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6. VANADIUM

E.M. PAGE

CONTENTS

INTRODUCTION

The purpose of this review is to summarise the reports on the coordination chemistry of vanadium published during 1981. The review therefore does not span the wide fields of organometallic and solid state chemistry, kinetics and catalysis, thorough reports of which can be found elsewhere. However, work in these areas is included where the results assist in the understanding of the coordination chemistry of vanadium.

The material is divided into five major sections according to oxidation state, commencing with vanadium(V). Within each section subdivisions of the content have been made depending upon the element bonded to the vanadium atom starting with elements at the right hand side of the periodic table. In the sixth section the chemistry of species formally containing oxo-anions is discussed.

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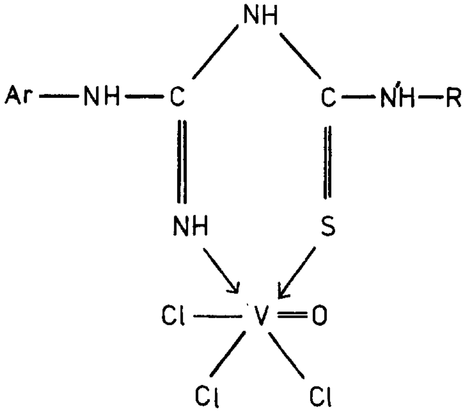
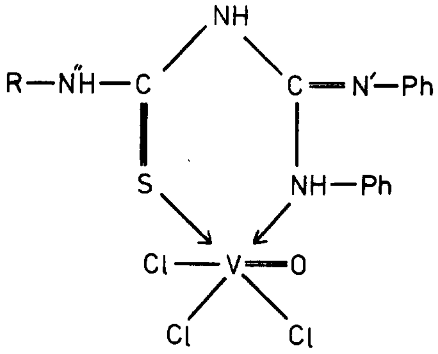
6.1 VANADIUM(V)

6.1.1 Species containing vanadium-halogen bonds

Further adducts of the oxide trichloride, $VOCl_3$, have been prepared and characterised. Reaction of $VOCl_3$ with substituted thiocarbamides having general formula $S{=}CNHR{-}NH{-}CArNH{-}NH$ ($R = C_6H_5$, $2{-}C_6H_4CH_3$, $4{-}C_6H_4CH_3$, CH_2CHCH_2; $Ar = C_6H_5CO$) led to complexes $VOCl_3.L$. The bidentate ligands are thought to be coordinated through the thioketo sulphur atom and the nitrogen atom of the secondary amine group, as shown in (*1a*) or (*1b*) [1]. By reacting 1,1'-diethanoylferrocene(def) with $VOCl_3$ in dry benzene or toluene the complex $VOCl_3.def$ has been synthesised [2].



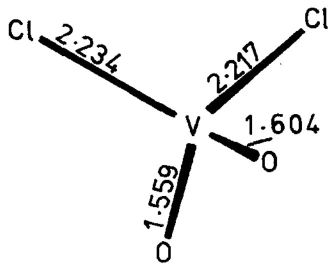
(1a)



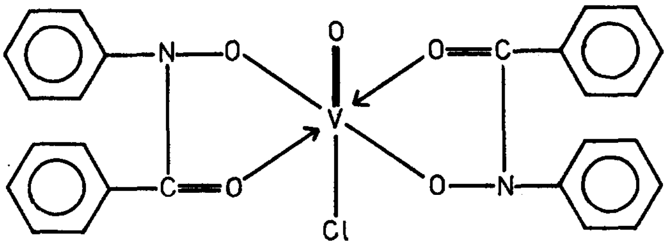
(1b)

The X-ray crystal structure of the salt $[PPh_3Me][VCl_2O_2]$ has been determined. Orange crystals of the compound were obtained from the reaction between VO_2Cl and $[PPh_3Me]Cl$ in CH_2Cl_2 solution. The anion, (*2*), has almost C_{2v} symmetry with V=O bond distances of 1.604(6) and 1.559(6) Å. The vibrational spectrum of the anion was assigned assuming C_{2v} symmetry, terminal ν(V=O) stretches being found at 959 cm^{-1} (b_1) and 970 cm^{-1} (a_1) [3].

A range of monochlorooxovanadium(V) complexes has been prepared by an unusual method which involves the reaction of ammonium vanadate(V) in concentrated hydrochloric acid with a solution of hydroxamic acid in trichloromethane. The compound, oxochlorobis-*N*-phenylbenzohydroxamatovanadium(V), was obtained by this method as a violet crystalline solid and the structure (*3*) was postulated on the basis of infra-red evidence [4].



(2; bond lengths in Å)



(3)

Force field and CNDO calculations performed on $ClNVCl_3$ are in agreement with a large $Cl\text{-}\hat{N}\text{-}V$ bond angle and short Cl-N distance in the molecule [5]. Vibrational analyses of $[VF_6]^{m-}$ spectra, having vanadium in a variety of oxidation states, have been carried out and various molecular characteristic constants calculated [6].

6.1.2 Species containing vanadium-oxygen bonds

The new compound $VO_2PO_2F_2$ has been prepared by treating V_2O_5 with $F_2OPOPOF_2$ under reflux for several hours. Reaction proceeds in accordance with equation (1).

$$P_2O_3F_4 + V_2O_5 = 2VO_2PO_2F_2 \qquad (1)$$

The excess of $P_2O_3F_4$ was removed by evaporation to leave a powdered hygroscopic solid stable up to 125 °C. Infrared and Raman spectra revealed the presence of bands attributed to the $\{VO_2\}^+$ moiety. The oxidising ability of the compound was measured at various temperatures and found to be much greater than that of V_2O_5 [7].

Further kinetic studies, using high pressure stopped-flow techniques, have been made on the reaction between the (nitriloethanoato)dioxovanadate(V) anion, $[V(O)_2(nta)]^{2-}$, and hydrogen peroxide [8]. The reaction is thought to proceed *via* an associative mechanism in which the H_2O_2 molecule is bonded as a monodentate ligand at one face of the octahedron of $[V(O)_2(nta)]^{2-}$. Oxo-peroxo oxygen exchange has been shown to occur in monoperoxo vanadium(V) species $(RO)VO(O_2)$ [9]. Enriched ^{18}O hydrogen peroxide was found to undergo fairly fast oxygen exchange (approximately 50% label loss in 10-20 h at 25 °C) in the presence of $[VO(acac)_2]$ acting as a catalyst. Two possible pathways were suggested for the exchange mechanism. A range of salts containing the $\{VO(O_2)\}^+$ moiety, *viz.* $M_3[VO(O_2)L].xH_2O$ (M = K, Na or NH_4; H_4L = edtaH_4; x = 2 or 3) has been prepared from MVO_3, MOH and H_4edta with 30% H_2O_2 according to equation (2) [10]. Interpretation of the

$$MVO_3 + 2MOH + H_4edta = M_3[VO(O_2)(edta)] + 3H_2O \qquad (2)$$

infrared spectra resulted in the proposal of monomeric structures having pentagonal bipyramidal coordination. The single oxygen atom of the {VO} group and a nitrogen donor atom of the edta ligand are thought to occupy the vertices of the bipyramid. This was claimed to be the first preparation of complexes having oxo(peroxo)vanadium(V) bonded to a tetradentate ligand. Further salts containing the $[VO(O_2)_2(L)]^{n-}$ ion have been prepared (L = NH_3, F, $OVO(O_2)_2$, $OHVO(O_2)_2$, CO_3 or C_2O_4) and their infrared spectra recorded [11]. The stretching vibrations of the $\{VO(O_2)_2\}$ group were found to depend upon the coordination number of the complex, different patterns of bands being observed when L was a monodentate or a bidentate ligand. The decomposition of one of these salts, $M[VO(O_2)_2(H_2O)]$ has been studied and is thought to proceed *via* the formation of a monoperoxo complex according to equations (3) and (4) [12]. Evidence to support this type

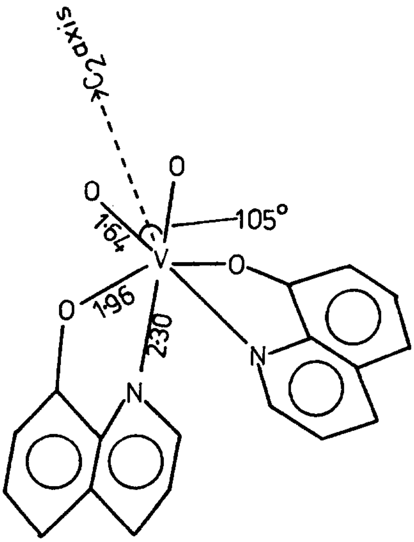
$$M[VO(O_2)_2H_2O] = M[VO_2(O_2)H_2O] + \tfrac{1}{2}O_2 \qquad (3)$$

$$M[VO_2(O_2)H_2O] = MVO_3 + H_2O + \tfrac{1}{2}O_2 \qquad (4)$$

of mechanism is derived from infrared spectra of the intermediates.

The ligand 4-(2-thiazolylazo)resorcinol (tarH_2) has been found to react with ammonium metavanadate, in weakly acidic solutions, to give intensely coloured species of the type $[V(O_2)(tar)]^-$. Stable crystalline salts were obtained with $[EPh_4]^+$ (E = P or As) corresponding to the formula $[EPh_4][V(O_2)(tar)].nH_2O$ (n = 0 or 1). These have been characterised by standard techniques including X-ray powder photography [13]. The X-ray crystal structure of a further complex having *cis*-(V=O) terminal bonds has been determined. Tetrabutylammonium dioxobis(8-quinolinolato)vanadium(V), $[NBu_4][VO_2(O\text{-}8\text{-}quin)_2]$, was prepared by mixing equimolar amounts of $VO(OH)(O\text{-}8\text{-}quin)_2$ and $[NBu_4]OH$ in ethanenitrile.

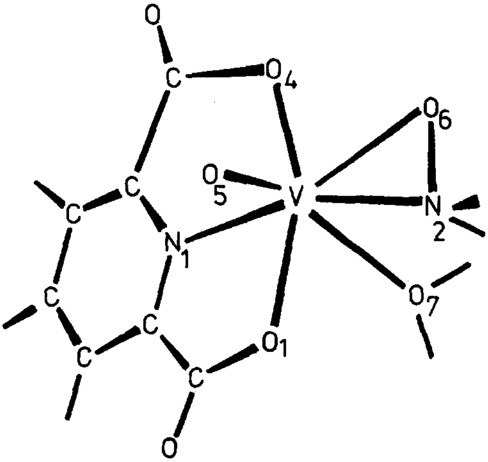
The $[VO_2(O\text{-}8\text{-quin})_2]^-$ anion, (*4*), exhibits C_2 symmetry with a *cis*-$(O\hat{V}O)$ angle of 105°. The nitrogen atom of the 8-quinolinolato ligand is *trans* to a terminal oxygen atom and the ligand oxygen atoms are *trans* to each other. The $(V{=}O)_t$ bond length, 1.64 Å, is slightly longer than those in a related complex $[PPh_4][VO_2(par)]$ ($parH_2$ = 4-(2-pyridylazo)resorcinol) in which the vanadium atom is five-coordinate. The vanadium atom and the nitrogen atom of the cation lie on the C_2 axis. The $[VO_2(O\text{-}8\text{-quin})_2]^-$ anion is chiral and both enantiomers were found in the crystal lattice, related by an S_4 axis. The mechanism of formation of a mixed valence anion, [μ-oxo{oxobis(8-quinolinolato)vanadium(V)}{oxobis-(8-quinolinolato)vanadium(IV)}], $[V_2O_3(O\text{-}8\text{-quin})_4]^-$ from $VO(O\text{-}8\text{-quin})_2$ and $[VO_2(O\text{-}8\text{-quin})_2]^-$ in CH_3CN was studied by polography and UV spectroscopy [14].



(4; bond lengths in Å)

Isomers of formula $Na_4[V_4O_8(C_4H_2O_6)_2].6H_2O$ have been prepared from the reaction between $NaVO_3$ and racemic *d*- and *l*- tartaric acids and their properties reinvestigated [15].

A series of studies have been made on the structural chemistry of the hydroxylamido(-1) ligand, and its *N*-substituted derivatives, with vanadium(V). Hydroxylamine is isoelectronic with hydrogen peroxide and structurally there have been found to be many similarities between the ligand properties of $[R_2NO]^-$ and those of the coordinated peroxo group. The crystal structure of the hydroxylamido complex $[VO(dipic)(H_2NO)H_2O]$ ($dipicH_2$ = $C_7H_3NO_4$ = pyridine-2,6-dicarboxylic acid) has recently been determined [16] and was found to be isostructural with the monoperoxo complex $[VO(dipic)(O_2)(H_2O)]^-$, the vanadium atom having a pentagonal bipyramidal environment as shown in (*5*). The terminal oxygen atom O(5) and the water molecule are *trans* to each other, the $O(5)-\hat{V}-O(7)$ angle being 172°. The dimeric μ-oxo complex $[O\{VO(Et_2NO)_2\}_2]$ has been prepared by two methods; the first involves the reaction of *N*,*N*-diethylhydroxylamine with V_2O_5 at 100 °C and the second the reaction between NH_4VO_3 and Et_2NOH in aqueous solution [17]. A structural investigation revealed that the complex had a peroxo- type structure [18]. (*6*) illustrates the coordination sphere around the vanadium atoms and shows that the structure consists of pairs of vanadium atoms, bridged by a single oxygen atom, each vanadium atom being *pseudo*-tetrahedrally surrounded by two (Et_2NO) groups, a terminal oxygen atom and the single oxygen atom of the bridge. Reactions of $[O\{VO(Et_2NO)_2\}_2]$ with oxalic acid were carried out and found to proceed according to equation (5) [17].



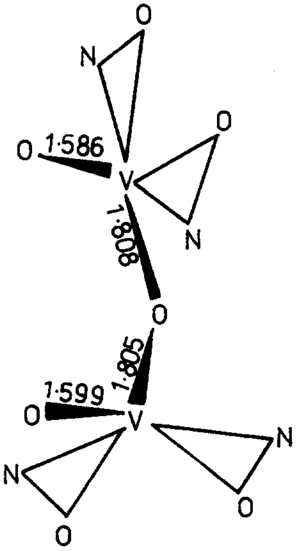
(5)

$$[(Et_2NO)_2V(O){-}O{-}(O)V(Et_2NO)_2] + H_2C_2O_4 = [\{VO(Et_2NO)_2\}_2(C_2O_4)] + H_2O \qquad (5)$$

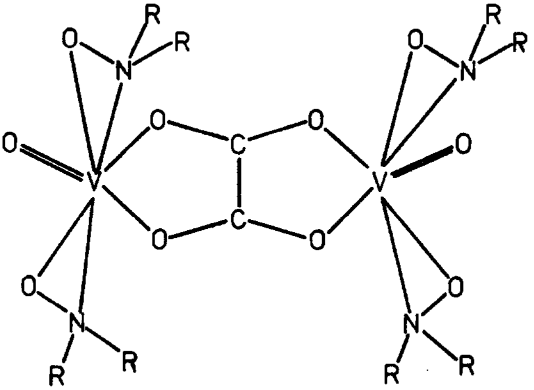
The authors used IR spectral data and the assumption that $[R_2NO]^-$ ligands behave as $[O_2]^{2-}$ ligands to propose a binuclear structure for the complex in which the vanadium atoms are bridged by a tetradentate μ_4-oxalato ligand as shown in (*7*).

Kinetic and equilibrium studies have been made on the esterification of μ-oxo dimeric vanadium(V) complexes, $[L_2V(O){-}O{-}(O)VL_2]$ (LH = 8-quinolinol, 5-chloro-8-quinolinol, 5,7-dibromo-8-quinolinol or isopropyltropolone) by butyl alcohols in chlorobenzene [19]. The reactions proceed according to equation (6)

$$[V_2O_3(L)_4] + 2ROH \rightleftharpoons 2[VO(OR)(L)_2] + H_2O \qquad (6)$$



(6; bond lengths in Å)



(7)

and rate and equilibrium constants were determined. The mechanism was thought to involve a monomeric vanadium species and so the rate of esterification of such a monomeric species with 2-methyl-8-quinolinol was investigated and was found to be five times greater than that observed for the dimeric species.

Photochemical studies have been carried out on solutions of [VO(acac)$_2$(EtO)] in EtOH or CCl_4 which showed that the vanadium atom is reduced in visible light (λ = 320 nm) by a two electron process. Ultraviolet light (λ = 254 nm) was found to initiate ligand substitution reactions in CCl_4 giving $[VO(acac)_2Cl]$, which is reduced to $[VO(acac)_2]$ by visible light [20]. The photochemical behaviour of a range of vanadium alkoxides $[VO(OR)_3]$ (R = Me, Et, $CHMe_2$, Pr, Bu or aryl) has been studied by the same group of workers [21].

EPR studies have been carried out on the red complex ion $[VO(O_2)]^+$, prepared from acidic solutions of $\{VO_2\}^+$ with H_2O_2. On increasing the pH, the red solutions became yellow and the EPR signal disappeared as the $[VO(O_2)_2]^-$ ion is formed. The authors remarked that the EPR signal of the red solutions (g = 1.97) was similar to that expected for vanadium(IV), despite the fact that a vanadium(V) species is believed to be formed [22].

6.2 VANADIUM(IV)

6.2.1 Species containing vanadium-halogen bonds

Reaction of $[VCl_4]$ with $[V(C_6F_5)_4]$ or with C_6H_5Li in thf has yielded pentafluorophenyl derivatives of vanadium(IV), $(C_6F_5)_nVCl_{4-n}$.thf (n = 1, 2 or 3). The V-C_6F_5 bond was found to be easily cleaved by compounds containing labile hydrogen, leading to the quantitative formation of pentafluorobenzene, according to equation (7). The chlorine atoms are also readily replaced by cyclopentadienyl or pentane-2,4-dionato groups [23]. Tetrachlorovanadium(IV) has been used in the preparation of $[VOCl_3]$ by reaction with $[OsO_4]$ in CCl_4 at -10 °C as in equation (8) [24].

$$(C_6F_5)_nVCl_{4-n}.\text{thf} + 4HCl \xrightarrow[0^\circ C]{\text{toluene}} C_6F_5H + VCl_4.\text{thf} \qquad (7)$$

$$4[VCl_4] + [OsO_4] \longrightarrow 4[VOCl_3] + OsCl_4 \qquad (8)$$

Thermogravimetric studies on the behaviour of $VOCl_2$ and VCl_3 with dichlorine showed that both compounds react, forming $[VOCl_3]$ and $[VCl_4]$ respectively, before disproportionation occurs. The reaction of $[VOCl_3]$ with Cl_2 on a charcoal bed was found to give $[VCl_4]$ in 97% yield at 700 °C. Thus a method for the formation of VCl_4 was suggested in which a mixture of $VOCl_2$ and VCl_3 is heated in dichlorine to 200 °C and the products, $[VOCl_3]$ and $[VCl_4]$, passed through a carbon bed at 700 °C [25].

A group of fluorooxalatovanadates(IV), $[LH][VOF(C_2O_4)(H_2O)]$ (L = morpholine), $[NH_4][VOF(C_2O_4)(H_2O)_2]$, $K_2[VOF_2(C_2O_4)(H_2O)].H_2O$ and $[NH_4]_3[VOF_3(C_2O_4)].H_2O$, has been synthesised. The magnetic moments, range 1.81-1.83 μ_B, are indicative of vanadium(IV) and IR spectra show the presence of terminal V=O bonds (ν(V=O) = 985±50 cm^{-1}) and chelating oxalate groups [26].

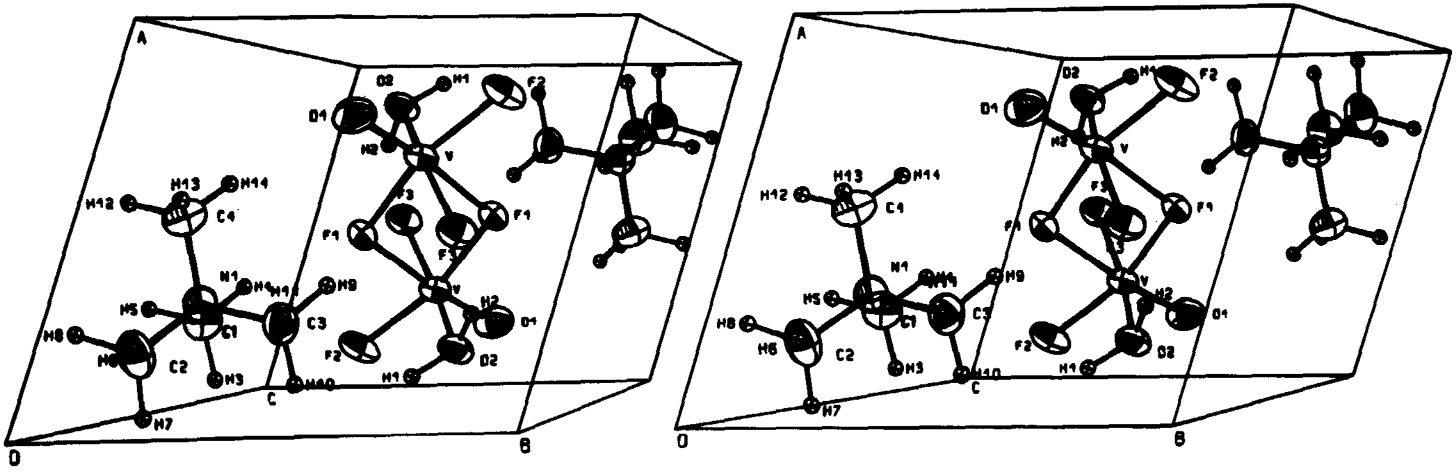


Fig. 1. Stereoscopic view of the unit cell of $[NMe_4]_2[V_2O_2F_6(OH_2)_2]$; reproduced, with permission, from ref. 27.

The first dimeric fluorooxovanadate has been prepared from an aqueous solution of [VF_4] and [NMe_4]F, and its crystal structure determined (see Fig. 1). The unit cell of [NMe_4]$_2$[$V_2O_2F_6(H_2O)_2$] consists of two octahedrally coordinated vanadium(IV) atoms bridged by two fluorine atoms, with two tetramethylammonium cations. The V=O bond length is characteristic of a double bond and the distance between the vanadium atoms is 3.292(1) Å. An assignment of the bands in the vibrational spectrum of [NMe_4]$_2$[$V_2O_2F_6(H_2O)_2$], and its deuterated and anhydrous derivatives has been made on the basis of the structure [27].

A series of oxovanadium(IV) and oxovanadium(V) dithiocarbamates, VOL_2, $VOLCl_2$, VOL_2Cl and VOL_3 (HL = *N*-cyclopentyl- or *N*-cycloheptyldithiocarbamic acid) has been prepared from the appropriate ligand plus $VOCl_3$ in benzene under reflux. The products were thought, from IR measurements, to be monomeric having terminal ν(V=O) and coordinated ν(V-S) stretches [28]. Oxovanadium(IV) complexes of the type [VOL_2X_2] (L = cyclohexanone, semicarbazone or thiosemicarbazone; X = Cl, Br or $\frac{1}{2}$[SO_4]) have been prepared and investigated by standard techniques [29]. A range of adducts of VOL_2 (L = Cl or $\frac{1}{2}$[SO_4]) with aromatic and aliphatic sulphoxides has been made; infrared studies indicate that the sulphoxide groups are bonded through the oxygen atom. A rough estimate of the S-O bond lengths and orders and the basicity of the sulphoxide ligands was made using the shift $\Delta\nu$(S-O). A further tentative estimation of the V=O bond lengths was made by applying Badger's rule to ν(V=O). However, no simple relationship was seen between the estimated V=O and S-O bond lengths [30].

X-ray powder diffraction measurements made on $VOCl_2$ and $VOBr_2$ have been used [31] to determine the structures of these compounds and the unit cell calculated is illustrated in Figure 2. Adducts of VOI_2 with dmso and dmf have been isolated and the structure of crystalline [VO(dmso)$_5$]I_2 determined. The coordination sphere of the vanadium atom is shown in (*8*) from which it can be seen that the five dmso molecules are bonded directly to the metal as in

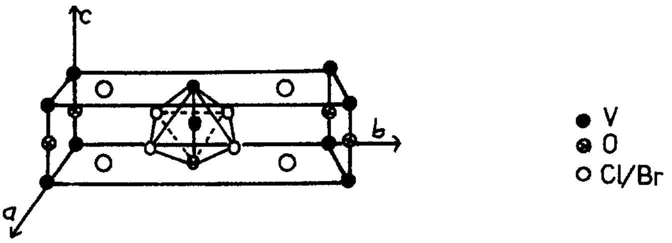
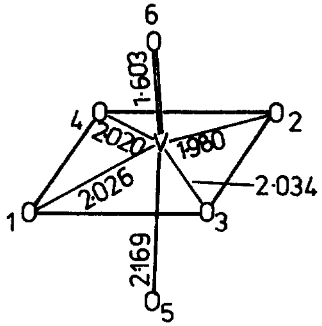


Fig. 2. The calculated unit cell of VOX_2 (X = Cl or Br); redrawn, with permission, from ref. 31.



(8; bond lengths in Å)

$[VO(dmso)_5][ClO_4]_2$. The complexes $VO(OCH_3)Br.3Py$ and $VOBr_2.2H_2O.2Et_2O$ are also reported [31].

Oxohalide adducts of vanadium(IV) have been the subject of several EPR studies. The EPR spectrum of $[VOF_4]^{2-}$ doped in single crystals of $[NH_4]_2[SbF_5]$ led to the determination of molecular orbital parameters which were compared with those from the MS-SCF-Xα method [32]. The series of *cis* and *trans* dihalogen vanadium(IV) complexes $[VX_2(L_4)]$ (L_4 = one quadridentate or two bidentate ligands; X = Cl or Br) prepared from SOX_2 and $[VO(L_4)]$ has been increased to include twenty members. Examples of the type of ligand used are pentane-2,4-dionate and tropolonate (O_4 donors); sal_2en {*N*,*N'*-ethylenebis(salicylideneiminate)} and $acac_2en$ {*N*,*N'*-ethylenebis(acetylacetiminate)} (O_2N_2 donors); and bipy and phen (two N_2 donors). The EPR solution spectra of the complexes were measured and in some cases differences were observed between spectral parameters of *cis* and *trans* isomers which could be used to characterise them. Conclusions drawn about the position of the unpaired electron are in accord with those reported in last year's review [33].

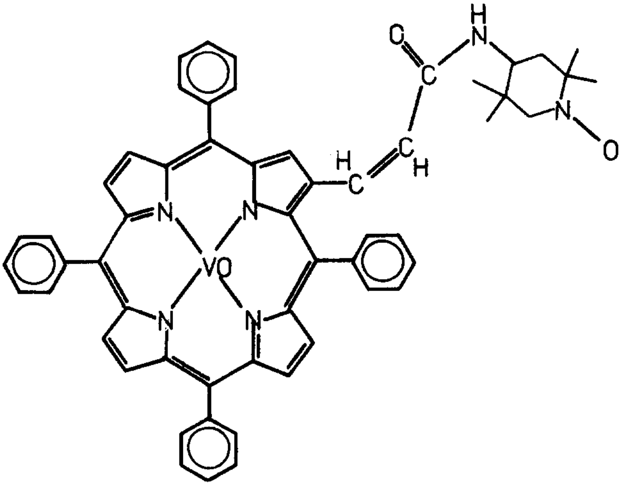
A whole range of oxochloride complexes of the type $[VOCl_2L_n]$ (L = neutral mono or bidentate ligand) and $A_2[VOCl_4]$ (A = $[NEt_4]$, $[pyH]$, $[NMe_4]$ or $[AsPh_4]$) have been prepared from $[VOCl_2(CH_3CN)_2]$ and their far IR and EPR spectra measured and used to classify the complexes according to their structural type. EPR spectroscopy has been successfully applied to relate the structure of the complex in a powdered sample to that in solution. However, solution spectra in solvents such as ethanenitrile and thf suggested displacement reactions may be occurring {see equation (9)} which must shed some doubt on some of the previously

$$[VOX_2(L)_2] \underset{L}{\overset{solv}{\rightleftharpoons}} [VOX_2(L)(solv)] \underset{L}{\overset{solv}{\rightleftharpoons}} [VOX_2(solv)_2] \qquad (9)$$

reported work in this field [34]. In a related study, the exchange reactions of ligands having different π donor/acceptor properties with $[VOCl_2(MeCN)_2]$ and $[VO(dmso)_4][ClO_4]_2$ have been studied by EPR spectroscopy in MeCN. Although coordinated MeCN could be substituted fairly readily, large excesses of fairly strong donor ligands such as dmso were required to substitute the chlorine atoms [35].

6.2.2 *Species containing vanadium-oxygen bonds*

Species having the oxovanadium(IV) (or vanadyl), $\{VO\}^{2+}$, moiety have been extensively studied by EPR spectroscopy. The *cis* and *trans* spin-labelled vanadyl(IV) porphyrins depicted in (*9*) have been synthesised and their EPR



(9)

spectra studied in order to determine the magnitude of metal-nitroxyl interactions and the extent of delocalisation of the unpaired electron into the porphyrin system. The results were compared with those of analogous Ag^{2+} and Cu^{2+} porphyrins [36]. The EPR signal of $[VO(O\text{-}8\text{-}quin)_2]$ (O-8-quin = 8-quinolinate) observed in a matrix of $[Zn(O\text{-}8\text{-}quin)_2(H_2O)_2]$ was found to be similar to that of $[VO(O\text{-}8\text{-}quin)_2]$ in toluene. This was thought to suggest that $[VO(O\text{-}8\text{-}quin)_2]$ in the matrix has no ligated H_2O to interact in the axial position [37]. Bis{di(4-tolyl)dithiophosphinato}oxovanadium(IV) has been prepared and its EPR spectrum recorded in trichloromethane and in the presence of pyridine bases. In the presence of base, the phosphorus hyperfine interaction disappears suggesting a breakdown of the four membered chelate structure with displacement of the equatorial sulphur donating ligands by pyridine [38].

The auto-oxidation of ascorbic acid is catalysed by vanadyl(IV) tetrasulphophthalocyanine, [VO(TSPc)], which is itself reduced to a vanadium(III) complex and then reoxidised. However, examination of the hyperfine structure of the EPR spectrum indicated that after reoxidation the equilibrium between dimeric and monomeric forms of [VO(TSPc)] is shifted towards the latter. This has been accounted for by the formation of adducts of [VO(TSPc)] with the products of the ascorbic acid oxidation which prevents dimerisation. Addition of dehydroascorbic acid to [VO(TSPc)] results in hyperfine splitting similar to that of the monomeric form in the EPR spectrum [39].

In a study of the vanadyl ion EPR spectra of mixed $\{VO\}^{2+}$, Fe^{3+}, conalbumin solutions, a pH dependent preference of the vanadium atom for different proton binding site configurations was found to exist [40].

Ligand exchange reactions between bis(diethyldithiocarbamato)oxovanadium(IV), $[VOA_2]$, and bis(diethyldithiophosphato)nickel(II), $[NiL_2]$, have been studied by EPR spectroscopy, which indicated the formation of mixed complexes such as [VOLA], [NiLA], and $[VOL_2]$ [41].

The vanadyl $\{VO\}^{2+}$ ion and its oxidative properties have been the subject of several kinetic studies. A method has been devised for the measurement of the rate constant for the reaction between $\{VO\}^{2+}$ and Cr^{2+}, {equation (10)}, in which

$$VO^{2+} + Cr^{2+} + 2H^+ \xrightarrow{k} V^{3+} + Cr^{3+} + H_2O \qquad (10)$$

the Cr^{2+} ions are generated slowly from $Cr(CH_2OH)^{2+}$, and a scavenger ion, $[Co(NH_3)_5X]^{2+}$ (X = F, Cl or Br), added which is known to react rapidly with Cr^{2+} according to equation (11). As the rate constants k and k' are of the same

$$[Co(NH_3)_5X]^{2+} + Cr^{2+} + 5H^+ \xrightarrow{k'} Co^{2+} + CrX^{2+} + 5[NH_4]^+ \qquad (11)$$

order of magnitude, and values of k' are already known, k was determined to be (1.3±0.3) or (1.4±0.2) x 10^6 $M^{-1}s^{-1}$, depending upon the nature of X [42]. The same group has studied the kinetics and mechanism of the vanadyl $\{VO\}^{2+}$ oxidation of $Cr(CH_2OH)^{2+}$ by measuring the disappearance of $Cr(CH_2OH)^{2+}$, equation (12),

$$Cr(CH_2OH)^{2+} + 2VO^{2+} + 3H^+ \longrightarrow Cr^{3+} + 2V^{3+} + CH_2O + 2H_2O \qquad (12)$$

spectrophotometrically. First order plots were obtained and the results suggested that reaction takes place *via* an inner-sphere mechanism by the formation of bridged activated complexes through the OH groups [43]. The reaction of $[HSO_5]^-$ with the vanadyl ion, in which the vanadium atom acts as a reducing agent, {equation (13)}, has been studied spectrophotometrically by monitoring the

$$2VO^{2+} + HSO_5^- + H_2O \xrightarrow{k''} 2VO_2^+ + HSO_4^- + 2H^+ \qquad (13)$$

appearance of vanadium(V). The rate was found to obey the second-order equation, (14), and competition reactions with HN_3 and cerium(III) indicated

$$-\frac{d}{dt}[HSO_5^-] = k''[HSO_5^-][VO^{2+}] \tag{14}$$

that a free radical mechanism involving $[SO_4]^{\bullet}$ takes place [44].

In an attempt to understand the catalytic oxidation of alkenes by $[VO(acac)_2]$, a study of the reactions between several oxo radicals (such as phenoxyl, iminoxyl, *etc.*) with $[VO(acac)_2]$ has been made by monitoring the EPR spectra of the mixtures. The rates were found to be first order with respect to each reactant, and ^{51}V NMR spectroscopy was used to investigate some of the products [45].

The kinetics of vanadium(IV) tartrate complex formation has received considerable attention. Potentiometric and polarographic measurements have been used to study the formation of the dimeric vanadyl tartrate complex $[(C_4H_2O_6)(VO)_2(C_4H_2O_6)]^{4-}$ with increase in pH. A stepwise mechanism was proposed for the neutralisation of the carboxylic and hydroxylic protons [46]. Equilibrium constants have been determined for the reactions between both the active and racemic dimeric vanadyl(IV) tartrate ions with active and racemic tartaric acid {equations (15) and (16)} at pH > 7. From the values of k_3 and k_4, equilibrium

$$[(VO)_2(d\text{-}C_4H_2O_6)_2]^{4-} + 2[d\text{-}C_4H_4O_6]^{2-} \underset{}{\overset{k_3}{\rightleftharpoons}} 2[VO(d\text{-}C_4H_3O_6)_2]^{4-} \tag{15}$$

$$[(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)]^{4-} + 2[dl\text{-}(C_4H_4O_6)]^{2-} \overset{k_4}{\rightleftharpoons} 2[VO(dl\text{-}C_4H_3O_6)_2]^{4-} \tag{16}$$

constants, K, for the interconversion of active and racemic binuclear complexes {equation (17)} have been derived for two different assumptions of the monomer

$$\tfrac{1}{2}[(VO)_2(d\text{-}C_4H_2O_6)_2]^{4-} + \tfrac{1}{2}[(VO)_2(l\text{-}C_4H_2O_6)_2]^{4-} \overset{K}{\rightleftharpoons} [(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)]^{4-} \tag{17}$$

isomer distribution in the racemic system [47]. Kinetic studies on the ligand substitution reaction {equation (18)} and ligand exchange reaction {equation (19)}

$$[(VO)_2(l\text{-}C_4H_2O_6)_2]^{4-} + [d\text{-}C_4H_4O_6]^{2-} \rightleftharpoons [(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)]^{4-} + [l\text{-}C_4H_4O_6]^{2-} \tag{18}$$

$$\tfrac{1}{2}[(VO)_2(l\text{-}C_4H_2O_6)_2]^{4-} + \tfrac{1}{2}[(VO)_2(d\text{-}C_4H_2O_6)_2]^{4-} \rightleftharpoons [(VO)_2(d\text{-}C_4H_2O_6)(l\text{-}C_4H_2O_6)]^{4-} \tag{19}$$

showed that the activation parameters for the two pathways are equal, suggesting identical dissociative steps may occur [48].

A reductive process in which $\{VO\}^{2+}$ is formed is thought to occur in the liver of rats which have been fed VO_3^-. In a reaction between $NaVO_3$ and cysteine at pH 6.8, in air, spectrophotometric and EPR measurements indicated that vanadium(V) is reduced to vanadium(IV), and cysteine simultaneously oxidised to cystine, followed by the formation of a stable vanadyl complex, the overall reaction being represented by equation (20) [49]. A similar complex,

$$3HSCH_2CH(NH_2)CO_2H + VO_3^- \longrightarrow [VO\{SCH_2CH(NH_2)CO_2\}_2]^{2-} + S_2\{CH_2CH(NH_2)CO_2H\}_2 + 2H_2O + H^+ \qquad (20)$$

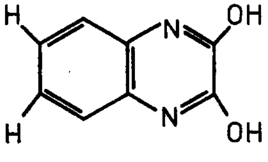
bis(cysteine methyl ester)oxovanadium(IV) has been isolated by the same group and identified by standard spectroscopic techniques. The purple solid obtained was thought to contain a mixture of *cis* and *trans* isomers on the basis of IR and EPR measurements [50].

A study made by cyclic voltammetry and controlled potential coulometry on the electrochemical reduction of $[VO(acac)_2]$ in dmso has been made and the reduction products and potentials identified [51].

6.2.3 Syntheses of complexes containing $\{VO\}^{2+}$

Again a vast number of coordination compounds containing the $\{VO\}^{2+}$ unit has been reported and studied by standard analytical techniques. The existence of most of these complexes will be mentioned only briefly in this section.

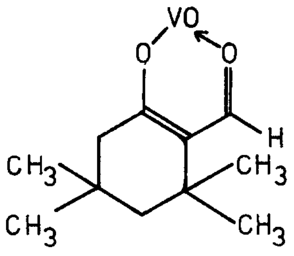
Complexes of oxovanadium(IV) with twelve β-diketones have been prepared and their magnetic properties studied between 80 and 300 K. As expected for complexes of the type $[VO(acac)_2]$, $[VO(bzac)_2]$ and $[VO(dbzm)_2]$ the values of μ_{eff} at 299 K were found to be in the range 1.71-1.76 μ_B. The moments decreased slightly as the temperature was lowered, indicating weak antiferromagnetic interactions [52]. Electron transfer reactions have been investigated in complexes of vanadium(IV) with quinoxalinic and naphthoquinonic ligands. Compounds of the type $[NBu_4]_2[VO(2,3\text{-dhq})_2]$ {2,3-dhqH₂ (*10*) = 2,3-dihydroxyquinoxaline} were characterised by various spectroscopic techniques including polography and powder EPR spectroscopy [53].



(10; 2,3-dhqH₂)

A number of new oxalatooxovanadates(IV) of the type $M_2[VO(C_2O_4)_2].xH_2O$ (M = Li, Rb, Cs, [pyH] or ½[enH₂]), $M'_2[V_2O_2(C_2O_4)_3].xH_2O$ (M' = $[NMe_4]$ or [3-MepyH]) and $[Co(NH_3)_6]_2[V_2O_2(C_2O_4)_5].5H_2O$ have been prepared from aqueous oxovanadium(IV) oxalate and the organic base or alkali metal carbonate [54].

A chelate of $\{VO\}^{2+}$, $[VOL_2]$ (*11*), with the β-ketoaldehyde 2-formyl-3,3,5,5-tetramethylcyclohexan-1-one, LH_2, has been isolated and its EPR spectrum recorded. However, vanadyl chelates with β-ketoaldehyde nitroxides {*e.g.* (*12*) and (*13*)} were unstable and could be observed only in solution by EPR spectroscopy [55].



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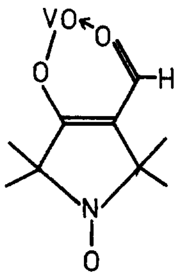

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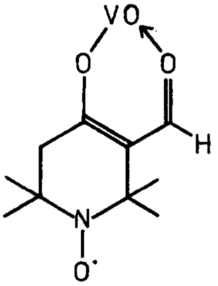
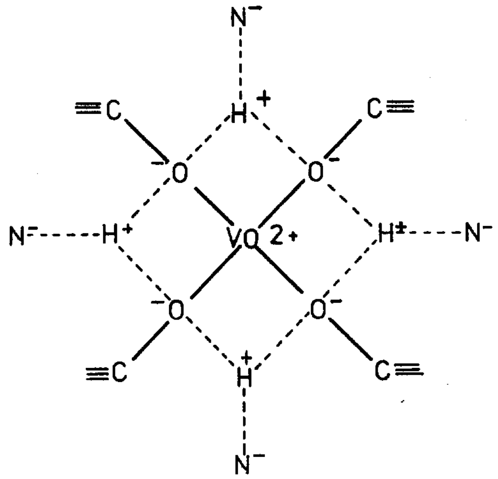


(13)

The IR spectra of a series of ternary complexes of $\{VO\}^{2+}$ and V^{3+} with the polyphenols pyrochatechol, pyrogallol and gallic acid and the amines aniline and aminopyridine showed that the vanadium atom is joined to the oxygen atoms of the ligands by the replacement of hydrogen atoms of the hydroxy groups to give structures as depicted in (*14*) [56].

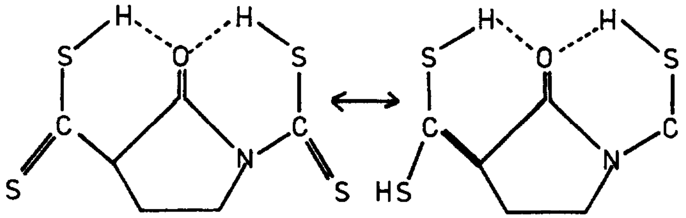
Complexes of $\{VO\}^{2+}$ with 4-benzoyloxime-3-methyl-1-phenyl-2-pyrazolin-5-one [57] and (α-benzoylmethylbenzylideneimido)ethane sulphonic acid [58] have been prepared and characterised by standard techniques.

A study of the replacement of the pentane-2,4-dionato groups in $[VO(acac)_2]$ by dithiolate ions from 3,4-dimercaptotoluene ($tdtH_2$) has been made and complexes having both *S* and *O* donor atoms in the equatorial plane have been observed by EPR spectroscopy [59]. Deprotonated and mixed ligand complexes of the type



(14)

$[VO(btH)_2]$ (btH_2 = *N*-phenyl-*N*'-benzothiazol-2-yl-thiocarbamide) and $[VO(btH)_2L']$ (L' = 2-methylbenzimidazole) have been prepared and characterised by molar conductance, and IR and electronic spectroscopy [60]. Binuclear complexes $(VO)_2(pdt)_2.2H_2O$ {pdtH = (*15*)} have been prepared from vanadium ethanoate and the ligand in methanol. From IR and electronic spectral data an octahedral environment is proposed for the vanadium atom [61].



(15)

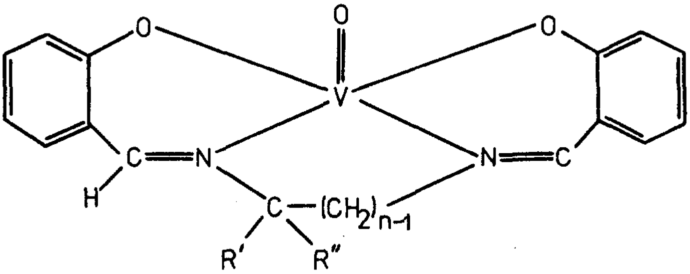
The reaction of vanadium(IV) with cyanide is purported to lead to the formation of $K_3[VO(CN)_5]$ by reaction (21) and not $K_2[V(CN)_6]$ as has been previously reported. The evidence for this proposition is based on the presence of a band at 935 cm^{-1} in the IR spectrum assigned to $\nu(V{=}O)$. Although this value is low for a $\nu(V^{IV}{=}O)$ stretch, the authors explain the value by evoking high electron

$$VO(OH)_2 + 3KCN + 2HCN \longrightarrow K_3[VO(CN)_5] + 2H_2O \qquad (21)$$

density on the central vanadium atom from the coordinated CN^- and O^{2-} which has the effect of decreasing ν(V=O) and ν(V-CN) [62].

Other complexes of oxovanadium(IV) with nitrogen donor ligands which have been reported this year include $[VO(acac)_2L]$ {L = various pyridine derivatives (including 2,3- and 4-Mepy), picolinamide, nicotinamide, isonicotinamide, quinoline, piperidine or Et_3N} [63,64].

A large number of Schiff base complexes of oxovanadium(IV) with a variety of donor atoms have been prepared in the past year. Quadridentate Schiff bases have been prepared from salicylaldehyde and polymethylenediamines and reacted with oxovanadium(IV) sulphate to give complexes of formula $[VO(OC_6H_4CH=N-CR'R''(CH_2)_{n-1}-N=CHC_6H_4O)]$ {(*16*); $n = 2$, R', R" = H or CH_3; $n = 3-10$, R' = R" = H}. Spectroscopic and magnetic data suggested that the geometries of the complexes vary with the length of the methylene chain [65].



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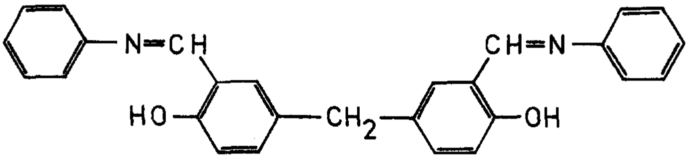
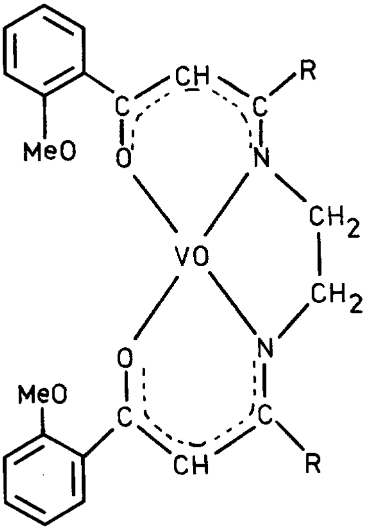
Polychelates of $\{VO\}^{2+}$ with the Schiff base derived from 5,5'-methylenebis(salicylaldehyde) and aniline (*17*) have been prepared as



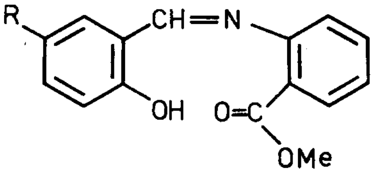
(17)

amorphous powders, insoluble in common organic solvents. The products showed a terminal ν(V=O) stretch at 970 cm^{-1} in their IR spectra and the electronic spectra suggested square-pyramidal configuration about the vanadium atom [66]. Mononuclear complexes of $\{VO\}^{2+}$ with the new acyclic Schiff bases derived from 2-methoxyphenylbutane-1,3-dione or 2-methoxyphenylpentane-1,3-dione with 1,2-diaminoethane have been prepared and are thought to have structure (*18*) by

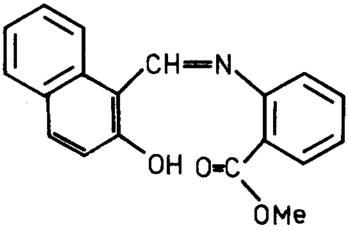


(18)

comparison with the nickel complex whose X-ray structure has been determined [67]. Other Schiff bases having *O*- and *N*- donor atoms which have been synthesised, and have been found to complex with the vanadyl(IV) ion, are shown in (*19*)-(*21*) [68,69] Square-pyramidal geometries were proposed for the complexes formed.



(19; R = H, Me or Cl)



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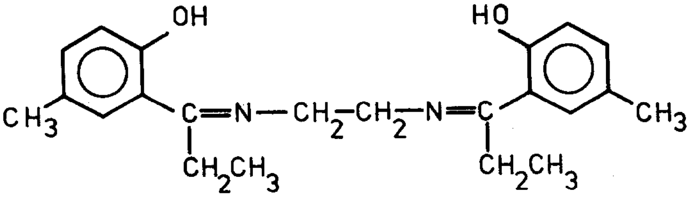

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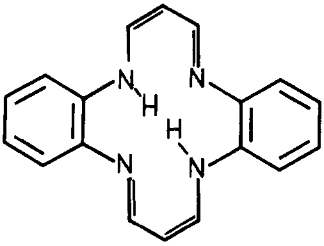
Quadridentate tetraaza[14]annulenes (*22*) and (*23*) have been prepared and



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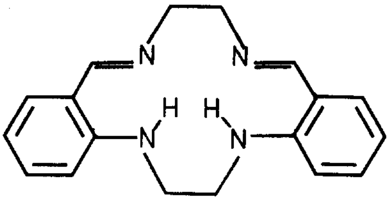


(23)

reacted with $\{VO\}^{2+}$. The products have been studied by electronic, vibrational, NMR, EPR, and XPES spectroscopy. The $\nu(V{=}O)$ vibrations were observed at 967 cm^{-1} {for (*22*)} and 940 cm^{-1} {for (*23*)} in their IR spectra, and EPR parameters suggested that the unpaired electron is in the $d_{x^2-y^2}$ orbital [70].

Complex formation between the vanadyl(IV) ion and a variety of ligands has been studied in order to determine stability constants. The reaction $VO^{2+} + 2A^{2-} + nH^{+} \rightleftharpoons$ products (H_2A = 2,5-dihydroxy-1,4-benzoquinone or 3,6-dibromobenzoquinone) has been studied and a relationship between the stability constants of the complexes and the basicities of the ligands observed [71]. Potentiometric measurements on the vanadyl(IV) chlorate/ethanoate system have been made to determine stability constants for the equilibria (22) and (23) [72].

$$VO^{2+} + [CH_3COO]^{-} \rightleftharpoons [VO(CH_3COO)]^{+} \qquad (22)$$

$$[VO(CH_3COO)]^{+} + [CH_3COO]^{-} \rightleftharpoons [VO(CH_3COO)_2] \qquad (23)$$

Stability constants for the formation of complexes of oxines with vanadium(IV) were found to increase in the order pyridine < 3-methylpyridine < 4-methylpyridine < isoquinoline. With chloro derivatives of oxines, the magnitude of the stability constant decreased with increasing substitution of chlorine atoms [73]. Formation constants have also been determined for complexes of $\{VO\}^{2+}$ with dicarboxylic acids [74], salicylic acid and its derivatives [75], substituted salicylaldehydes [76], 2,3-dihydroxynaphthalene [77], 3-bromo-2-hydroxy-5-methyl acetophenone [78] and 3,7-dimethyl-7-hydroxyoctan-1-al [79]. Potentiometric techniques have been used to estimate stability constants for chelates between $\{VO\}^{2+}$ and 3-(α-benzoyl methyl benzylideneimino)propanoate [80] and {(5-benzoyl-2-hydroxy-3-methoxybenzyl)imino}bis(ethanoic acid) [81].

Finally in this section are included two reactions in which the vanadium-oxygen moiety is destroyed. Irradiation of $[VO(C_2O_4)_2]^{2-}$ in oxalic acid with

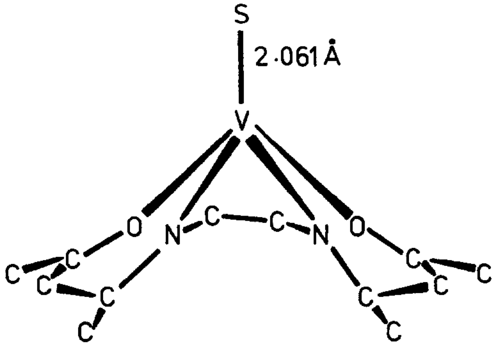
UV light caused reduction to vanadium(III) with the evolution of a stoicheiometric quantity of CO_2, represented by equation (24) [82].

$$[VO(C_2O_4)_2]^{2-} + 2H^+ + \tfrac{1}{2}[C_2O_4]^{2-} \overset{h\nu}{\rightleftharpoons} [V(C_2O_4)_2]^- + CO_2 + H_2O \qquad (24)$$

The complex $[VO(C_{22}H_{22}N_4)]$, shown in Figure 3, has been deoxygenated by treatment with anhydrous HCl to give $VCl_2(C_{22}H_{22}N_4).HCl$. Treatment of this complex with H_2S yielded the thioxo derivative $[VS(C_{22}H_{22}N_4)]$. A μ-nitrido complex $[(C_{22}H_{22}N_4)V\text{-}N\text{-}V(C_{22}H_{22}N_4)]^+$ was obtained by treatment of the chloro derivative with ammonia [83].

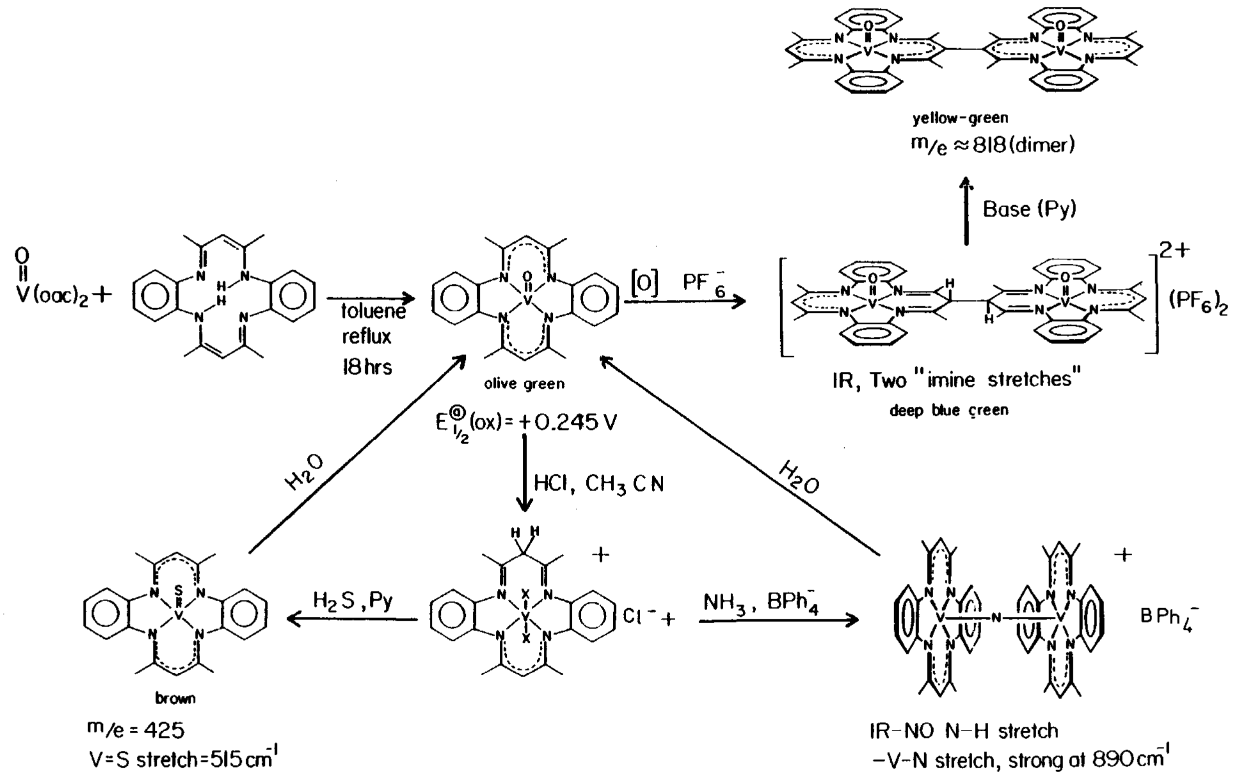
6.2.4 Species having vanadium to sulphur bonds

One species having a multiple {V=S} bond has already been mentioned in the preceding section [83]. The crystal structure of a complex whose preparation was mentioned last year, {*N,N'*-ethylenebis(acetylacetonylideniminato)}thiovanadium, [S=V(acac$_2$en)] (*24*), has been determined [84]. The {V=S} bond distance of 2.061(1) Å is thought to correspond to a double bond analogous to the $\{V=O\}^{2+}$ moiety. However the bond length is longer than would be expected from comparison with the {V=O} distance in the corresponding vanadyl complex, [O=V(acac$_2$en)]. This is in agreement with molecular orbital calculations which predict that the {V=S} bond should be markedly weaker than the stable {V=O} bond [84].



(24)

A layered compound of formula $V(CH_3CS_3)_2$ has been prepared from the reaction of $VOCl_2$ with thioethanoic acid at 60 °C for two days. The X-ray diffraction pattern of the product was indexed on the basis of a monoclinic cell. Reaction of the complex with a 50% molar excess of butyl lithium at 60 °C produced a compound formulated as $LiV(CH_3CS_3)_2$ which was thought to be an intercalation compound of lithium [85].



@ vs. SCE with 0.1 M electrolyte

Figure 3. A reaction scheme for the formation of vanadium(IV) complexes of the dibenzotetramethyltetraaza[14]annulene ligand. Reproduced with permission from ref. 83.

^{51}V NMR studies have been used to investigate the microscopic magnetic properties of $BaVS_3$ at different temperatures. The compound exhibits vastly different conducting properties depending upon the temperature. Results suggested that at the metal-insulator transition (∿70 K), a gradual pairing of the magnetic vanadium atoms into linear chains occurs with decrease in temperature [86].

6.3 VANADIUM(III)

6.3.1 Species containing vanadium-halogen bonds

The effects of small composition changes upon the structural and magnetic properties of the tungsten-bronze like compounds $A_xV^{II}_x\,V^{III}_{(1-x)}F_3$ (A = Cs or K; x = 0.19-0.558) have been studied [87].

A fluoride ion selective electrode has been used to study M^{3+}/F^- systems (M = first row transition element) and a value of $\log\beta = 5.00 \pm 0.03$ obtained for the reaction $V^{3+} + F^- \rightarrow \{VF\}^{2+}$ [88]. The crystal structure of the high temperature β-phase of $LiVF_6$ has been determined and was found to represent a new structural type. The vanadium atoms are in octahedral environments of two different symmetry types (see Fig. 4). However 7/9 of the lithium atoms occupy octahedral sites and the remaining 2/9 occupy distorted tetrahedral sites forming binuclear $\{Li_2F_6\}$ groups. The octahedra are linked to one $\{VF_6\}$ and two $\{LiF_6\}$ groups forming a three-dimensional network similar to those in some heteropolyanions [89].

A series of aquahalo complexes of vanadium(III), $M_3VCl_6.4H_2O$ (M = Cs, Rb) and $Cs_2VBr_5.4H_2O$ have been prepared and the structure of $Cs_3VCl_6.4H_2O$ determined by X-ray diffraction (see Fig. 5). Considerable hydrogen bonding within the structure was suggested by the O-H···Cl distance of 3.038 Å and the unusual stability of the crystals. The low temperature polarised absorption spectra of the compounds were recorded and interpreted in terms of D_{4h} symmetry, which is the symmetry of the *trans*-$[VX_2(H_2O)_4]^+$ chromophore found in the compounds [90] Substitution reactions have been carried out between the complexes $H_3VCl_6.6Et_2O$ and $H_3VCl_3Br_3.6Et_2O$ and nitrogen bases. Reaction with pyridine was thought, from IR spectral evidence, to give ionic complexes of the type $[pyH]_3[VX_6]$. However aniline and quinoline were thought to coordinate directly to the metal, yielding structures such as $H[VX_4L_2].2L$ (L = $PhNH_2$ or quinoline) [91].

Reaction of anhydrous VCl_3 with phen or bipy, LL, have been found to give complexes of the type $[VCl_2(LL)_2]^+$ and $[VCl_4(LL)]^-$. Conductance measurements suggested that, at higher vanadium concentrations, polynuclear complexes (possibly with bridging diimine groups) are formed [92]. The species

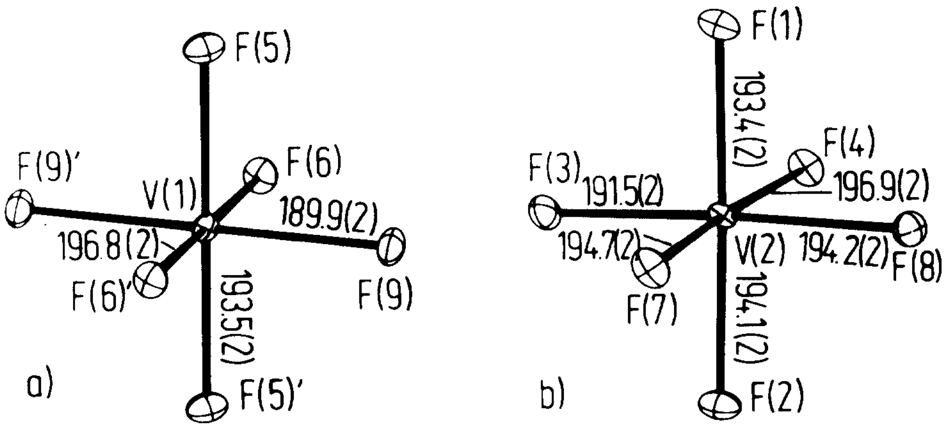


Fig. 4. The coordination spheres of the two types of vanadium atoms in Li_3VF_6; (a) $\{V(1)F_6\}$ (symmetry $\bar{1}$), (b) $\{V(2)F_6\}$ (symmetry $\bar{2}$). Reproduced with permission from [89]. The bond lengths are given in pm.

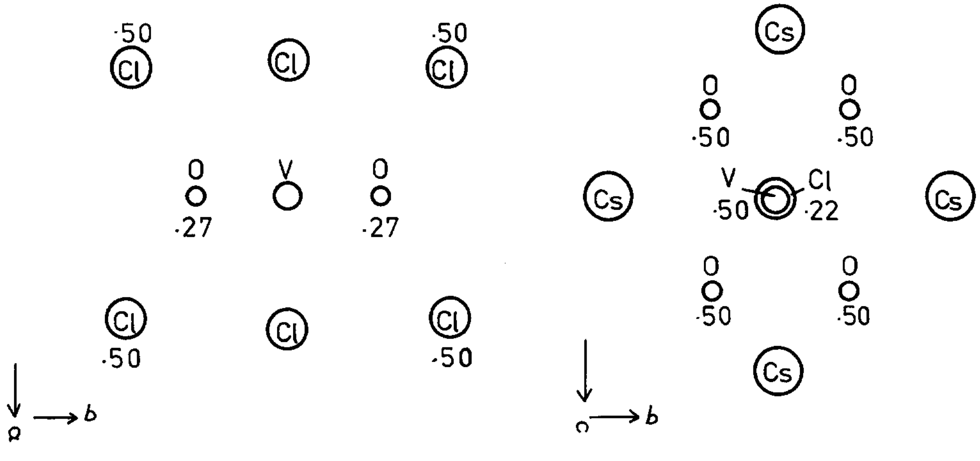


Fig. 5. The coordination sphere of the vanadium atom in the unit cell of $Cs_3[VCl_2(H_2O)_4]Cl_4$, (a) looking down the *c* axis and (b) looking down the *a* axis. The numbers are the positions above and below the appropriate planes in fractions of the unit cell *c* or *a* dimensions, respectively. Drawn with permission from [90].

$[VCl_3(hmpa)_3]$ {hmpa = tris(dimethylamino)phosphine oxide} has been prepared as a pink crystalline solid from VCl_3 and hmpa in dry thf. Shifts in ν(P=O) observed in the IR spectrum indicate coordinated phosphine oxide. ^1H, ^{13}C and ^{31}P NMR spectroscopic measurements were made [93]. In an attempt to obtain pure vanadium(III) phosphates from VCl_3 and Na_2HPO_4 or NaH_2PO_4, mixtures of acidic and neutral compounds were obtained, the composition of the mixture being determined by the washing procedure. Hydrolysis of the phosphates formed prevented isolation of single products [94]. The systems VCl_3/Al_2Cl_6 and VCl_2/Al_2Cl_6 have been studied by mass spectrometry and values obtained for thermodynamic parameters as $\Delta H°$, $\Delta S°$, ΔC_p. Chemical transport experiments were also carried out on $VCl_3/VCl_2/Al_2Cl_6$ mixtures [95].

6.3.2 *Species having vanadium-oxygen or vanadium-carbon bonds*

Kinetic studies have been made on the reaction between $[V(H_2O)_6]^{3+}$ ions and 5-nitrosalicylic acid (H_2L), using a stopped flow technique. Equilibrium constants were determined for the formation of $\{V(HL)\}^{2+}$ and $\{VL\}^+$, and rate constants obtained for the reactions (25) and (26). A comparison of the results

$$V^{3+}_{aq} + HL^- \rightarrow \{V(HL)\}^{2+} \qquad (25)$$

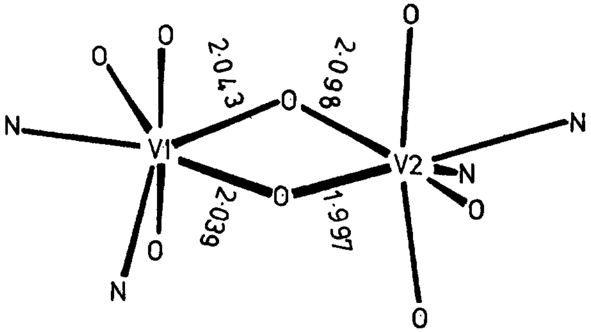
$$V^{3+}_{aq} + H_2L \rightarrow \{V(HL)\}^{2+} + H^+ \qquad (26)$$

with those previously obtained for salicylic and 4-amino-salicylic acids showed a strong ligand dependence of both the rate and equilibrium constants [96].

Ligand exchange reactions of $[V(acac)_3]$ in acacH have been investigated and rate constants determined. The exchange process was found to occur without side reactions and no deuterium isotope effect was observed on the rate. The rates of reaction were also measured in different solvents (such as dmso, MeCN, $CHCl_3$, CH_3OH and C_2H_5OH) and were found to depend upon the electrophilicity of the substrate molecule [97].

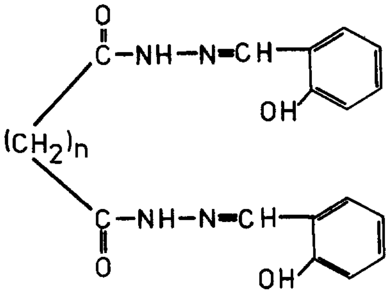
The photodecomposition of oxalic acid is known to be sensitised by (oxalato)vanadium(III) complexes. From a spectrophotometric study on this system, a reaction scheme has been proposed in which the vanadium(III) complex is decomposed to a vanadium(II) ion and an oxalate radical, *via* a charge transfer to metal route. The vanadium(III) ion is then thought to reduce the methanoic acid radical, formed by decarboxylation of the oxalate radical, to carbon monoxide [98].

In a study on the kinetics of oxidation of $[Ti(hedta)(H_2O)]$ {hedta = *N*(hydroxylethyl)ethylenediaminetriacetate} by $[VO(hedta)]^-$, two new binuclear ions containing mixed oxidation states and resultant charge transfer interactions have been observed. One of them is an orange species represented by $\{Ti^{IV}V^{III}(hedta)_2\}$ formed in the pH range 2.5-7.5. It can also be generated by the combination of $[V(hedta)(H_2O)]$ and $[TiO(hedta)]^-$. The binuclear complex is thought to be formed in the cross reaction following an outer sphere electron transfer step [99]. The same group have determined the X-ray crystal structure of the binuclear complex $[enH_2][V(hedta-H)]_2.2H_2O$; the anion, (*25*), displays several features uncommon to other known transition metal edta complexes. Each vanadium(III) atom was found to be seven-coordinate, having a distorted pentagonal bipyramidal configuration. The bridging atoms are the alkoxy oxygens from the $[hedta-H]^{4-}$ ligands. The V-V distance is 3.296 Å and the angles of the $\{V_2O_2\}$ core ($V\hat{O}V$ = 108°; $O\hat{V}O$ = 72°) suggest very little strain is present [100].



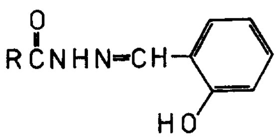
(25; bond lengths in Å)

Some vanadium(III) complexes with flexidentate dihydrazide Schiffs bases (*26*; L), of formula $V(HL)SO_4$, have been prepared and characterised. Although the ligands exist in the keto- form, IR spectra suggested that they coordinate through enolised carbonyl and azomethine groups [101].

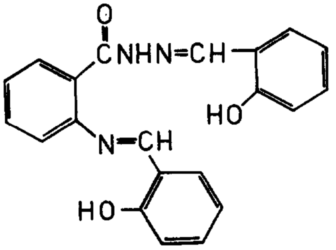


(26; *n* = 0, 1 or 2)

Complexes of the type VL_3 {L = methylphenylphosphinate, (*27*) or (*28*)} have been synthesised and investigated by standard techniques [102,103].



(27; R = Ph, C_6H_4-2-OH or C_6H_4-2-NH$_2$)



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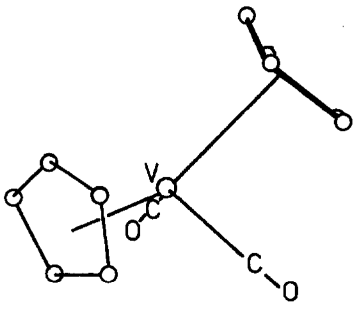
Further attempts have been made to measure the EPR spectrum of $[V(CN)_7]^{4-}$, but decomposition to $[VO(CN)_5]^{3-}$ and $[V(CN)_6]^{4-}$ rendered them unsuccessful [104] The X-ray crystal structure of $[(\eta^5\text{-}C_5H_5)_2V(CO)_2][BPh_4]$ has been determined but disorder in the cations prevented accurate location of all the atoms. Two possible orientations were found for the $[(\eta^5\text{-}C_5H_5)_2V(CO)_2]^+$ ion which are depicted in (*29*) and (*30*). The disorder was thought to be due to the distribution of the cyclopentadienyl rings [105].



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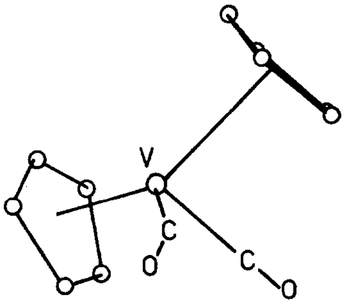

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6.4 VANADIUM(II)

6.4.1 Reactions of $[V(H_2O)_6]^{2+}$, and related complexes

The reaction of $[V(H_2O)_6]^{2+}$ with hydrogen peroxide and dmso was found to yield methane with traces (2%) of ethane. Methyl radicals, produced by attack of hydroxyl radicals on dmso, are thought to be reduced by $[V(H_2O)_6]^{2+}$, possibly *via* the formation of a seven coordinate vanadium species [106].

The reduction of nitroamine by $[V(H_2O)_6]^{2+}$ ions was found to proceed *via* a two electron transfer, yielding dinitrogen according to equation (27). When

$$NH_2NO_2 \xrightarrow[2e^-]{2H^+} N_2 + 2H_2O \qquad (27)$$

$NH_2{}^{15}NO_2$ was used, $^{14}N{-}^{15}N$ was produced, suggesting N-N bond fission does not occur [107]. Rate data for the reduction of $[Co(dmg)_2(N_3)_2]^-$ by $[V(H_2O)_6]^{2+}$ showed a very small dependence of the rate upon H^+, and some evidence for oxime bridging [108]. The reactions of molecular nitrogen, and other substrates such as ethyne, but-2-yne, ethene or butadiene, with vanadium(II) pyrocatechol, VL, complexes are thought to proceed *via* monomeric vanadium(II) centres. Vanadium(II) pyrocatechol complexes act as powerful reducing agents, and reaction was found to proceed according either to equation (28) or (29), the path followed being

$$V^{II}L + sub + 2H^+ = V^{IV}L + subH_2 \qquad (28)$$

$$2V^{II}L + sub + 2H^+ = 2V^{III}L + subH_2 \qquad (29)$$

dependent on both the reactivity and the concentration of the substrate (sub). Nitrogen reduction was found to occur in a stepwise fashion, with N_2H_2 and N_2H_4 being formed as intermediates. The yields of NH_2 produced were extremely dependent on the pH and the solvent [109]. A second group have studied the mechanism of nitrogen reduction by vanadium(II) pyrocatechol complexes in the presence of a varying concentration of Li[OMe]. The rate constants were found to be at a maximum at 0.57 *M* Li[OMe] [110]. The kinetics and mechanism of the oxidation of $[V(H_2O)_6]^{2+}$ ions with trichloroethanoic acid have been studied in varying concentrations of $H[ClO_4]$. The reaction, which is represented by equation (30), was found to proceed in a similar manner to the analogous one involving the oxidation of U^{3+}_{aq} [111].

$$2[V(H_2O)_6]^{2+} + CCl_3COOH + H^+ = 2[V(H_2O)_6]^{3+} + CHCl_2COOH + Cl^- \qquad (30)$$

6.4.2 *Species containing vanadium-halogen bonds*

Crystalline vanadium dihalides VX_2 (X = Cl, Br or I) having layered structures have been investigated by Raman and IR spectroscopy. At low temperatures, additional Raman scattering to the group theoretical modes was observed, which was attributed to a spin dependent electron-phonon coupling. The Raman spectrum of VI_2 was found to be different to those of VCl_2 and VBr_2, which was thought to be due to a difference in the magnetic properties of the compounds [112].

The reductive hydrolysis of 2,4-dinitrophenylhydrazones, $Ph_2C=NNHC_6H_3(NO_2)_2$, by VCl_2 in thf has been employed to yield various aromatic and cycloaliphatic ketones in almost 100% yield [113].

6.4.3 Other vanadium(II) species

The hexaammine complex $[V(NH_3)_6]Br_2$ has been prepared by bubbling ammonia through solutions of $[V(H_2O)_6]Br_2$ in ethanol or liquid ammonia. The X-ray powder pattern obtained for the complex was indexed according to a face-centered cubic unit cell, isomorphous with $[Ni(NH_3)_6]Br_2$. Three bands in the diffuse reflectance spectrum were assigned as spin-allowed transitions expected for a species having O_h symmetry [114].

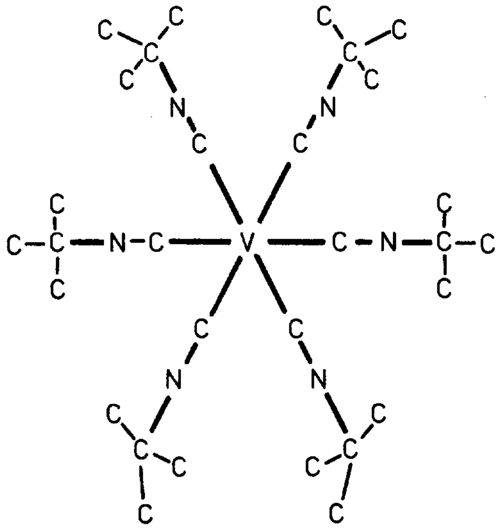
Vanadium(II) β-diketonate complexes have been found to deoxygenate both cyclic and acyclic epoxides to give alkenes in good yields. Vanadyl, $\{VO\}^{2+}$, containing complexes were the ultimate products in the deoxygenation reactions. Stereospecificity in the reactions was variable, and a mechanism was proposed in which a metallooxetane intermediate was formed. The observed stereospecificity seemed to depend upon the size of the substituents of the oxirane ring and the β-diketonate ligand, which was consistent with the mechanism [115].

The complex $[V(NCS)_2(tpyea)]$ {tpyea = tris(3,5-dimethyl-1-pyrazolylethyl)amine} has been prepared from $V(NCS)_2$ and the ligand, in either ethanol or CH_2Cl_2, under anaerobic conditions [116].

The X-ray crystal structure of a complex whose preparation was mentioned last year, $[V(CNCMe_3)_6][V(CO)_6]_2$, has been determined. A second preparative route is given to the complex, which involves the reaction between $[Et_4N][V(CO)_6]$, Me_3CNC, and iodobenzene dichloride in ethanol. The crystal structure was found to consist of $[V(CNCMe_3)_6]^{2+}$ cations, (*31*), lying on an inversion centre at the origin of the unit cell, and $[V(CO)_6]^-$ anions situated in general positions. Because of problems occurring from deterioration of the crystal in X-rays, two sets of data were measured using both Mo Kα and Cu Kα radiation. Structure solutions from both sets of data exhibited a large variation in the C-C distances of the CMe_3 groups; however, disordered structures were not explored due to there being insufficient data [117].

A new compound of vanadium, VP_4, in which the vanadium is thought to be in the +2 oxidation state, has been prepared by high pressure, high temperature reactions between elemental phosphorus and vanadium [118].

The change in lattice parameters of ZrV_2 and HfV_2 on hydrogenation has been studied by neutron diffraction. With these two intermetallic compounds no



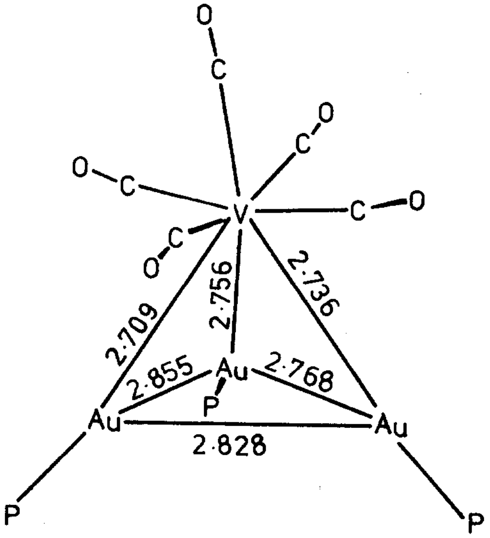
(31)

rearrangement of the metal lattice was thought to occur but a clearly defined correlation was observed in the arrangement of the hydrogen atoms [119].

6.5 LOW OXIDATION STATES

The emission spectrum of VF has been photographed in the region 3440-3660 Å, and a tentative assignment of the bands made [120]. A multinuclear NMR study carried out on $[V(PF_3)_6]^-$ showed well resolved multiplets and enabled a determination of coupling constants to be made ($^1J_{VP}$ = 510, $^2J_{VF}$ = 10.3, $^1J_{PF}$ = 1200 Hz). A decrease in nuclear shielding, characterised by a downfield shift in the ^{51}V NMR spectrum, was observed in the $[V(PF_3)_6]^-$ ion relative to $[V(CO)_6]^-$ which was thought to imply that PF_3 is slightly weaker than CO in π-acceptor power [121].

Although it is not the purpose of this article to review the organometallic chemistry of vanadium, a few interesting examples of this type of chemistry are included to indicate recent developments. Details of the preparations of a series of "super-reduced" vanadium species containing the $[V(CO)_5]^{3-}$ ion have been published. These complexes contain vanadium in its lowest known formal oxidation state. The compounds were prepared by sodium reduction of $[Na(diglyme)_2][V(CO)_6]$, followed by the addition of the alkali metal iodide at low temperature. The rubidium and caesium salts were found to be relatively stable at room temperature, unlike the lithium, sodium and $[EPh_4]^+$ (E = P or As) analogues. The potassium salt, $K_3[V(CO)_5]$, was found to be extremely shock sensitive and pyrophoric [122]. The X-ray crystal structure of a gold-vanadium cluster, $[\{(Ph_3P)Au\}_3\{V(CO)_5\}]$, (*32*), prepared by the treatment of the above sodium or caesium salts with chloro(triphenylphosphine)gold has been determined. The molecule shows the vanadium atom to be effectively eight coordinate, being bonded to a triangular cluster of gold atoms. The geometry about the vanadium atom is *pseudo*-octahedral, the complex resembling others of the type $[V(CO)_5L]$, where L is a large ligand (in this case, $\{(Ph_3P)Au\}_3$). The infrared spectrum is in agreement with that expected for an octahedral complex of the type $[V(CO)_5L]^-$ [123].



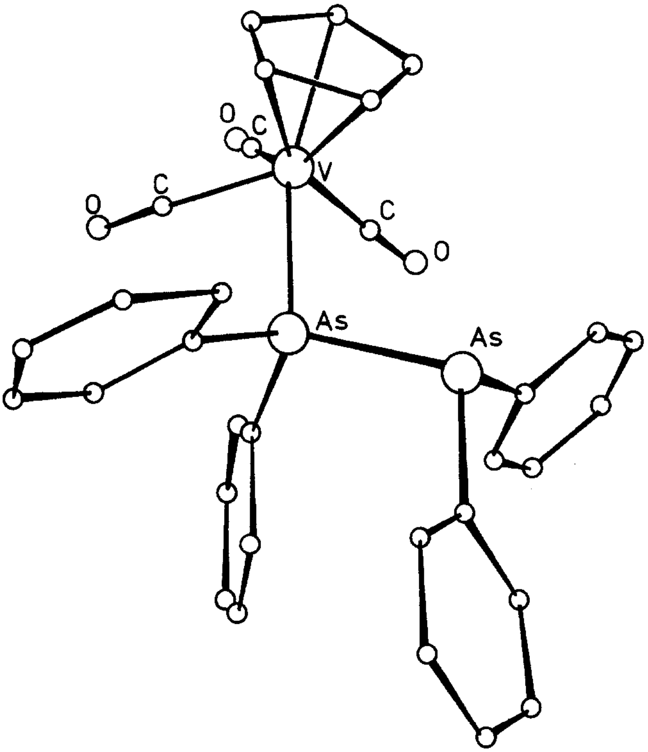
(32; bond lengths in Å)

Moderately high yields of the new organometallic derivatives $[(R_3E)V(CO)_5]^{2-}$ (R = alkyl or aryl; E = Sn or Pb) and $[(R_3E)_2V(CO)_5]^-$ have been prepared from R_3EX and $[V(CO)_5]^{3-}$ [122,124]. The structure of $[Et_4N][(Ph_3Sn)_2V(CO)_5]$, synthesised from the photolysis of $[Et_4N][V(CO)_6]$ in the presence of Ph_6Sn_2, has been determined. The seven coordinate geometry about the vanadium atom approaches very closely to three of the known hepta-coordinate structural arrangements. The molecule contains two V-Sn bonds {2.757(3) and 2.785(3) Å} and five V-C bonds, averaging 1.94 Å.

A general synthesis has been reported for carbonyl complexes of V(0), stabilised by diphosphine ligands. The reaction involves the oxidation of $[V(CO)_4(LL)]^-$, {LL = $Ph_2P(CH_2)_nPPh_2$ (n = 1-4), $Ph_2As(CH_2)_2PPh_2$ or 1,2-$C_6H_4(PPh_2)_2$}, as shown by equation (31) [125]. A series of complexes containing the ligands

$$cis\text{-}[Et_4N][V(CO)_4(LL)] + [C_7H_7][BF_4] = [V(CO)_4(LL)] + [Et_4N][BF_4] + \tfrac{1}{2}(C_7H_7)_2 \quad (31)$$

$Ph_2ECH_2EPh_2$ (E = P, As or Sb) has been investigated by ^{51}V NMR spectroscopy in order to study the effect of the ligand upon nuclear shielding. The crystal structure of the complex $[CpV(CO)_3(Ph_2AsAsPh_2)]$ (*33*) has been determined, but the nuclear shielding found for this complex did not agree with that predicted for the ligand, which was attributed to steric crowding around the vanadium atom [126].



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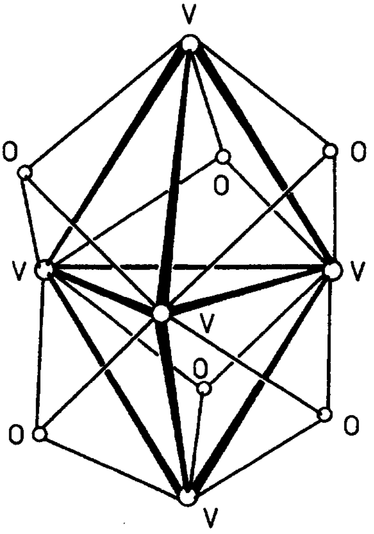
The synthesis and structure of bis(benzene)tetracarbonyldivanadium $[(C_6H_6)_2V_2(CO)_4]$ prepared by the decomposition of $(C_6H_6)_2V_2(CO)_4V(CO)_6$ in benzene has been reported [127].

Finally, an interesting structure consisting of a trigonal bipyramidal cluster of vanadium and oxygen atoms, $[(\eta^5\text{-}C_5H_5)_5V_5O_6]$ has been reported. The structure has some similarities to known homonuclear metal carbonyl clusters and to the few cyclopentadienyl-oxo clusters of the early transition metals. Black crystals of $[(cp)_5V_5O_6]$ were obtained from the reaction between $[V(cp)_2]$ and N_2O in toluene at -78 °C. Each vanadium atom in the bipyramid is capped by a cyclopentadienyl ring with V-Cp(eq) = 1.973 Å and V-Cp(ax) = 1.997 Å. Each oxygen is bound to three vanadium atoms and is at an average distance of 1.128 Å above the faces of the bipyramid [128]. The structure of the $\{V_5O_6\}$ core is illustrated as (*34*).



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6.6 SPECIES FORMALLY CONTAINING OXO-ANIONS OF VANADIUM

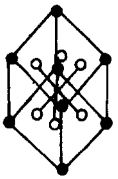
This final section reviews work that has been carried out in the past year on complexes that contain vanadium-oxygen anions. Because of the variety of oxidation states that can be exhibited by the vanadium atom in some of these species, no further subdivision of the section has been made according to valency.

Reports on the solid state structures and spectral properties of species containing the vanadate, $[VO_4]^{3-}$, ion are again numerous. The Raman spectra of a range of orthovanadates, $LnVO_4$ (Ln = Pr-Lu), as well as those of $ScVO_4$ and YVO_4, have been recorded [129]. An assignment of the Raman and previously reported IR bands was made assuming D_{4h} symmetry for the anion. The 4d and valence electron X-ray photoelectron spectra of several of these rare earth vanadates (Ln = Y, Nd, Eu, Gd, Tb, Dy or Yb) have been investigated and the results used to make calculations on the electronic structures of $LnVO_4$ [130]. The X-ray structure of a mixed vanadate $In_{0.6}Li_{1.2}VO_4$, prepared from $InVO_4$ and Li_3VO_4 at 800 °C, has been determined (see Fig. 6). The structure was found to be isomorphous with that of $InVO_4$. Partial substitution of In^{3+} by Li^+ in the $\{InO_6\}$ octahedra and insertion of Li^+ in tetrahedral sites occurs. This has the effect of producing two short {2.167(1) Å} and four long {2.181(1) Å} In-O (or Li^6-O) bonds in the $\{InO_6\}$ octahedra [131].

The range of double vanadates $M_3Ln(VO_4)_2$ (Ln = Gd-Lu, Sc or Y; M = K or Rb) has been synthesised by a ceramic method which involves heating stoicheiometric amounts of Ln_2O_3, M_2CO_3 and V_2O_5 at 400-700 °C for fifteen hours. X-ray powder photographs of the products showed the structures to be trigonal and derived from that of $K_3Na(SO_4)_2$ [132,133].

The solid state high pressure, high temperature reactions between Ln_2O_3 (Ln = Er or Yb) and VO_2 to produce $LnVO_3$ by reduction of vanadium have been studied [134]. Two structural types of $ErVO_3$ were formed, depending upon the pressure used. At 30 kbar $ErVO_3$ having the rhombohedral, calcite type structure, (*35*), was formed, whereas at 50 kbar hexagonal, vaterite type $ErVO_3$ was obtained (*36*). With Yb_2O_3 pure perovskite type $YbVO_3$ (*37*) was formed, only after prolonged heating of the initial product from the high pressure reaction at 1400 °C under vacuum.

● Er^{3+} · V^{3+} ○ O^{2-}



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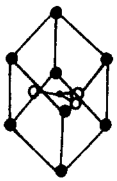

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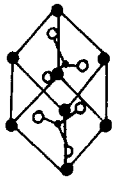

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The mixed valence decavanadate, $SrV_8^{III}V_2^{II}O_{15}$, has been prepared in crystalline form from SrO and V_2O_3 at 1900 °C. The structure was found to consist of a $V^{3+}/V^{2+}/O^{2-}$ octahedral framework. The arrangement of twelve $\{VO_6\}$ octahedra forms a large cavity which resembles the $\{V_{12}O_{50}\}$ groupings in polyacids [135].

X-ray diffraction studies carried out on the spinel type compound AlV_2O_4 showed it to be rhombohedral, with vanadium atoms occupying the octahedral sites and aluminium atoms occupying the tetrahedral ones [136]. Various other phase

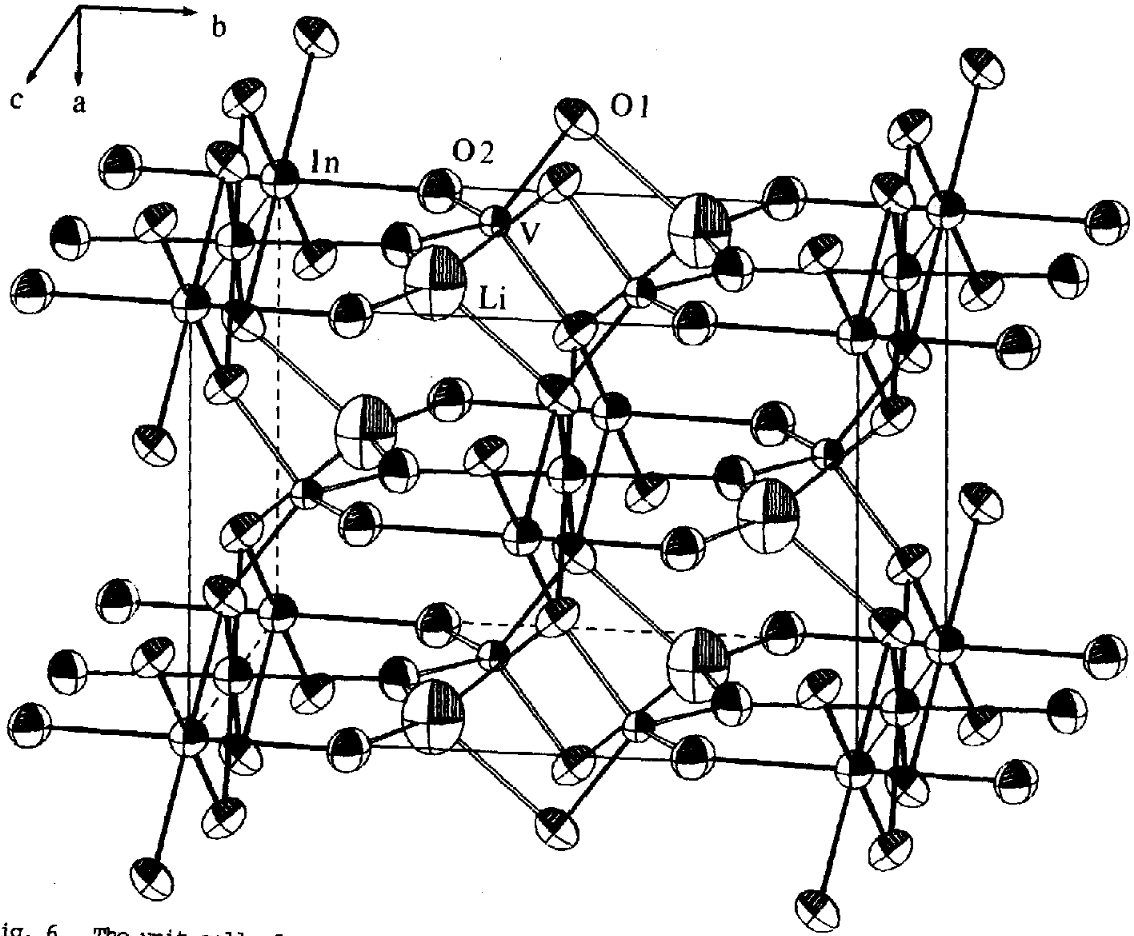


Fig. 6. The unit cell of $In_{0.6}Li_{1.2}VO_4$, reproduced with permission from [131].

equilibria between vanadium oxides and metal oxides (*e.g.* Ho_2O_3 [137], Er_2O_3, TeO_2 [138], Fe_2O_3 [139]) have been investigated by X-ray diffraction, differential thermal analysis and other standard techniques.

Numerous studies have been carried out on aqueous orthovanadate/acid systems to determine the effect of the variation of parameters such as pH, temperature, *etc.* upon the nature of the products.

The system $NaVO_3/Ca(NO_3)_2/HNO_3/H_2O$ was found to yield $Ca_3V_{10}O_{28}.xH_2O$ as the main product at 20-40 °C. A new double vanadate $Na_4CaV_{10}O_{28}.19H_2O$ was isolated from the system [140]. Aqueous solutions of $NaVO_3/HNO_3$ and $Ca(VO_3)_2/HClO_4$ were studied at varying temperatures (20-85 °C), $[VO_3]^-$ concentrations and acidities. At lower temperatures and acidities, decavanadates were found to be the major products, whereas at higher temperatures and acidities, mixtures of hydrated hexavanadates were formed [141]. Mixed cation systems of $NaVO_3/M^{II}X_2$ and $NaVO_3/TlX$ (M^{II} = Cd or Pb; X = CH_3COO) in ethanoic acid have been investigated at a range of temperatures (20-60 °C) and acidities. Again, low temperatures favoured the formation of decavanadates and higher temperatures led to the formation of penta-, hexa- and divanadates [142]. The same group have established the preferred conditions for the precipitation of $La_2V_{10}O_{28}.xH_2O$ (x = 24 or 25) from the $La(CH_3COO)_3/NaVO_3/HX$ (X = ClO_4 or CH_3COO) aqueous systems. Investigations upon the thermal decomposition of the decavanadate showed that at temperatures greater than 500 °C, $LaVO_4$, V_2O_5 and V_4O_7 are formed [143]. A study has been made on the reactions of Fe^{3+} cations with dodecavanadic acid ($H_2V_{12}O_{31}$) and with sodium deca-, meta-, pyro- and ortho-vanadates at various Fe:V ratios. Investigation of the products by chemical analysis and IR spectroscopy confirmed the formation of $FeVO_4.3H_2O$ from the orthovanadate system. Two types of iron dodecavanadates were formed from the $FeCl_3/H_2V_{12}O_{31}/H_2O$ system [144].

A relationship between the cation, M^+, and the structural parameters of a range of pentavanadates, $M_3V_5O_{14}$ (M = K, Tl or Rb) has been observed. An increase in the cationic radius was found to result in an expansion of the *c* axis, decrease in thermal stability and a shift in ν(V-O) to lower frequency [145]. Other workers have synthesised various heteropolyvanadates, namely $M_7[SbV_{12}O_{36}]$ [146] (M = NH_4, Na or K), $[NH_4]_5[MoV_6O_{19}].12H_2O$ [147] and $K_2[CrV_6O_{19}].12H_2O$ [148], starting from MVO_3.

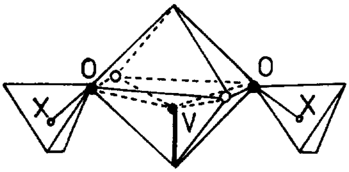
The series of tungsten vanadophosphoric heteropolyacids containing the $[PV_nW_{12-n}]$ (n = 1-11) moiety have been synthesised from the respective sodium salt $Na_{3+n}PV_nW_{12-n}O_{40}.xH_2O$. However, acids where $n > 4$ were obtained only with great difficulty and in very low yields [149].

The systems $Fe_2O_3/V_2O_5/Na_2CO_3$ and $NaVO_3/FeVO_4$ have been studied at various temperatures from 400 °C upwards to determine the sequence of formation of components. Depending upon the ratio of starting materials, either $NaFe_3V_4O_{15}$

or $NaFeV_2O_7$ is the overall product [150]. In a study on the $Mn_2O_3/V_2O_5/MoO_3$ system, it was found that molybdenum atoms may substitute vanadium atoms in MnV_2O_6, producing Brannerite type vanadates having formula $Mn_{1-x}{}_{x}V_{2-2x}Mo_{2x}O_6$, in which represents a vacancy at the Mn^{2+} site. The reaction path taken during the formation of phases having $0 \leqslant x \leqslant 0.33$ has been studied by X-ray and thermogravimetric techniques [151]. In a further study the same group have determined the X-ray crystal structure of the compound having $x = 0.53$. The structure was found to consist of Mo-O- -O-Mo clusters distributed at random in the host vanadate lattice [152].

An extensive ^{51}V and ^{17}O high field (105.2 MHz) NMR study has been carried out on a variety of vanadate and polyvanadate species in the pH range 7-14, in which several new vanadate species were detected. Most of these species were thought to consist of $\{VO_4\}$ tetrahedra in either linear or cyclic arrangements having up to six vanadium atoms. However, no branched or triprotonated species and no cyclic trimer was detected which was thought to confirm the postulate that tetrahedral vanadium(V) prefers to be coordinated to at least two terminal oxide ligands. Several equilibrium constants and pK_a values were measured [153]. A study of the kinetics of decomposition of decavanadates $[H_nV_{10}O_{28}]^{(6-n)-}$ in the pH range 2-6 suggested that the mechanism involved the breaking of the decavanadate structure into octahedral monomeric species of the type $[H_7VO_6]$ [154].

The syntheses of two types of α-$VOPO_4$ have been repeated and the cell parameters obtained from the X-ray powder diffraction patterns. The structural form obtained seemed to depend upon the method of preparation. In α_I-$VOPO_4$, (*38*), prepared by dehydration of $VOPO_4.2H_2O$ at low temperature (280 °C), the vanadium and phosphorus atoms are thought to be on the same side of the equatorial chain V-O(2)-P-O(2)-V, whereas in α_{II}-$VOPO_4$, (*39*), from a high temperature preparation, these atoms are found on alternate sides of the chain [155].



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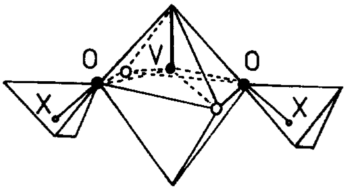
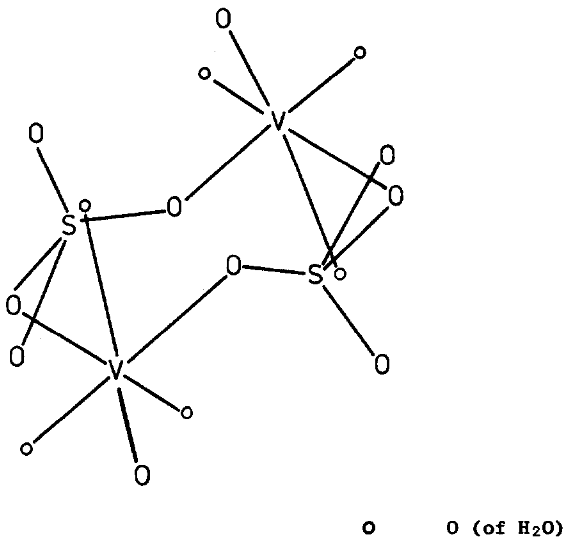


(39)

The X-ray crystal structure of a further hydrate of vanadyl sulphate, $VOSO_4.3H_2O$, has been determined and was found to consist of blocks of dimers of $\overline{S-O-V-O-S-O-V-O}$. The structure is represented in (*40*). The mean values of the bond lengths and the structural relationships between other hydrated vanadyl sulphates were compared [156].



(40)

The crystal structure of V_2GaO_5 has been determined and was found to consist of β-gallia like columns containing the gallium atoms and chains of $\{VO_6\}$ octahedra, the vanadium atoms being formally in the +3 and +4 oxidation states [157].

A vanadium niobate, $V_2Nb_6O_{19}$, has been prepared by sintering mixtures of VO_2 and Nb_2O_5 at 1123 K for fifty hours. The X-ray powder diffraction pattern was indexed in a tetragonal unit cell and values were determined for the cell axes [158]. A series of mixed niobates, $Fe_{1-x}V_xNbO_4$, has been prepared from the solid state reaction between Fe_2O_3, Nb_2O_5 and V_2O_3 at 1000 °C. X-ray diffraction patterns, magnetic susceptibilities and resistivities were measured for the samples. For $x \leqslant 0.2$, the compound was found to have the wolframite structure, but for $x \geqslant 0.4$, a phase transformation to the rutile structure occurs [159].

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