen coordinated to the vanadium in a superoxide-type manner. Thus, the authors remarked that the use of such low-valent complexes as dioxygen carriers may be a feasible process.

The crystal field parameters ($10Dq$, B and C) have been used to calculate d-d transitions in $[V(CN)_6]^{4-}$ by both angular overlap and ligand-field theory [129]. These parameters were also applied in semi-empirical calculations to obtain charge-transfer transitions.

4.5 LOW OXIDATION STATE COMPLEXES OF VANADIUM

The EPR spectra of $[V(CO)_6]$ have been measured in frozen cyclohexane and in $[Cr(CO)_6]$ hosts, and EPR parameters g_x, g_y and g_z and A_x, A_y and A_z reported for the species in cyclohexane [130]. The EPR spectra obtained were non-axial in both media and the highest symmetry distortion possible (consistent with the measured parameters) was proposed to be a D_{2h} angle bending distortion. A different group of workers have investigated the EPR spectra of $[V(CO)_6]$ and $\{V(CO)_n\}^{2+}$ in single crystals of $[Cr(CO)_6]$ [131]. The $\{VO\}^{2+}$ radical was detected at 90 K following γ irradiation of the sample. This latter showed almost axial g and ^{51}V hyperfine tensors.

An improved synthesis has been reported for the cationic arene complexes of vanadium(I), $[V(CO)_4(C_6H_6\text{-}n\text{-}Me_x]^+$ [132]. The reaction, equation (27),

$$2[V(CO)_6] + C_6H_{6-x}Me_x \longrightarrow [V(CO)_4(C_6H_{6-x}Me_x)]^+[V(CO)_6]^- + 2CO \qquad (27)$$

involves treatment of $[V(CO)_6]$ in heptane with, say, 1,2,4,5-tetramethylbenzene under argon for forty-eight hours. An X-ray crystal structure determination was carried out on the product where $x = 4$, $[V(CO)_4(C_6H_2Me_4)][V(CO)_6]$, and the ^1H NMR spectrum reported for the species. The structure is depicted in Figure 20; the C_4 axis of the $\{V(CO)_4\}$ moiety passes through the centre of the aromatic ring and the vanadium atom is equidistant from each of the six ring carbon atoms {r(V–C) = 2.33 Å}. The $\{V(CO)_4\}$ unit has approximate C_{4v} symmetry with C–V–C angles in the range 72.9–76.3°. In an extension of studies on heptacoordination, the structure

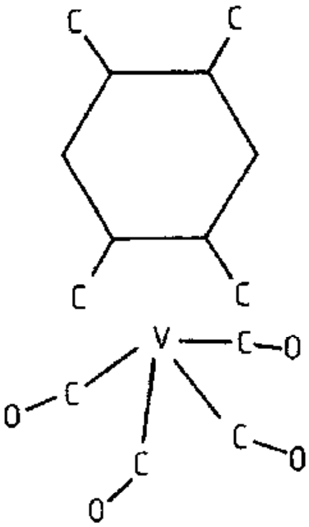

Figure 20: The structure of the cation in $[V(CO)_4(C_6H_2Me_4)][V(CO)_6]$ [132].

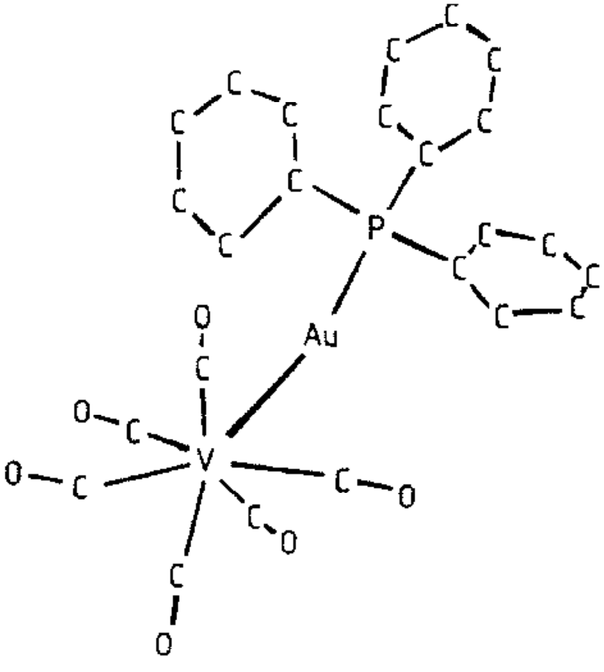

Figure 21: A perspective view of the $[V(CO)_6(AuPPh_3)]$ molecule [133]

of the complex $[V(CO)_6(AuPPh_3)]$, in which all the ligands are monodentate, has been reported [133]. The molecule, Figure 21, has crystallographically imposed 3 symmetry with the vanadium and gold atoms on the axis. The vanadium atom is seven-coordinate in a capped octahedral environment, the gold atom assuming the capping position at a distance of 2.690(3) Å. This was thought to be the first V-Au bond distance reported. The effect of the gold capping on the geometry of the octahedron was discussed and compared with related molecules.

The reaction between $(cp_2)VX$ (X = Br or I) and NO in toluene yielded two products, both of which analyse as $[(cp)_2V(NO)X]$ [134]. The IR and EPR spectra of each product were studied over a range of temperatures and the results lead the authors to conclude that an equilibrium must exist between $[(cp)_2V(NO)I]$ with a linear VNO group and $[(cp)_2V(NO)I]$ with a bent VNO group. A solution of $[(cp)_2V(NO)I]$ in thf was found to yield brown-gold crystals after several days, which were shown to be $[\{(cp)VI\}_2\{(cp)V(NO)\}_2(\mu\text{-}O)_4]$ by crystallography. The structure, Figure 22, can be seen to contain an eight-membered ring of four vanadium atoms and four oxygen atoms. The fluxional nature of $[(cp)_2V(NO)I]$ was thought to be in some way responsible for the formation of the complex.

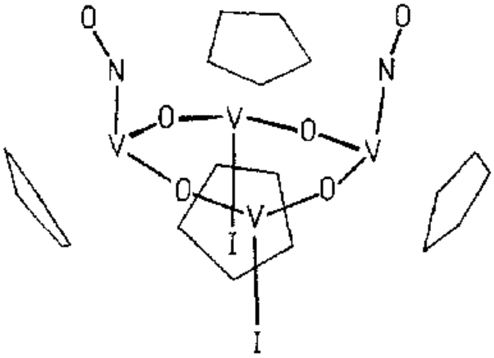

Figure 22: The molecular structure of $[\{(cp)VI\}_2\{(cp)V(NO)\}_2(\mu\text{-}O)_4]$ [134].

A more detailed report of the structure of $[(cp)_5V_5O_6]$, whose preparation was referred to in last year's review, has been published and compared to the structrue of $[(cp)_4Cr_4O_4]$ [135]. The preparation of the first vanadium-sulfide cluster, $[(Mecp)_2V_2S_4]$, similar to the oxygen cluster above, has been reported [136]. Treatment of $[(Mecp)_2V_2S_5]$ with PBu_3 in CH_2Cl_2 yielded purple crystals of $[(Mecp)_2V_2S_4]$ after precipitation by hexane. Several structures were postulated for the complex on the basis of ^1H NMR and mass spectrometric results. Reaction of $[(Mecp)_2V_2S_4]$ with $[Fe(CO)_5]$ yielded $[(Mecp)_2V_2S_3\{Fe(CO)_3\}]$ (see Figure 23). Furthur reactions of this complex

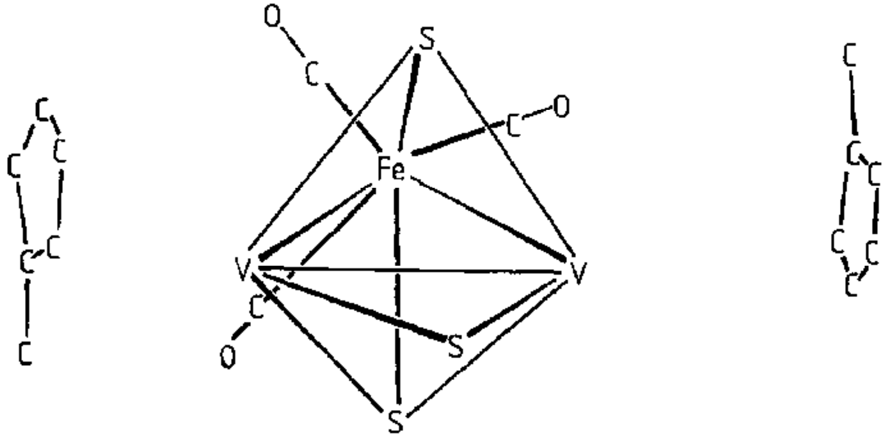

Figure 23: One of the two independent molecules in $[(MeC_5H_4)_2V_2S_3\{Fe(CO)_3\}]$ [136].

were carried out, which convinced the authors that there is a wide scope of chemistry to be revealed in the field of cyclopentadienyl vanadium sulfide clusters.

4.6 SPECIES THAT FORMALLY CONTAIN OXO-ANIONS OF VANADIUM

Once again the vanadate, $[VO_4]^{3-}$, ion has received much attention and numerous reports have been made on different complexes containing the anion, detailing their structures, and spectral and physical properties.

A calculation has been made of the vibrational spectra of $Ca(VO_4)_2$ by a matrix method assuming three crystallographic non-equivalent $[VO_4]^{3-}$ groups [137]. The structure is known to be rhombohedral, containing $[VO_4]^{3-}$ anions which are distorted to different degrees from true tetrahedral geometry. The predicted spectrum was compared with that observed by experiment. In an extension of the study, calcium ions were replaced by larger atoms (M = Sr or Ba) to give a mixed-metal vanadate $(Ca_xM_{1-x})_3[VO_4]_2$. This caused the shorter V–O bonds in $[VO_4]^{3-}$ to lengthen, and hence the wavenumber of the associated ν(VO) vibrations to decrease. Conclusions were drawn from the changes in wavenumber about the interchange of cationic positions. The X-ray crystal structure of copper(II)vanadate, $Cu_3(VO_4)_2$, has been determined and is shown in Figure 24 [138]. The complex is triclinic, space group $P1$ and isotypic

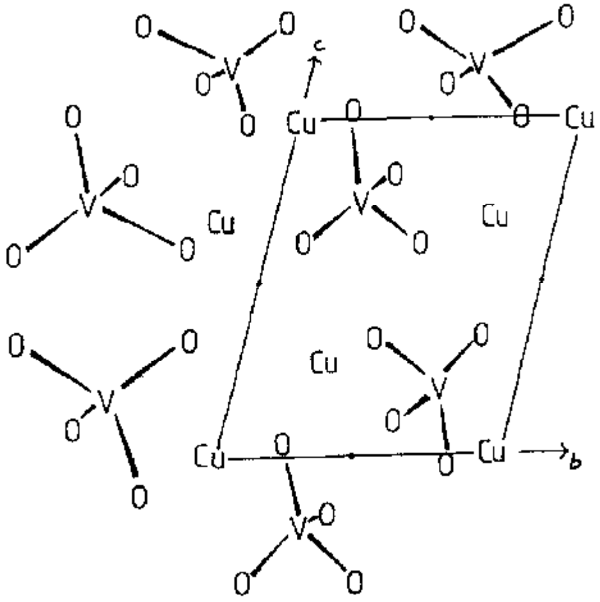

Figure 24: The crystal structure of the triclinic $Cu_3(VO_4)_2$ [138].

with the corresponding phosphate. The V–O distances were found to vary from 1.643 to 1.783 Å, and the lengths seemed to depend upon the relative positions of the oxygen atoms to the nearest copper atoms.

By mixing solutions of $Na_3[VO_4]$ and $Ga[NO_3]_3$ at various pH's, complexes of moleculer masses corresponding to $GaVO_4.3H_2O$, $Ga_4(V_2O_7)_3.15H_2O$ and $Ga_2V_4O_{13}.9H_2O$ were obtained [139]. The water molecules were thought to have different adsorption centres in the complexes. Infrared spectra of the products suggested that they contain $\{GaO_6\}$ octahedra and $\{VO_4\}$ tetrahedra. The complexes were heated in an attempt to obtain anhydrous crystalline structures, but all decomposed above 550°C to Ga_2O_3 and V_2O_5. In a similar study, solutions of $Sc[NO_3]_3$ and $Na_3[VO_4]$ were mixed and the precipitates obtained were studied [140]. However, considerable contamination of the solid phases with sodium salts was observed, although some pure compounds were thought to be obtained, one of which was represented by the formula $\{[\{Sc(OH)\}_3(VO_4)_2](H_2O)_{4.5}\}(H_2O)_3(H_2O)_m$. The same group also studied the dependence of the compositions of yttrium and lanthanum vanadates upon pH by mixing solutions of the nitrates with $Na_3[VO_4]$ [141].

The structure of a salt, calcium sodium vanadate, $CaNa[VO_4]$ has been studied by powder neutron diffraction [142]. The salt was obtained by heating sodium oxalate, calcium carbonate and V_2O_5 for thirty minutes at 600 K and then for two days at 973 K: the resulting material was annealed for one week at 773 K. The structure was found to be of the $Na_2[CrO_4]$(II) type and was described as being built from $\{CaO_6\}$ octahedra sharing parallel edges, giving slightly staggered chains along [001]. These chains are arranged in parallel planes normal to [010] and linked by $\{VO_4\}$ tetrahedra. Various double vanadates of thallium and rare earth elements, such as $TlLn(VO_4)_2$, have been synthesised and characterised by X-ray diffraction and IR spectroscopy [143]. The thermal stability of the complexes was studied and each was found to decompose at temperatures above 450 °C to Tl_3VO_4 and $LnVO_4$. The spinel system $Zn_{1-x}Fe_x(Fe_{1+x}V_{1-x})O_4$ has been prepared by heating mixtures of $ZnFeVO_4$ and Fe_3O_4 at 1000 °C and the distribution and valency of the cations investigated. A transition from a near normal to an inverse distribution of Fe(II) and Fe(III) was found to exist [144].

The range of mixed cationic and anionic apatites of general formula $Ca_{10-x}Sr_x(PO_4)_{6-s}(VO_4)_s(OH)_2$ ($x = 2$, 5 or 8; $s = 1$, 2, 3, 4, 5 or 6) has been the subject of a spectroscopic study. The point group of the 'tetrahedral' ions appeared to depend upon the value of s. For instance in the case of $x = 5$ and $s = 1$, the $[VO_4]^{3-}$ ion appeared to have C_{2v} symmetry from the IR bands observed ($3\nu_3$ and $1\nu_2$). When $s = 2$, the point group changed to C_{3v}, and as s increased to 5 a loss of symmetry was observed so eventually most of the $[VO_4]^{3-}$ ions belonged to the C_s group. The X-ray diffraction pattern of the salts showed a decrease in crystallinity as the amount of $[VO_4]^{3-}$ present increased [145]. The IR spectra of the series of mixed anionic strontium apatites $Sr_{10}(PO_4)_{6-z}(VO_4)_z(OH)_2$ ($z = 1$, 2, 3, 4, or 5) again showed that the symmetry of the anions depended on the composition of the complex [146].

X-ray powder data has been reported for the decavanadates of pyridinium, $[C_5H_5NH]_3H_3[V_{10}O_{28}]\cdot MH_2O$ [147].

The structure of the first mixed valence isopolyvanadate ion, $[V_{10}O_{26}]^{4-}$ which exists as a discreet entity has been published [148]. The tetraethylammonium salt of the ion, whose preparation was reported some time ago, was recrystallised from ethanenitrile. Figure 25 shows the structure of

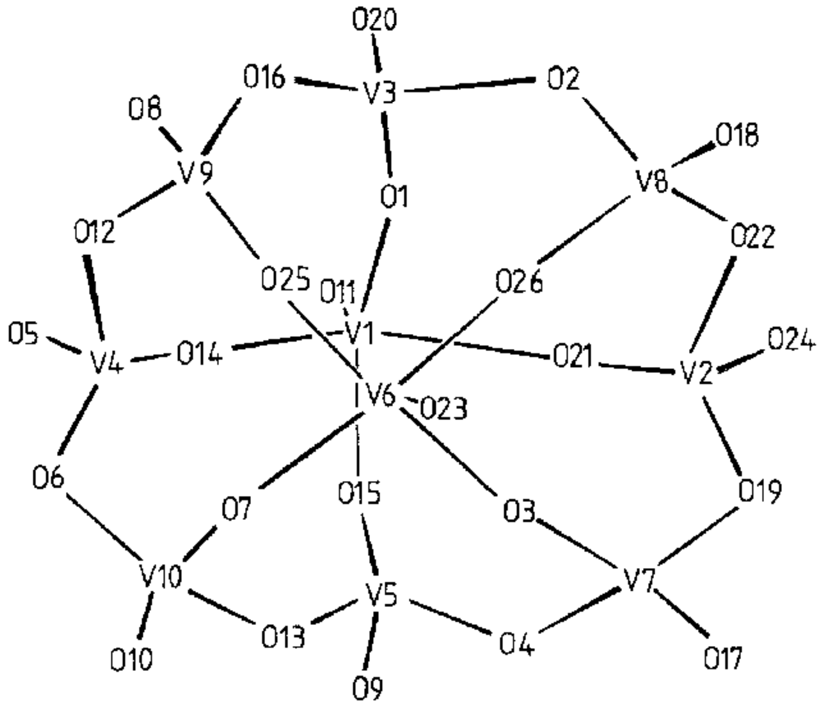

Figure 25: One view of the $[V_{10}O_{26}]^{4-}$ anion [148].

$[V_{10}O_{26}]^{4-}$, which comprises one asymmetric unit of the structure. The atoms V(1) and V(2) are in tetragonal pyramidal geometry, and thought to be quadrivalent with V–O distances similar to those found in the other vanadium(IV) complexes. These two tetragonal pyramids of $\{VO_4\}^{4-}$ units are considered to be above and below a crown of eight vertice shared tetrahedra containing $\{VO_4\}$ units. These eight vanadium atoms are thought to be formally pentavalent, with V–O distances typical of a vanadium(V) complex. The distance between the two central vanadium(IV) atoms is quoted as approximately 4.44 Å, which is similar to that found in other dimeric vanadium(IV) complexes.

The polymerisation of decavanadic acid by an autocatalytic process is known to yield polyvanadic acid gels, free from foreign ions such as Na^+ or $[NO_3]^-$ [149]. During the polymerisation, some vanadium reduction is thought to occur which resulted in mixed valence vanadium(IV) and vanadium(V) polymers. When layers of this polymer gel were deposited on glass, semiconductor properties were observed due to electron transfer betweeen vanadium(IV) and vanadium(V) atoms. The authors suggest that the polyvanadic acid colloids exist as polydispersed coils rather than rods from the interpretation of both the EPR spectra and light scattering experiments.

The polyvanadates $Na_2V_{12}O_{31}.7.7H_2O$ and $Na_2V_6O_{16}.4H_2O$ have been characterised by IR, EPR and NMR studies, and the loss of water molecules on heating studied [150]. The complete dehydration of $Na_2V_{12}O_{31}.7.7H_2O$ was observed at 280 °C, when a structural change occurs with formation of $Na_2V_6O_{15}$ bronze.

Monophasic vanadium antimonate, $VSbO_4$, has been prepared by carefully heating an equimolar mixture of V_2O_5 and Sb_2O_3 in O_2-free dinitrogen at 750 °C [151]. However, traces of Sb_2O_3 were observed to sublime out from the reaction mixture, suggesting the formation a non-stoicheiometric product such as $VSb_{1-y}O_{4-1.5}$ ($0 \leqslant y \leqslant 0.1$). Calcination of the product at 810 °C led to the formation of β-Sb_2O_4 crystals which, when heated at 670 °C, produced crystalline outgrowths of $VSbO_4$, β-Sb_2O_4 and V_2O_5. The system V_2O_5/MoO_3 has been studied in order to characterise the β-phase, which was found to have the composition $V_9Mo_6O_{40}$. X-ray powder diffraction studies were carried out to demonstrate that the crystals $V_9Mo_6O_{40}$ were monoclinic and cell dimensions were calculated [152]. The crystal structure determination of the ammonium vanadium molybdenum oxides, $[NH_4]_xV_xMo_{1-x}O_3$, has been carried out by complete profile analysis and refined by least squares to $R = 10\%$ [153]: when $x \leqslant 0.2$, the crystals were found to be hexagonal, space group $P6_3/n$ with $Z = 6$. Crystals of the compound $Cs_3Mn_3V_4O_{16}$ have been obtained by electrolysis in a melt of initial molar composition $Cs_2[CO_3] = 36.4\%$, $V_2O_5 = 54.6\%$ and $Mn[CO_3] = 9.0\%$ at 420 °C [154]. The structure was found to contain $\{CsMn_3V_4O_{16}\}_n$ layers parallel to the *ab* plane, with two Cs atoms per cell between them. The layers are made of flat ribbons of $\{Mn_3O_{10}\}_n$ bridged by $\{V_2O_7\}$ double tetrahedra, which leave large cavities inside the layers which are occupied by caesium atoms. The oxide vanadium bronze $Ca_xV_2O_5$ of type β, has been studied by EPR and IR spectra and magnetic susceptibility measurements [155]. A sudden change in physico-chemical properties of the bronze was found close to the composition $Ca_{0.25}V_2O_5$, thought to be due to the redistribution of calcium ions in the possible positions in the crystal lattice. Oxide vanadium bronzes of alkali metals $M_xV_2O_5$-β (M = Li, Na or K) have been obtained during crystallisation of melts of alkali metals and vanadium(V) oxide in air and the Gibbs free energy of formation calculated for the compounds [156].

A new complex $K_3VO_2[SO_4]_2$ has been obtained in the K_2O-SO_3-V_2O_5 system and has been studied by X-ray powder diffraction, IR spectroscopy and crystal optics [157]. The unit cell parameters of a related complex $K_2S_2O_7.V_2O_5$ have been determined from X-ray powder photographs [158].

A study has been made of the behaviour of oxovanadium, $\{VO\}^{2+}$, ions in tungstic acid [159]. In aqueous dmso, the $\{VO\}^{2+}$ ion was found to insert itself into the most stable tungstic acid, $H_4W_{10}O_{32}$, according to equation (28) and in the presence of excess $\{VO\}^{2+}$ the complex $VO(W_{10}VO_{33})$ crystallised

$$H_4W_{10}O_{32} + \{VO\}^{2+} \longrightarrow H_2W_{10}VO_{33} + 2H^+ \qquad (28)$$

out. When the reaction was carried out in water, there was competition between the insertion reaction and floculation of the associated tungstic acid.

High resolution solid state NMR spectra of the quadrupolar nucleus ^{51}V ($I = 7/2$) in $[NH_4]VO_3$ and $NaVO_3$ have been reported. The spectra were obtained by observing the $(\frac{1}{2},-\frac{1}{2})$ spin transition under conditions of rapid 'magic-angle' rotation and are thought to be the first of their kind reported for ^{51}V [160].

The optimum experimental conditions for the preparation of $TlVO_3$ and $Tl_3V_5O_{14}$ have been ascertained by investigating the systems $NaVO_3/CH_3COOTl/CH_3COOH/H_2O$ and $NaVO_3/CH_3COOTl/HNO_3/H_2O$ [161]. The existence of a new pentavanadate, $KV_5O_{13}.2H_2O$, has been verified by analysis of the precipitate formed in the system $K_2SO_4/KVO_3/H_2SO_4/H_2O$ [162]. The reaction of aqueous NH_4VO_3 with H_3PO_4 and oxalic acid was found to yield the complex $[NH_4](VO)(VO_2)(HPO_4)_2.1\frac{1}{2}H_2O$, which was characterised by thin layer chromatography, X-ray diffraction, IR spectroscopy, and thermal analysis: this complex was found to act as a catalyst in oxidizing C_4 fragments to maleic anhydride [163].

The X-ray structure of the high temperature modification of V_3O_5 has been determined. The structure is described as comprising hexagonal close-packed oxygen atoms with octahedral interstices which are partially filled with vanadium atoms. These vanadium filled octahedra form two chains of two types which run parallel to [001] and which alternate in the directions [100] and [010]. One type of chain is composed of double octahedra coupled together by having edges in common, the other type consists of single octahedra coupled by sharing corners. This is similar to the low temperature V_3O_5 structure, in that it has a sheer structure derived from the rutile structure [164].

A single crystal ENDOR study of the $[VO(H_2O)_5]^{2+}$ ion in $Mg[NH_4]_2[SO_4]_2.6H_2O$, where $[VO(H_2O)_5]^{2+}$ substitutes for Mg^{2+} in the lattice, has been carried out to determine whether hydrogen bonding with $[SO_4]^{2-}$ ions plays a dominant role in determining the positions of the water molecules, or whether the geometry is determined by the binding forces in the aqua complex itself [165]. ENDOR data on $[VO(H_2O)_5]^{2+}$ in Tutton's salt and in frozen aqueous solution were compared and showed that the cation has a similar geometry to the hexaaqua complexes $[Cu(H_2O)_6]^{2+}$ and $[Zn(H_2O)_6]^{2+}$, where planes of H_2O molecules are almost perpendicular to each other. The geometry of $[VO(H_2O)_5]^{2+}$ is retained in frozen aqueous solution. It was concluded that internal hydrogen bonding forces have a large effect in determining the geometry, because of the lack of pronounced solvent effects on $[VO(H_2O)_5]^{2+}$.

Vanadate sulfate trihydrate, $VOSO_4.3H_2O$, has recently been the subject of a single crystal X-ray determination, but in the study three of the hydrogen atoms were not located absolutely. Therefore the same group have made a study by neutron profile analysis on the structure of $VOSO_4.3D_2O$ [166]. The coordinates of the non-hydrogen atoms were found to agree well between both sets of data. The previous location of the hydrogen atoms was confirmed as being quite good, with the exception of one atom which was found to be shifted towards one oxygen atom to give a normal hydrogen bond.

The sucessful formation of phases from the reaction of $Na_2[CO_3]$ with VO_2 and V_2O_3 has been studied by DTA [167]. Carbon dioxide, which is evolved during the reaction, was found to play a vital part in the oxidation/reduction reactions. Products obtained from the reaction of Na_2CO_3 and VO_2 are V_2O_3, $Na_2V_2O_5$, $Na_4V_2O_7$, Na_2VO_3 and Na_3VO_4. In the reaction with V_2O_3, only $Na_4V_2O_7$ and Na_2VO_3 were observed.

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