Introduction

The highest oxidation state of vanadium is + (V). Vanadium (V) forms two oxo-species, the \( \text{VO}^{3+} \) and \( \text{VO}_2^+ \) ions, and none of these disproportionate because of their being better oxidants. The \( \text{VO}^{3+} \) unit occurs in the oxyhalides \( \text{VOX}_3 \) (\( X = F, \text{Cl} \) or \( \text{Br} \)) in which the V-O stretching frequencies are at 1058, 1035 and 1025 cm\(^{-1}\) respectively. In addition, however, a number of complexes of the types \( \text{VOCl}_3 \cdot L \) and \( \text{VOCl}_3 \cdot 2L \), in which \( L \) can be an oxygen-donar or a nitrogen-donar ligand, have been characterized.\(^1,2\) The complexes appear to be either five- or six-coordinate monomers.

Vanadium oxychloride, \( \text{VOCl}_3 \), has been shown to react\(^1\) with ligands containing replaceable hydrogen atoms to give rise to substitution products of the type \( \text{VO(O} \text{Me})_3 \), \( \text{VOCl}_2 \cdot \text{O} \text{Me} \), \( \text{VOCl}_2 \cdot \text{O} \text{Et} \), \( \text{VOCl} \cdot \text{O} \text{Et})_2 \), \( \text{VOCl}_2 \cdot \text{acac} \), \( \text{VOCl} \cdot \text{acac})_2 \) (\( \text{Hacac} = \text{acetylacetone} \)). Very little structural information is available for these complexes. The structure of the alkoxide \( \text{VO(O} \text{Me})_3 \) has, however, been determined, and it has been shown that the molecule is a linear polymer, with a dimeric repeat unit and alkoxide bridging.\(^3\)
The second cationic vanadium(v) species, the $\text{VO}_2^+$ ion, is not very much characterized, but it is believed to occur discretely in the complexes $\text{VO}_2(\text{NO}_3)$, $\text{VO}_2\text{F}$, and $\text{VO}_2(\text{SbF}_5)$, and as a cis-$\text{VO}_2$ unit in the complexes $^4$ $\text{K}_3\text{V}_2\text{O}_2(\text{C}_2\text{O}_4)_2\text{F}_2$ and $\text{K}_3\text{V}_2\text{O}_2\text{F}_4\text{I}$. The other example of complex compounds formed under non-aqueous conditions include the salts of $\text{VOCl}_4^-$ and $\text{VOF}_4^-$ (Ref 5).

The complex species, $\text{VOF}_4^-$, is particularly interesting because this exhibits fluxional behaviour$^5$ in solution. However, no simple method is available for the synthesis of oxotetrafluorovanadate(v) complexes. The only compound $\text{CsVOF}_4$ was prepared by Howell and Moss$^5$ under non-aqueous conditions and carrying out the reaction at $-30^\circ\text{C}$.

Chapter 1 of the present thesis describes a new and simple general method for the synthesis, and isolation in the solid state, of $\text{AVOF}_4$ ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$ or $\text{NH}_4$) compounds from aqueous media, together with the characterization of these compounds.

The chemistry of vanadium(IV) is largely dominated by the formation of cationic species, and a wide range of compounds with $\text{VO}^{2+}$ groups is known. Although many oxometal species have been characterized to date, the
diatomic ion VO$^{2+}$ is thought to be the most stable ion known. The ion VO$^{2+}$ forms a wide variety of complexes which may be cationic, neutral or anionic.$^{6,7}$

The oxovanadium(IV) complexes are generally of the type$^{3,8}$ $\sum$VO$_5$$^+$$^\text{n}$$^+$$,$ $\sum$VO$_4$$^+$$^\text{n}$$ ^+$$,$ $\sum$VO$_{5-x}$L$_x$$^+$$^\text{n}$$^+$$ or $\sum$VO$_{4-x}$L$_x$$^+$$^\text{n}$$^+$$ e.g. A$_3$ $\sum$VOF$_5$$^+$, A$_2$ $\sum$VOF$_4$$^+$, VOCl$_2$, DMSO (DMSO = dimethylsulphoxide) and VOCl$_2$$^\cdot$$^2$C$_5$H$_5$N. The VO$^{2+}$ entity bonds most effectively to the most electronegative atoms, e.g. F, Cl, O, or N, although bonds to S and P are also known.

The structures of several oxovanadium(IV) species have been determined by X-ray crystallography. The characteristic coordination polyhedron is the tetragonal pyramid, in which the axial V=O bond has a length of 1.57 - 1.68 Å, the equatorial V-O bonds are ~ 0.4Å longer, the O=V-O angles are ~ 106°, and the vanadium atom lies ~ 0.55 Å above the plane formed by the four singly-bonded oxygen atoms. In some complexes, octahedral coordination is completed by the formation of a further relatively long bond trans to the V=O bond. Some of the structures are of particular interest. The complex VO(H$_2$O)$_5$SO$_4$ occurs in three forms, one monoclinic and two orthorhombic. The structure of the monoclinic form indicates that the VO$^{2+}$ group is bound
to four water molecules and to one of the oxygen atoms of the sulphate group. The latter is in the cis-position to the $\text{VO}^{2+}$ group, and not the trans-position.

The most characteristic feature of the infrared spectra of oxovanadium(IV) complexes is the very strong, sharp band at $985 \pm 50 \text{ cm}^{-1}$. This band is assigned to the $\text{V}=\text{O}$ stretching frequency, and as expected lies near the upper frequency limit for those complexes which are known from X-ray work to have the shortest $\text{V}=\text{O}$ bonds. Coordination of ligand to the sixth octahedral position, i.e. the position trans to the $\text{V}=\text{O}$ bond, brings about a drop of $\sim 50 \text{ cm}^{-1}$ in the $\text{V}=\text{O}$ stretching frequency of the parent complex.

The magnetic moments of oxovanadium(IV) complexes lie almost invariably in the range $1.70 - 1.73$ B.M. This result is to be expected since the ligand field around the vanadium(IV) ion ($d^1$ configuration) is strongly axial, and hence all the orbital contribution to the moment is quenched. The magnetic moments of discrete oxovanadium(IV) complexes should thus be, and indeed are, independent of temperature.

The e.s.r. $g_{av}$ values for oxovanadium(IV) complexes occur in the range $1.95 - 2.00$, i.e. close to the
spin-only value of 2.00. Both these results and the fact that the anisotropy of the g-values is small in comparison with that for the magnetically similar $d^9$ complexes, indicates that the axial component to the ligand field is high. The unpaired electron lies in an orbital of $b_2$ symmetry.

The optical spectra of oxovanadium(IV) complexes are characterized by three $d$-$d$ transitions ($5 \lesssim E \lesssim 100$) in the range 8000-32,000 cm$^{-1}$. The first band lies in the range 11,000 - 14,700 cm$^{-1}$, the second in the range 14,800 - 20,400 cm$^{-1}$, and the third in the range 21,000 - 31,250 cm$^{-1}$ and are assigned to $e \leftarrow b_2$, $b_1 \leftarrow b_2$ and $a_1 \leftarrow b_2$ transitions respectively. The third band is frequently obscured by strong charge transfer transitions, and the first band in the spectra of some complexes shows vibrational structure ($\sim 700$ cm$^{-1}$ spacings, corresponding to the V=O stretching frequency in the excited state).

A number of attempts have been made at detailed interpretations of the ligand field spectra of oxovanadium(IV) complexes. The most successful of these is the molecular orbital treatment of the VO($H_2O$)$_5^{2+}$ ion by Ballhausen and Gray. The bonding scheme in the
Ballhausen-Gray treatment is described as follows:

a strong $\sigma$-bond of $a_1$ symmetry between the $sp^6$ oxygen hybrid orbital and the $(4s + 3dz^2)$ hybrid orbital on the vanadium atom;

two $\pi$ bonds of $e$ symmetry between the $2px$ and $2py$ oxygen orbitals and the $3dz^2$ and $3dy^2$ vanadium orbitals;

four $\sigma$-bonds between the four equivalent $sp^6$ (water) oxygen hybrid orbitals and the $(4s - 3dz^2)$ ($a_1$), $4px$, $4py$ ($e$) and $3dx^2-y^2$ ($b_1$) vanadium orbitals;

the fifth water molecule is bound to the $4pz$ ($a_1$) vanadium orbital, leaving the $3d_{xy}$ ($b_2$) orbital non-bonding and free to hold the single d-electron of vanadium(IV).

The order of the energy levels is thus $b_2 < e^* < b_1 < a_1^*$. Thus, the $\pi$-bonding in the ion VO(H$_2$O)$_5^{2+}$ is essentially axial, giving rise to a triple bond between the vanadium and the unique oxygen atom.

Our interest in the field of fluorometalate chemistry led us to synthesise the hitherto unreported oxotrifluorovanadate(III) complexes, VOF$_3^-$. We were particularly interested in the VOF$_3^-$ species because
such a species has no reported evidence in the literature, although the corresponding VOCl$_3^-$ ion has been known.$^{11}$ Further we were interested in the structure and chemistry of oxotrifluorovanadate(IV) complexes.

Chapter 2 of the thesis presents the synthesis of the VOPO$_3^-$ ion and its isolation in the solid state as hydrazonium and alkali-metal salts. The Chapter 2 also reports the results of structural assessment of the newly synthesised compounds.

It has been known$^{12}$ for over a century that characteristic colour reactions may take place when hydrogen peroxide is added to solutions of transition metal derivatives, and many peroxy transition metal compounds have been isolated in the solid state. Peroxy derivatives of metals, besides having an intrinsic interest of their own, are of considerable and growing importance particularly in relation to the catalysis of oxidations involving hydrogen peroxide or oxygen gas, the catalytic decomposition of H$_2$O$_2$ itself, and the storage and transport of oxygen in biological systems.$^{13,14}$

Although the term molecular oxygen refers only to the free uncombined O$_2$ molecule with the ground state
3. The term dioxygen has been used as a generic designation for the \(O_2\) moiety in any of its several forms, and can refer to \(O_2\) in either a free or combined state. For use of this term it is essential that a covalent bond has to exist between the oxygen atoms. Thus, a metal-dioxygen complex refers to a metal containing \(O_2\) group coordinated to the metal centre, and no distinction is made between neutral dioxygen or dioxygen in any of its reduced forms. Accordingly, a metal-peroxide complex is one in which the \(O_2\) coordinated dioxygen resembles a peroxide \((O_2^{2-})\) anion. The incorporation of \(O_2\) into a metal complex to form a metal-dioxygen compound is called oxygenation, and the reverse is known as deoxygenation.

Simple peroxo compounds of transition metals are the ones which contain peroxides, hydroperoxides and water molecules, whereas heteroligand peroxo complexes are mixed ligand metal complexes containing one to three coordinated peroxo groups, and one or more monodentate or polydentate ligands. Heteroligands range from monodentate halide ions to bulky porphyrin (F, Cl, NH\(_3\), C\(_2\)O\(_4\), NTA, EDTA, dipy, O-phen, oxine, porphyrin, pyridine-2,6-dicarboxylate etc.) The stability of peroxo complexes is generally enhanced by
specific heteroligand combinations. Thus, many simple transition metal peroxides often explode spontaneously; some are sensitive to shock or decompose above 0°C and several do not exist at all as stoichiometric compounds. Many heteroligand peroxo complexes, on the other hand, survive recrystallisation from boiling aqueous solutions, heating in vacuo, and remain unchanged for prolonged periods in closed containers.

The biochemical significance of peroxo-metal complexes has been emphasized recently in the literature. The reactivity of peroxides and the lability of metal-oxygen bonds in special heteroligand environments in solutions are of particular interest to biochemistry, but are not easy to measure directly.

A comparison between the peroxo and unreduced dioxygen heteroligand complexes reveals that the chemistry of the two is very different owing to the presence of two extra electrons in the antibonding O-π* orbitals of the peroxide ion. The electron rich O$_2^{2-}$ ion therefore preferably forms complexes with metal ions of low d$^n$ electron configuration, while the neutral dioxygen molecule favour higher d$^n$ metal acceptors. However, there are at least two things that these two oxygen species have in common: both are
stabilised by specific heteroligand spheres, and both are of importance in biochemistry.

The importance of neutral dioxygen complexes in biochemistry is well known, but the biochemical connection of the metal peroxo complexes with biological processes is not very well understood. The transition metals, Sc, Ti, V, Cr, Y, Zr, Nb, Mo, La, Hf, Ta, W, form stable heteroligand peroxo complexes, and there is increasing evidence that vanadium has a significant biological role. It is reasonable to assume that the participation of vanadium will depend upon parameters such as pH, and the availability of inorganic or organic molecules that can act as heteroligands.

Molecular oxygen is a paramagnetic molecule, having a triplet $3\Sigma^-$ ground state. A molecular orbital description of $3\Sigma^-$ level is

$$O_2 \text{KK}(2s \sigma_g)^2 (2s \sigma_u^\ast)^2 (2p \sigma_g)^2 (2p \sigma_u)^4 (2p \sigma_g^\ast)^1 (2p \pi_g^\ast)^1$$

where the KK term indicates that the K shells of the two oxygen atoms are filled. The two unpaired electrons in the $3\Sigma^-$ ground state are found in the two degenerate antibonding $2p \pi_g^\ast$ orbitals (Fig.1), leaving $O_2$ with a formal bond order of two.
Fig. 1.

The MO description of \( O_2 \, (3\Sigma^\text{-}) \) shows a vacancy for the addition of a single electron in both of \( 2p_g \) orbitals. The addition of one or two electron to
a neutral \( \text{O}_2 \) results in formation of the superoxide \( \text{O}_2^- \) and peroxide \( \text{O}_2^{2-} \) species, respectively, leaving \( \text{O}_2^- \) with a bond order of 1.5, and the peroxide \( \text{O}-\text{O} \) link with a normal bond order of one. Some of the salient features for \( \text{O}_2^- \), \( \text{O}_2^- \) and \( \text{O}_2^{2-} \) are summarized in Table 1.

Table 1. Some Properties of \( \text{O}_2^- \), \( \text{O}_2^- \) and \( \text{O}_2^{2-} \)

<table>
<thead>
<tr>
<th>Bond order</th>
<th>Compound</th>
<th>O-O distance (Å)</th>
<th>Bond energy (Kcal/mol)</th>
<th>O-O cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>( \text{O}_2 )</td>
<td>1.20(^{22})</td>
<td>117.2</td>
<td>1554.7(^{24})</td>
</tr>
<tr>
<td>1.5</td>
<td>( \text{KO}_2 )</td>
<td>1.28</td>
<td>-</td>
<td>1145(^{25})</td>
</tr>
<tr>
<td>1</td>
<td>( \text{Na}_2\text{O}_2 )</td>
<td>1.49(^{23})</td>
<td>48.8</td>
<td>842(^{26})</td>
</tr>
</tbody>
</table>

The way in which a peroxo group is expected to coordinate to metals (Fig. 2) can range from a symmetrical bidentate to a terminal monodentate position, including all the possible angles in between.
The bridging $\mu$-peroxo could vary from \textit{cis}-planar and \textit{trans}-planar to \textit{trans}-nonplanar configurations. An unusual symmetrical double bridging was also found.\textsuperscript{27} Deviations from the ideal symmetry are common. In the cases of heteroligand fields they are due to the inherent symmetry of different donor atoms. Additional $p\pi^*$ electron delocalization to the metal ion is
anticipated, which would therefore favour \( d^3 \) or low \( d^n \) metal ion configurations.

The stereochemical polyhedra in heteroligand peroxo complexes are fairly predictable. For the second row elements Nb and Mo, coordination number 8 with dodecahedral (D\(_{2d}\)) symmetry has invariably been observed in the absence of \( \text{oxo} \) groups. In \( \text{oxo} \)peroxo heteroligand surroundings, the pentagonal bipyramidal arrangement is the most common, usually with two coordinated peroxo groups in the cis positions and one \( \text{oxo} \) group in an axial position. There is an interesting non-octahedral example of coordination number 6 for a vanadium complex.\(^{28}\)

Infrared spectra are essential for the characterisation of complexes containing coordinated peroxo groups. For a bidentate peroxide, regarded as a C\(_{2v}\) unit, three i.r. active modes are expected:\(^{29}\) the peroxo stretching (\( A_1 \)), and symmetric asymmetric M-O\(_2\) stretchings (\( A_1 \) and \( B_2 \)). The \( \nu(0-0-) \) band is the most sensitive and intense one and characteristically occurs between 800 and 900 cm\(^{-1}\). The frequency of this band remains fairly independent of the heteroligand environment, but is affected by the mass of the metal.
ion, indicating coupling of the \( \mathcal{J}(\sigma-\sigma^-) \) with \( M-O_2 \) vibrations. This most familiar way of bonding of \( O_2^{2-} \) groups, in a triangular bidentate manner, is similar to that proposed by Griffith \(^{30}\) for the bonding of \( O_2 \) in oxyhemoglobin, and the \( \mathcal{J}(\sigma-\sigma^-) \) values, which are similar to those observed for free \( O_2^{2-} \) ion.

The dimeric \( \text{per}_\text{ox}_\text{co} \) complex is often more stable than the monomeric complex and will generally form unless its formation is inhibited. (e.g. \( \mathcal{J}(\text{NH}_3)_5-\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_5^{4+} \)). These complexes are diamagnetic with the oxygen being viewed as "peroxide-like" with a concomitant oxidation of the metal centres to low-spin \( d^6 \) (\( \text{Co}^{3+} \)). The \( \mathcal{J}(\sigma-\sigma^-) \) for such complexes span a range of \( 790-844 \text{ cm}^{-1} \) with an average value of \( 810 \text{ cm}^{-1} \) (c.f. \( \mu-\text{per}_\text{ox}_\text{co} \)).

Heteroligand complexes of Nb and Ta are rather easily formed. Structural analysis of some such niobium complexes show that the coordination polyhedron is dodecahedral.\(^{31}\) Vanadium, however, presents a different story. Several \( \text{per}_\text{ox}_\text{co} \) and \( \text{ox}_\text{per}_\text{ox}_\text{co} \) vanadium(\( V \)) species occur,\(^{12}\) but only few heteroligand complexes are known.\(^{28,32}\) Unlike Nb and Ta, vanadium has a strong tendency to form \( \text{ox}_\text{per}_\text{ox}_\text{co} \) species.
The reaction of concentrated alkali hydroxide with concentrated solutions of $\text{V}_2\text{O}_5$ in $\text{H}_2\text{O}_2$ at $>0^\circ\text{C}$ gives blue solutions which contain the ion $\text{V}(\text{O}_2)_4^{3-}$. The salts of $\text{V}(\text{O}_2)_4^{3-}$ can also be obtained by addition of alcohol to such solutions. The salts are stable only at low temperatures, the stability decreasing with increasing cation size. The potassium salt which is isomorphous with $\text{K}_3\text{Cr}(\text{O}_2)_4^-$, has a magnetic moment of 0.6B.M., consistent with the presence of vanadium(V). The i.r. spectra of the $\text{(NH}_4)_3\text{V}(\text{O}_2)_4^-$ and $\text{K}_3\text{V}(\text{O}_2)_4^-$ contains bands in the region 800-900 cm$^{-1}$ that have been assigned to $\delta(\text{O}^{-}\text{O}^{-})$ modes of peroxo groups.

It is suggested that slight excess of a base causes the destruction of the tetraperoxy species and the formation of the yellow triperoxo anion $\text{V}_3(\text{O}_2)_3^{3-}$:

$$\text{V}(\text{O}_2)_4^{3-} + \text{OH} \rightarrow \text{V}_3(\text{O}_2)_3^{3-} + \text{HO}_2^-$$

which is stable at room temperature.

The yellow colour produced by addition of $\text{H}_2\text{O}_2$ to a dilute solution of a metavanadate has been shown to be due to be a diperoxy anion by cryoscopy and spectrophotometry as well as by thermochemical studies. There is, however, some controversy as to how the anion should be formulated, although the results of cryoscopic
and spectrophotometric studies have been interpreted in terms of the monobasic anion \( \text{VO}(O_2) \). The addition of \( H_2O_2 \) to \( V_2O_5 \), to an acid solution of a metavanadate, to a vanadium (V) salt in weakly acid solution, and to a decavanadate produces a red colour due to the monomeric monoperoxyvanadate cation \( \text{VO}(O_2)^+ \). The red colour is stable in moderately acid media. In excess \( H_2O_2 \) the red cation is converted to the yellow peroxo anion \( \text{VO}(O_2)^- \) (Ref. 38,39). It has been concluded that,

(i). the number of peroxo groups per vanadium atom increases with alkalinity;

(ii). increasing acidity increases polymerisation and decreases the number of peroxo groups per vanadium atom;

(iii). increasing the concentration of \( H_2O_2 \) decreases the degree of polymerization.

Vanadium peroxo complexes are of special interest because of the function of V in living cell is unknown, and is selectively toxic in mammals. From biochemical point of view, the most interesting aspect of peroxo-vanadium chemistry remains the experimental approach to measuring the reactivity of the coordinated peroxo group in an environment of various heteroligand fields.
The reactivity of coordinated peroxo groups means essentially the ease of electron-transfer to and from the dioxygen anion \( \text{O}_2^{2-} \). Thus, studies involving heteroligand peroxo complexes of vanadium requires an immediate attention. The chemistry of these compounds embraces a fascinating, rewarding and worthwhile area of investigation.

Chapters 3-6 of the present thesis describe syntheses, characterization structural assessment and some chemistry of a number of heteroligand (viz., fluoro and chloro) peroxo complexes of vanadium(V) and (IV).

Complexes of vanadium (III) are usually prepared by direct reaction between the vanadium trihalide and the ligand, all operations being carried out on a vacuum line. The complexes are unstable towards air and moisture. All three types of complexes viz., cationic, anion and neutral have been known. The magnetic moments of octahedral vanadium (III) complexes \( \text{^{3}T_{1g}} \) ground term are expected to be \( \sim 2.8 \) B.M. at room temperature and to fall appreciably with a lowering of temperature. In practice, however, the temperature dependence of these magnetic moments is less pronounced than is expected for an orbital triplet ground term; indeed, it is
consistent with a splitting of the ground triplet by some 500 - 2000 cm\(^{-1}\). The splitting is most obviously brought about by a non-equivalence of all six ligands.

Tetrahedral vanadium(III) complexes, with a \(3\)\(A_2\) ground term, are expected to show a temperature independent magnetic moment of \(\sim 2.7\) B.M. and do so in practice.\(^8\)

The electronic structure and spectra of octahedrally coordinated vanadium(III) (\(d^2\)) complexes have been interpreted satisfactorily in terms of the ligand-field model, although in general it has been found necessary to take account of the effects of a trigonal distortion (to \(D_2d\)) of the octahedral field.\(^{42}\)

Vanadium trihalides form various neutral complexes, and the known examples can be classified into \(VL_3X_3\) and \(VL_2X_3\) types.\(^8\) No example of neutral complex of the type \(V(L-L')_2X\) (where \(L-L'\) is a bidentate uninegative ligand and \(CX\) is a halide) is known. Moreover, no report has been available on the synthesis of a neutral complex of vanadium(III) from a higher valent vanadium species through electron-transfer reactions.

Chapter 7 presents an account of the synthesis of bis(acetylacetonato) fluorovanadate(III) complex achieved by an electron-transfer reaction between a
vanadium(IV) compound and acetylacetone (Hacac). This 
Chapter also reports the results of various physico-
chemical studies, including mass spectrometry, of the 
newly synthesised neutral complex of vanadium(III).

As part of a programme of the laboratory, in which 
the whole work was done, a new method of synthesis of 
tris(acetylacetonato) iron(III), Fe(C₅H₇O₂)₃, has been 
developed. This compound has been known for quite some-
time, but the methods used for its synthesis suffer from 
many difficulties. For example, the reaction between 
metallic iron and Hacac in the presence of oxygen⁴³ is 
extremely slow. The reaction between iron(III) chloride 
and Hacac in the presence of a large amount of sodium 
acetate as buffer⁴⁴,⁴⁵ may contaminate the product. 
The reaction between Fe(CO)₅ and Hacac⁴⁶ requires the 
preparation and handling of the toxic air-sensitive 
metal carbonyl.

Chapter 8, indeed the last Chapter of this thesis, 
reports a novel synthesis and mass spectrometric studies 
of tris(acetylacetonato) iron(III), Fe(C₅H₇O₂)₃. 
Advantages of the new synthesis have been discussed.
Attempts have been made to make each Chapter a self-contained one. Thus, every Chapter has been provided with a brief introduction, experimental section, results and discussion section, and the relevant bibliography.
References


