CHAPTER 1
Vanadium with the outer electronic configuration $3d^{3}4s^{2}$ belongs to the periodic group VB. Besides its utility as a catalyst in industrial purposes, there is considerable evidence which suggests that vanadium is also an essential element for mammals of an unknown biochemistry. Further, it is established that vanadium in moderate levels has a significant impact on the function of enzymes and of biological systems.

Vanadium can attain a highest oxidation state of +5. 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 $\text{VO}^{3+}$ (aq) cation is probably best represented as $[\text{VO(H}_{2}\text{O})_{5}]^{3+}$, with the oxygen occupying one co-ordination position in the octahedral complex. The $\text{VO}^{3+}$ unit is found in the oxyhalides $\text{VOX}_{3}$ ($X = \text{F, Cl or Br}$) 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 type $\text{VOCl}_{3}.\text{L}$, which appears to be five or six co-ordinated monomer have been characterised in which $\text{L}$ can be either an oxygen donor or a
nitrogen donor ligand.\textsuperscript{9,10} Vanadium oxytrichloride also reacts\textsuperscript{9} with ligands containing replaceable hydrogen atoms to give substitution products of the type \(\text{VO(OMe)}_3\), \(\text{VOC}_1\text{(OEt)}_2\), \(\text{VOC}_1\text{(acac)}\), and \(\text{VOC}_1\text{(acac)}_2\) (\(\text{acac}^- = \text{acetylacetonate}\)). The \(\text{VO}^{3+}\) entity is also very commonly encountered in peroxo-vanadium chemistry\textsuperscript{11} and there are some X-ray crystallographic evidences for the occurrence of \(\text{V=O}\) in the peroxo-vanadate(V) compounds, viz., \((\text{NH}_4)_2[\text{VO(O}_2)(\text{C}_2\text{O}_4)_2]_{\text{H}_2\text{O}}, \) \(\text{[VO(O}_2)\text{C}_2\text{O}_4]^{3-}\) (Ref.\textsuperscript{12}), \((\text{NH}_4)_2[\text{VO(O}_2)\text{bipy}]\text{.H}_2\text{O}, \) \((\text{NH}_4)_2[\text{VO(O}_2)(\text{C}_4\text{H}_5\text{O}_4\text{N})],\) \text{in addition to a few published earlier.}\textsuperscript{15-19} Some other complexes containing \(\text{VO}^{3+}\) include \(\text{VOC}_1^{-}\), \(\text{VOF}^{-}\) (Ref.\textsuperscript{20-22}) and \(\text{[VOF}_3(\text{H}_2\text{O})]\).\textsuperscript{23}\)

The second oxo-vanadium(V) species, the \(\text{VO}_2^+\) ion, is not very much characterised, but it is believed to occur discreetly in the complexes, \(\text{VO}_2(\text{NO}_3), \text{VO}_2\text{F}, \text{and VO}_2(\text{SbF}_6)\) and as a cis-\(\text{VO}_2\) unit in the complexes \(\text{K}_3[\text{VO}_2\text{F}_4]\) and \(\text{K}_3[\text{VO}_2(\text{C}_2\text{O}_4)_2]\).\textsuperscript{25}\)

Vibrational spectroscopy plays an important role in the study of oxo-vanadium compounds. The most characteristic feature of the vibrational spectra of oxovanadium complexes is the occurrence of very strong and sharp bands at 980±50 cm\(^{-1}\). Such bands are assigned to the V=O stretching frequencies\textsuperscript{24} and as expected it lies near the upper frequency limit for those complexes which are known, from X-ray work, to have the shortest V-O bonds.

One of the most interesting aspects of vanadium chemistry, which has also engaged the attention of several groups of contemporary researchers, is its peroxo chemistry.\textsuperscript{28-38} Peroxo-transition
metal complexes in general have received continued attention over several years because of their important roles in biological processes as well as in catalytic oxidations.

It has been known for over a century that characteristic colour reaction may take place when hydrogen peroxide is added to solutions of transition metal derivatives and many peroxo transition metal compounds have been isolated in the solid state. Peroxo-metal complexes besides having an intrinsic interest of their own constitute an important class of reactive intermediates in catalytic oxidations and are involved as potential oxygen donors in the oxygen transfer reactions to organic substrates including hydrocarbons. Also, the research leading to gain an insight into the roles of peroxo-transition metal compounds in the storage and transport of oxygen and oxidase functions in biological systems is of growing interest.

Molecular oxygen functions both as a ligand and as a reagent in transition metal chemistry. Recent interest in the chemistry of molecular oxygen has involved biochemists interested in biological oxygen transport and oxygen function as well as industrial chemists interested in developing homogeneous analogues to heterogeneous metal-catalysed oxidation reactions. The isolation and characterisation of stable dioxygen complexes and the variety of reactions that they themselves undergo are beginning to yield general information about bonding, structure, and reactivity of co-ordinated molecular oxygen.
Fig. 1 Molecular orbital diagram for $O_2$
Owing to the importance of molecular oxygen as a reagent in biological and industrial processes and also because dioxygen is an interesting ligand in its own right, current research in this area has been directed towards understanding the bonding of dioxygen to transition metal complexes and the effect of this bonding upon its reactivity towards other substrates, or in other words the extent to which the O-O bond of co-ordinated O₂ is activated.

The bonding in molecular oxygen is best described by MO theory. According to this theory, the valence orbitals of the two oxygen atoms (2s²2p⁴) combine to give molecular orbitals whose relative energies are shown in Fig. 1. The ground state of molecular oxygen is predicted and observed to be a triplet state (³Σ) with two unpaired electrons occupying a pair of degenerate Π* antibonding orbitals. The two lowest excited states are formed by redistributing the two electrons in these 2pΠ* orbitals. The configuration and energies for the ground state and first two excited states are shown in Fig. 2.

![Fig. 2](image)

Fig. 2 Π* orbital occupancy and energies of the first two electronically excited states of O₂
MO theory also predicts bond orders of 2.5, 2, 1.5, and 1 for the dioxygenyl cation \( \text{O}_2^+ \), molecular oxygen \( \text{O}_2 \), superoxide \( \text{O}_2^- \), and peroxide \( \text{O}_2^{2-} \), respectively. Some of the salient features for \( \text{O}_2^+ \), \( \text{O}_2 \), \( \text{O}_2^- \) and \( \text{O}_2^{2-} \) are summarised in Table 1-1.

Table 1-1. Some Properties of \( \text{O}_2^+ \), \( \text{O}_2 \), \( \text{O}_2^- \), 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>( \nu (\text{o-o}) ) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>( \text{O}_2^+ \text{PtF}_6 )</td>
<td>1.12</td>
<td>-</td>
<td>1905(^{70})</td>
</tr>
<tr>
<td>2</td>
<td>( \text{O}_2 )</td>
<td>1.207</td>
<td>117.2</td>
<td>1554.7(^{71})</td>
</tr>
<tr>
<td>1.5</td>
<td>( \text{KO}_2 )</td>
<td>1.28</td>
<td>-</td>
<td>1145(^{72})</td>
</tr>
<tr>
<td>1</td>
<td>( \text{Na}_2\text{O}_2 )</td>
<td>1.49</td>
<td>35</td>
<td>842(^{73})</td>
</tr>
</tbody>
</table>

Although the term molecular oxygen refers only to the free unco-ordinated \( \text{O}_2 \) molecule with the ground state configuration \( ^3\Sigma_g^- \), the term dioxygen has been used as a generic designation for \( \text{O}_2 \) moiety in any of its several forms and can be referred to \( \text{O}_2 \) in either a free or combined state.\(^74\) 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
O₂ group co-ordinated to the metal centre, and no distinction is made between neutral dioxygen in any of its reduced forms. According to the rationalisation made by Vaska, transition metal peroxide involve co-valently bound dioxygen resembling O₂⁻ in peroxo configuration. A common characteristic of these complexes is the O-O distance, which occurs between 1.4 and 1.52Å (1.49 for O₂⁻), and the corresponding infrared frequency (0-0) which lies between 800 and 950 cm⁻¹ (802 cm⁻¹ for O₂⁻). 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 co-ordinated peroxo groups and one or more monodentate or polydentate ligands. Heteroligands may range from monodentate ions to bulky porphyrins (F⁻, Cl⁻, NH₃, C₂O₄²⁻, SO₄²⁻, CO₃²⁻, NTA, EDTA, bipy, o-phen, oxine, porphyrins, pyridine-2, 6-dicarboxylic acid etc).

The stability of peroxo complexes is generally enhanced by specific heteroligand combinations. Many simple 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 but many heteroligand peroxo complexes, on the other hand, survive recrystallisation from boiling aqueous solutions, heating in vacuo, and remain unchanged for prolong periods in closed containers. The biochemical significance of peroxo metal complexes has been emphasised in recent literatures. The reactivity of peroxides and the lability of metal-oxygen bonds in special heteroligand environments in solutions are of particular interest to biochemistry although not easy to measure directly.
A comparison between the peroxy and unreduced dioxygen heteroligand complexes reflects 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 peroxydianion. The electron rich O$_2^{2−}$ ion therefore preferably forms complexes with metal ion of low d$^n$ including d$^0$, and also f$^0$ electronic configurations, while the neutral dioxygen molecule favours higher d$^n$ metal acceptors. However, there are at least two things that these oxygen species have in common, viz., both are stabilised by specific heteroligand spheres and both are of importance in biochemistry.

The way in which peroxy group is expected to co-ordinate to metals can range from symmetrical bidentate to a terminal monodentate position, including all the possible angles in between them. The structural classification of dioxygen complexes, rationalised by Vaska, can be represented as shown in Fig. 3. The bridging peroxy could vary from cis-planar and trans-planar to trans-nonplanar configuration. An unusual symmetrical double bridging was also found, however, such complexes are very rare. Deviations from the ideal symmetry are also observed very often. In the cases of heteroligand fields they are due to the inherent symmetry of different donor atoms. Additional π$^*$ electron delocalisation to the metal ion is anticipated, which could therefore favour d$^0$/f$^0$ or low d$^n$ metal ion configuration. The stereochemical polyhedra in heteroligand peroxy complexes are often fairly predictable. In oxoperoxo heteroligand surroun-
<table>
<thead>
<tr>
<th>Structural type</th>
<th>Structural designation</th>
<th>Vaska Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Structure" /></td>
<td>$\eta^2$ dioxygen</td>
<td>Type a (superoxo)</td>
</tr>
<tr>
<td><img src="image2" alt="Structure" /></td>
<td>$\eta^2$ dioxygen</td>
<td>Type IIa (peroxo)</td>
</tr>
<tr>
<td><img src="image3" alt="Structure" /></td>
<td>$\eta^1: \eta^1$ dioxygen</td>
<td>Type Ib (superoxo)</td>
</tr>
<tr>
<td><img src="image4" alt="Structure" /></td>
<td>$\eta^1: \eta^1$ dioxygen</td>
<td>Type IIb (peroxo)</td>
</tr>
<tr>
<td><img src="image5" alt="Structure" /></td>
<td>$\eta^2: \eta^2$ dioxygen</td>
<td>-</td>
</tr>
<tr>
<td><img src="image6" alt="Structure" /></td>
<td>$\eta^1: \eta^2$ dioxygen</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 3. Structural Classification of dioxygen complexes
 ding, the pentagonal bipyramidal arrangement is most common\textsuperscript{12,13} for transition metal complexes, usually with two co-ordinated peroxo groups in cis position. There is also an interesting non-octahedral example of co-ordination number 6 for a peroxy-vanadium complex.\textsuperscript{19}

Infrared spectra are essential for the characterisation of complexes containing peroxo groups. For, a bidentate peroxide, regarded as a $C_2v$ unit, three IR active modes are expected,\textsuperscript{25} the peroxo stretching ($A_1$) and symmetric and asymmetric M-O\textsubscript{2} stretching $A_1$ and $B_2$. The $\tilde{\nu}$ (O-O) band is the most sensitive and intense one and characteristically occurs between 800 and 950 cm\textsuperscript{-1}, but generally observed below 900 cm\textsuperscript{-1}. The frequency of this band remains fairly independent of the heteroligand environment but is effected by the mass of the central metal ion, indicating some degree of coupling of the $\tilde{\nu}$ (O-O) with M-O\textsubscript{2} vibrations. Although, peroxide may bind metal centres in different manners as mentioned earlier in this Chapter, the most familiar way of bonding of O\textsubscript{2} groups is a triangular bidentate manner which is similar to the one proposed by Griffith\textsuperscript{86} for the bonding of O\textsubscript{2} in oxyhemoglobin, and the $\tilde{\nu}$ (O-O) values, which are similar to that observed for O\textsubscript{2} ions. While the importance of infrared spectroscopy in this field has been emphasised, the usefulness of Raman spectroscopy should not be underestimated. All the three IR active modes as mentioned above are also Raman active. Thus the results of Raman spectral studies not only complement the IR results but also augment them. Moreover, Raman spectroscopy can also be easily
applied to solutions, and the results of which provide further
information concerning identity and structure of a complex
species in solutions.

The importance of neutral dioxygen complexes in biochemistry
is well known, but the biochemical connection of the metal peroxy
complexes with biological processes is not very well understood.
The metals, Sc, Ti, V, Cr, Y, Zr, Nb, Mo, La, Hf, Ta, W, and
U form stable heteroligand peroxy complexes and there is increa-
sing 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 species that can act as heteroligands.

The behaviour of vanadium(V) in hydrogen peroxide solution
is not analogous to its congeners niobium(V) and tantalum(V)
under similar conditions. Unlike niobium and tantalum, vanadium
has a strong tendency to form oxoperoxo species. Oxodiperoxovanadate
complexes have been reported previously and by composition
he correspond to some chromium(VI), molybdenum(VI) and tungsten(VI)
peroxo complexes which exhibit co-ordination number of 6 or 7. Heteroligand complexes of niobium and tantalum are rather easily
formed and they commonly exhibit eight co-ordination with a dode-
cahedral co-ordination polyhedron. Although, some information
concerning peroxy, oxoperoxo and heteroligand peroxo complexes
of vanadium(V) are now available, nevertheless some funda-
mental aspects of peroxy-vanadium chemistry still seem to be
unattended to.
Vanadium-hydrogen peroxide system appears to be complicated owing to the formation of a number of different complexes with a small change of pH of the reaction solutions. The addition of aqueous $\text{H}_2\text{O}_2$ to (i) $\text{V}_2\text{O}_5$, (ii) an acid solution of a metavanadate, (iii) a vanadium(V) salt in a weakly acid solution, or a decavanadate produces in each case a red colour which was believed to be due to the formation of a monomeric monooxo-peroxovanadate(V) cation $[\text{VO(O}_2\text{)}]\text{}^+$. The red colour thus obtained is stable in moderately acid media. However, very recently it has been shown that red colouration of the vanadium-hydrogen peroxide system owes its origin to the formation of a peroxovanadate(IV) complex. In an excess of $\text{H}_2\text{O}_2$ the red species is converted to the yellow oxodiperoxovanadate(V) anion $[\text{VO(O}_2\text{)}_2\text{]}^-$.

The yellow colour produced by the addition of aqueous hydrogen peroxide to a dilute solution of a metavanadate was shown to be due to a diperoxo anion by cryoscopy as well as by thermochemical studies more than a few decades ago. There was, however, some controversy as to how the anion should be formulated although the results of cryoscopic and photometric studies were interpreted in terms of the anion $[\text{VO(O}_2\text{)}_2\text{]}^-$. Various attempts made in the past to ascertain the existance of this species through isolation in the solid state were unsuccessful thereby leaving some doubt regarding its actual composition. Therefore it was considered quite imperative to synthesise this species in solid state and to ascertain its composition.
The reaction of concentrated alkali hydroxide with a concentrated solution of vanadium pentoxide (V₂O₅) in aqueous hydrogen peroxide at low temperature (0° or below 0°C) gives a deep blue solution owing to the formation of tetraperoxy vanadate(V) species, [V(Ο₂)₄]³⁻. The salts of the complex [V(Ο₂)₄]³⁻ ion were obtained by the addition of ethanol to such a solution. The salts are stable only at low temperatures, and their stability decreases with increasing cation size. The potassium salt, K₃[V(Ο₂)₄], which is isomorphous with K₃[Cr(O₂)₄], presumably having a dodecahedral structure, has a magnetic moment of 0.6 μ_B, consistent with the presence of vanadium(V). Albeit the tetraperoxovanadate(V) species is evidently a blue complex, it was not known until recently as to what is the minimum number of Ο₂²⁻ bonded to vanadium(V) centre, required for the formation of the blue colouration of vanadium —— H₂O₂ systems leaving some fundamental questions unanswered.

The notable point emerged out of the earlier studies include the following:

(i) The number of peroxy groups per vanadium atom increases with alkalinity.

(ii) Increasing acidity increases polymerisation and decreases the peroxy groups per vanadium atom.

(iii) Increasing concentration of H₂O₂ decreases the degree of polymerisation.
Studies involving vanadium peroxy complexes are of special interest because the actual function of vanadium in living cell is unknown. From the biochemical point of view, the most interesting aspect of peroxy-vanadium chemistry remains the experimental approach to measuring the reactivity of the co-ordinated peroxy group in an environment of various heteroligand fields. An essential factor in the biochemical activity of peroxy-heteroligand vanadates is the heteroligand. Recently, a few peroxy-vanadates of the type, $M_4[O(VO(O_2)_2)_2]$, $M_3[VO(O_2)_2C_2O_4]$ and $M_3[VO(O_2)L]$ ($L =$ malate, citrate, iminodiacetate, nitrilotriacetate and EDTA), have been tested for toxicity and antitumour activity and such activity of peroxovanadates(V) has been shown to depend upon the type of heteroligand present. Peroxo-heteroligand vanadates(V) behave differently from analogous non-peroxo complexes. The heteroligands determine the biological activity of these complexes, presumably because it can shift the $V(V)/V(IV)$ redox potential ($E^0_{298} = 1.00$V) towards the point where an intramolecular electron-transfer could occur within the $[V(V)-peroxo]$ moiety. Such a process reduces vanadium(V) to vanadium(IV) and oxidises peroxy group to superoxide radical. Consequent upon this bonds to co-ordinated dioxygen ligand weaken, and superoxide ion generated in the process could trigger further biological events. This is further supported by the fact that peroxy heteroligand complexes of niobium(V) and tantalum(V) do not exhibit analogous bio-activity because the metal ion does not allow intramolecular electron transfer probably due to unfavourable $M(V)/M(IV)$ redox potential. These observations cause one to infer that the
[V(V)-peroxo] moiety is unique. It has also been suggested that the tendency of vanadium(V) to form stable heteroligand complexes could be extended to vanadium chemistry in the cell or membranes where complexes of this type may form wherever vanadium happens to accumulate.\textsuperscript{102} Apart from their biological activity peroxovanadium compounds, like some other similar compounds of transition metals play a significant role in catalytic oxidation reactions.\textsuperscript{15} It has been reported, from the results of limited studies, that they are highly active and stereoselective in the oxidation of various organic substrates.\textsuperscript{15} In a very recent report Mimoun et al. have given a good account of the synthesis of oxo-[N-(2-oxodiphenyl)salicyldenaminato]vanadium(V) alkyl peroxides, their use in the selective epoxidation of olefines, and discussed the results in relation to the mechanism of Halcon epoxidation process.\textsuperscript{84} However, much remains yet to be explored.

In view of the importance of heteroligand peroxovanadates, in biochemistry as well as in catalysis, it appeared that, suitably chosen heteroligands may give rise to peroxo-vanadium complexes which are of interest in biochemistry. Amino acids are the alphabet of protein structure and determine many of the important properties of proteins. The increasing interest in metal-amino acid systems is attributed to their potentials as models for understanding biologically important molecules. To us it appears that peroxo-amino acid complexes of vanadium(V) will be of interest because they would contain three biological important components: peroxo group, \(\alpha\)-amino acid and vanadium(V). Besides, possibility
of their exhibiting catalytic properties cannot be ruled out. According to a recent report\textsuperscript{103} some attempts to synthesise peroxo-amino acid complexes of vanadium(V) were unsuccessful. We, however, considered it worthwhile to reinvestigate this aspect of vanadium chemistry and to work out appropriate experimental conditions leading to the synthesis of heteroligand peroxo-vanadium(V) compound containing an amino acid.

Added to all that have been mentioned so far regarding the peroxo-vanadium chemistry, there remains another important point which deserves a due consideration. This addresses to the nature and mode of bonding of $\text{SO}_4^{2-}$ with oxodiperoxovanadate(V) in the complex species formed in the reaction of vanadium(V) with hydrogen peroxide in the presence of $\text{SO}_4^{2-}$. This reaction is of considerable practical importance in the context of spectrophotometric determination of vanadium.

It may be inferred from the above non-exhaustive discussion, that the chemistry of peroxovanadates(V) in general embraces a fascinating, rewarding and worthwhile area of investigation. Also it is evident that the synthesis and structural assessment of well defined peroxovanadate(V) complexes are above all prerequisites following which other aspects can be developed in this field of chemistry.

Accordingly, such studies were undertaken as a major part of the present Ph.D. programme. Following selective aspects of peroxovanadium(V) chemistry have been identified for the present research:
(i) isolation in the solid state of oxodiperoxovanadate(V) complexes, $A[VO(O_2)_2]$ ($A =$ alkali metal or $NH_4$); 
(ii) reactions of vanadium(V) with alkali sulphate or thiocyanate and hydrogen peroxide;
(iii) synthesis and characterisation of heteroligand-oxodiperoxovanadate(V) complexes containing an amino acid (e.g. glycine(GlyH) as the heteroligand; and 
(iv) synthesis and structural assessment of alkali triperoxovanadates(V) and studies of their reactivity.

Chapter 3 of the present thesis describes the first isolation in the solid state of the yellow complex, $[VO(O_2)_2]^-$, its characterisation and structural assessment. Two reactions highlighting the scope for the use of the compounds in synthesis are also included. Also reported in this Chapter are the results of the studies involving the reactions of vanadium(V) and $H_2O_2$ in the presence of $SO_4^{2-}$ or $SCN^-$. 

Chapter 4 presents the synthesis, characterisation and structural assessment of peroxo complexes of vanadium(V) having amino acid (e.g. glycine) as a heteroligand. 

Studies of reactivity of a co-ordinated dioxygen of low valent transition metal compounds have received considerable attention in the recent years. The nature of metal-dioxygen bonding was the subject of several theoretical studies as well. The various studies indicate that the reactivity of dioxygen increases upon co-ordination for which three possible explanations were advanced.
(i) Co-ordinated dioxygen (Type IIa) is in general diamagnetic; therefore reactions with diamagnetic substrates to form diamagnetic products are not hindered by the requirement for spin conservation.

(ii) The metal may hold dioxygen and the substrate in cis positions, lowering the activation energy for oxidation of the substrate.

(iii) Co-ordinated dioxygen is, in most cases, partially reduced since a considerable charge is transferred to the $O_2$ ligand and increased electron density on the $O_2$ may activate it.

Information concerning the reactivity of $O_2$ bonded to metals has relevance in understanding the processes involved in the activation of molecular oxygen by metallo-enzymes in biological systems. The reactivity of low valent, group VIII transition metal complexes with respect to their ability to oxidise organic and inorganic substrates, viz., olefins,\textsuperscript{104,110-112} acetylenes,\textsuperscript{104} carbonyls,\textsuperscript{113,114} $CO_2$,\textsuperscript{114,115} $SO_2$,\textsuperscript{64,116-120} $NO$\textsuperscript{119,120} etc. have been studied to a certain extent, in recent years. As a case in point, for example, it is evident from the literature, that in most cases co-ordinated dioxygen behaves as a nucleophile and reaction of $SO_2$ with such complexes leads to the corresponding sulphato complexes, which is generated from the insertion of $SO_2$ into a M-$O_2$ bond as evidenced by the isotopic IR study.\textsuperscript{44,117}\textsuperscript{44}\textsuperscript{117} This has been further supported by theoretical studies based on MO theory.\textsuperscript{109}
However, to the best of our knowledge, no work, except for the one involving a peroxo-titanium compound, has been reported on the reactions of $\text{SO}_2$ with non-group VIII transition metal peroxo compounds, leaving curiosity regarding the course of such reactions under similar conditions, and the nature of the products obtained thereof. Moreover, it is relevant to mention that none of the earlier investigations relating to $\text{SO}_2$ reactions with peroxo-metal compounds seem to have involved compounds containing more than one peroxo group per metal centre thereby leaving some questions unanswered in this context.

In view of the above, it was considered imperative to study the reaction between inorganic polar species, $\text{SO}_2$, with higher valent vanadium compounds containing more than one peroxo groups. The results of which might enable one to rationalise the reaction sequence of the peroxo groups in the parent compounds. An additional interest adhered to this was to find out whether the co-ordinated peroxyde or the high valent metal centre would react with $\text{SO}_2$ in preference over the other particularly when both are susceptible to attack by $\text{SO}_2$. Such studies may also
provide an access to synthesis of newer ternary compounds of vanadium when carried out in presence of suitable ligands.

In line with the contention such a study was undertaken as a part of the whole programme. Alkali-metal triperoxovanadates(V), A[V(O_2)\_3].3H_2O (A = Na or K), have been synthesised and their structural assessment made, thereby enabling us to ascertain the minimum number of peroxide groups necessary for the formation of blue peroxovanadates(V). Making use of alkali-metal triperoxovanadates(V) as the precursors, reactions of SO_2(g) in an aqueous medium were carried out. In addition, similar reactions were also conducted in the presence of F\(^-\) leading to the synthesis of newer ternary complexes of vanadium(IV).

A detailed account of the synthesis, structural assessment and the reactivity of alkali triperoxovanadates(V) constitutes the subject matter of Chapter 5.

Quite apart from the vanadium chemistry, research involving chemistry of fluoro-containing transition metal compounds appears to be one of the areas of contemporary interest.\(^{122-139}\) Interest in this field of chemistry seem to be never diminishing. Studies of the fluoro-compounds of different metals are interesting not only for the sake of science but also for use in practice. Inorganic fluoro compounds are successfully used in optical instrument making, laser technology, microelectronics, in the production of pure metals by thermal reduction, in the manufacture of electrochemical cells with solid electrolytes and in some other
fields of technology. Quite exciting is also to draw attention to a recent development in the history of fluorine chemistry is the chemical synthesis of elemental fluorine ($F_2$) from a fluoro complex of transition metal. However, over and above the utility of metal-fluorides in various fields of science and technology, fluoride ions are also subjected to much controversy. "Fluoride ions, despite their similarity to the biologically ubiquitous chloride ions, and the necessary role that they play in various biological systems, are also blamed by some, for several biologically harmful processes, including cancer".

Three main factors mostly explain why the chemistry of fluorine is different from that of other halogens. These are:

- The low dissociation energy of the fluorine molecule ($D(F_2) = 37.7$ Kcal/mol);
- Relatively high strength of bonds formed between fluorine and metallic or non-metallic elements; and
- The relatively small ionic size of the fluorine atom and the fluoride ion.

With most transition metals a variety of stoichiometries are possible, leading to a versatility of structures and physical properties. Metal fluorides are generally well behaved, with structure depending largely on stereochemical factors. Further, as a result of high electronegativity of the fluoride ion, metal-fluoro complexes are generally insulators or large band gap semiconductors. The lack of electron delocalisation leads to a
certain simplicity in the interpretation of physical properties such as magnetism, and in consequence metal fluorides have often been studied as model systems. 144

The ready dissociation of fluorine into atom is at the root of its high reactivity. The overall energy release in the formation of a fluoride is considerably greater than the other halides. 143 The fundamental properties of fluorine, viz., its extreme electronegativity and small ionic size render it suitable for stabilising higher oxidation states of metals, and knowledge on fluoro-compounds of transition metals has been increasing considerably, mainly because fluorine itself has ceased to be a laboratory curiosity as a result of simplification of its preparation and purification. New materials and improved techniques have made newer synthetic methods very effective. 122,127,146-152 Although much of the very recent activity in this area of fluoro-metal chemistry is devoted to studies related to kinetics 153 and magnetic properties, 154-157 a great deal of effort is still required for the search for direct, and easier to manipulate, synthetic procedures for the synthesis of novel fluoro and mixed-fluoro species,

Success has been achieved by other workers in the laboratory where the present work has been carried out in searching out simple and direct methods for the synthesis of fluoro-nickelates(II), 151,158 fluoromanganates(III), 122,127 and mixed fluoromanganates(III), 135,149 fluoro and mixed fluorocobaltates(II) 159 and also their structural assessment have been made. However, such
aspects of iron chemistry were unattended to. As a sequel of studies on fluoro and mixed-fluoro complexes of transition metals, and fluoro compounds of non-metals, viz., boron, phosphorus etc. as a part of a general programme of the laboratory, it was considered worthwhile to undertake such studies on iron so that the information obtained thereof would enrich the existing wealth of knowledge of fluoro metalate chemistry.

It is known that iron is the first row group VIII transition metal, fourth most abundant element in the earth's crust, occurring to the extent of \( \sim 5.1\% \). Besides its various utilities in industrial purposes, iron is by far the most widespread and important transition metal also with intrinsic functional role in living systems. Iron containing proteins participate in two main processes: oxygen transport and electron-transfer. Iron in the animal body is present as heme proteins which include hemoglobin in the blood, myoglobin and the heme enzymes, and in non-heme proteins as transferrin, ferritin, and hemosiderin. Iron also occurs in conjunction with molybdenum in enzymes that catalyse nitrogen fixation.

The metal has the ground state electronic configuration \([\text{Ar}]^3d^64s^2\) which can attain oxidation states ranging from -2 to +6. The lower oxidation states are generally found in the carbonyl, nitrosyl and organometallic derivatives of iron. Rather surprisingly the higher oxidation states of iron Fe(IV) \(d^4\), Fe(V) \(d^3\) occur when iron is in combination with oxygen but generally not with fluorine.
In aqueous solution, the principally occurring oxidation states of iron are +2 and +3. These two states of iron are the two important and relatively more studied oxidation states of the metal. Iron in its +3 state forms a large number of complexes, mostly octahedral ones, and the octahedron may be considered its characteristic co-ordination polyhedron. Iron (III) also forms complexes with co-ordination number ranging from 3 to 8 with various geometries.

The metal in its +3 oxidation state has the free ion electronic configuration in the ground state of 3d⁵. Most of the iron(III) complexes are high spin and in high-spin complexes (S = 5/2) this gives rise to ⁶S free ion ground term. Since this is the only sextuplet term arising from d⁵ and since this is not split in a crystal field all the terms of higher energy are of a different spin multiplicity to the ground term. All the electronic transitions are thus spin forbidden so that the ligand field bands in the spectra of these complexes are very weak. The magnetic properties of high spin iron(III) complexes of cubic symmetry are fairly straightforward. As the ground term is ⁶A₁, the magnetic moments are expected to be close to the spin only value of 5.92 \( \mu_B \) and to be independent of temperature and this is found to be the case experimentally for magnetically dilute complexes.

It has been established that like some other transition metals iron(III) also forms binary fluoro complexes. The affinity of iron(III) for \( F^- \) is quite high as shown by equilibrium
constants,\(^{169}\) which may also be accounted for by the hard acid
hard base concept.\(^{170}\) Three principal types of binary fluoro
complexes have been reported, viz., \(M^3_3\text{FeF}_6\), \(M^2_2\text{FeF}_5\cdot\text{H}_2\text{O}\), and
\(M^1\text{FeF}_4\).\(^{172}\) Typical members of the series are \(\text{NH}_4\text{[FeF}_4\text{]}\),
\((\text{NH}_4)_2\text{[FeF}_5\text{]}\), \((\text{NH}_4)_3\text{[FeF}_6\text{]}\). The corresponding salts of the
alkali metals and certain of the heavy metals, e.g. Tl, Co, Ni
are also known.\(^{145}\) In some cases salts of these types form
hydration, but in others water molecules make up part of the
complex, e.g. \(\text{Ag}_2\text{[FeF}_5\cdot\text{H}_2\text{O}].\text{2H}_2\text{O}\), \(\text{Tl}_2\text{[FeF}_5\cdot\text{H}_2\text{O}].\text{2H}_2\text{O}\).\(^{145}\) Also
the pentafluoroferrates(III) have shown very interesting magnetic
properties.\(^{154}\) The ready formation of stable fluoroferrate complexes
has important applications in analytical chemistry.\(^{145}\) If a
solution containing fluoride ions is added to a solution containing
a coloured ferric compound such as ferric thiocyanate the colour
of the latter decreases in intensity owing to the formation of the
stable \([\text{FeF}_6]^{3-}\) ion. In addition the position of the absorption bands is shifted to shorter wavelengths and are broadened.
The decrease in colour intensity is proportional to the fluoride
concentration and this bleaching effect forms the basis of a
colorimetric method for the determination of fluoride.\(^{145}\)

In the context of synthesis of the fluoro-compounds of
iron(III), the tetrafluoroferrates(III) are obtained from
aqueous hydrofluoric acid solutions by using 1:1 mole ratios of
the univalent cation and iron(III) fluoride.\(^{172}\) The pentafluoro-
ferrate(III) is the most easily accessible. The reactions between
iron(III) hydroxide and alkali-metal fluorides in aqueous hydro-
fluoric acid yields principally the aquopentafluoroferrate(III),
e.g. \(\text{Na}_2\text{[FeF}_5\cdot\text{H}_2\text{O}]\).\(^{173}\)
The hexafluoroferrate(III) compounds are magnetically dilute high spin complexes with room temperature magnetic moment of \(~5.9\mu_B\). The ammonium salt is cubic, while the potassium salt, \(K_3FeF_6\), has a slightly distorted cubic unit cell.\(^{174}\) To obtain the cryolite like hexafluoroferrate(III), the recommended method\(^{174}\) requires first the synthesis of the \([FeF_5]^{2-}\) complex, which on treatment with molten alkali-metal hydrogen fluoride, AHF\(_2\), yields the corresponding hexafluoroferrate(III), \(A_3[FeF_6]\). Moreover, it is mentioned in the literature\(^{175}\) that cryolite like compounds in general are difficult to obtain in a pure state directly from aqueous solution probably owing to the contamination of hydrates such as \(A_2MF_5\cdot H_2O\).\(^{175}\)

It is evident from the above discussion on fluoroferrates(III) chemistry that no direct and simple route to hexafluoroferrate(III) seems to be available thus limiting their accessibility. The currently used methods involve steps which require high temperature heating.\(^{174}\) Thus it is imperative and necessary to improvise suitable methods for the synthesis of alkali metal hexafluoroferrate(III).

When a solution contains a metal ion and at least two different ligands, there exists always a finite possibility of formation of a mixed-ligand complex. In view of the potential donating ability of many counter anions and solvents, there are very few cases indeed when this possibility is out of consideration.\(^{176}\) Various types of mixed-ligand complexes of different
metals have been studied, methods regarding the determination of their stability constants have been worked out in details, and their importance in chemical\textsuperscript{177,178} and by biosystems\textsuperscript{179,180} have been emphasised by others. The relationship between the stability of a mixed-ligand complex and its parent complex has been long disputed and it was thought that the mixed-ligand complexes are always more stable that could be expected on statistical grounds, but there are now many examples of the opposite behaviour. Statistically however mixed-ligand complex formation is always favoured,\textsuperscript{181} which has been later supported\textsuperscript{177} by elementary electrostatic consideration, steric effect and back co-ordination. A survey of literature shows that mixed ligand complexes of iron in its different oxidation states are known. However, one finds that there is a paucity of information regarding mixed-fluoro complexes of iron not only in its +3 but also in +2 oxidation states of the metal. It appears, therefore, that studies directed to mixed ligand fluoro complexes of iron(III) may generate some valuable information rendering it to be a rewarding aspect of investigation. A planning of synthetic strategies and working out of appropriate experimental conditions are important prerequisites for this.

Sulphate was thought to be an appropriate ligand for this purpose, because $SO_4^{2-}$ is an important spectroscopic probe amenable to direct structural assessment by IR and Raman spectroscopy. Also the corresponding fluoro-sulphato compounds of manganese(III) and cobalt(II), viz.,$A_2[\text{MnF}_3(SO_4)]$\textsuperscript{149} $A[\text{CoF}(SO_4)(H_2O)_2]$,$^{159}$
respectively, synthesised in the laboratory where the present work was carried out, have shown some interesting physical properties different from those of the corresponding parent binary fluoro complexes.

Strategically three different reaction pathways may be considered for the synthesis of fluoro(sulphato)iron(III) complex from an aqueous medium. These are:

(i) Direct reaction of sulphate and fluoride with iron(III) in an acidic medium.

(ii) In situ generation of $\text{SO}_4^{2-}$ by reacting $\text{H}_2\text{O}_2$ in the medium with $\text{SO}_2(g)$ and reaction of this with iron(III) and $\text{F}^-$ ion, already made available in the reaction solution.

(iii) Chemical oxidation of $\text{SCN}^-$ to $\text{SO}_4^{2-}$ by $\text{H}_2\text{O}_2$ in the presence of $\text{F}^-$ ions and iron(III).

In case strategy (iii) has to be exploited in the context of synthesis of fluoro-sulphato complexes of iron(III), evaluation of the optimum conditions for the hydrogen peroxide oxidation of thiocyanate to sulphate is the pre-requisite. It was known that hydrogen peroxide oxidation of thiocyanate in solution to yield sulphate is an electron-transfer reaction\textsuperscript{182} but the optimum conditions like pH, molar ratio between $\text{SCN}^-$ and $\text{H}_2\text{O}_2$ etc. required for the quantitative oxidation have not been known so far.

Accordingly, in line with the scope highlighted in the above discussion, studies involving fluoro and mixed-ligand fluoro
complexes of iron(III) were undertaken as the other part of the research programme. A new and direct method for the synthesis of $A_3[\text{FeF}_6]$ ($A = \text{NH}_4$, Na or K) from aqueous solution has been developed. Mixed-ligand fluoro-ferrate(III) compounds of the type $K_3[\text{Fe(SO}_4\text{)}F_4]$ and $(\text{NH}_4)_2[\text{Fe(SO}_4\text{)}F_3]$, have been synthesised for the first time and their structural assessment has been made by various physico-chemical techniques. Since a direct interaction of fluoride and $\text{SO}_4^{2-}$ with iron(III) did not lead to success, an indirect reaction involving the oxidation of SCN$^-$ with hydrogen peroxide in the presence of $\text{F}^-$ and iron(III) had to be adopted. In order to utilise the reaction of hydrogen peroxide oxidation of thiocyanate to $\text{SO}_4^{2-}$ in the context of synthesis of the afore mentioned complexes, optimum conditions for the quantitative conversion of SCN$^-$ into $\text{SO}_4^{2-}$ have been worked out. The knowledge obtained from this reaction was made use of for the synthesis of the above mentioned mixed-ligand fluoro complexes of iron(III), and the synthesis of the desired mixed-ligand complexes has been achieved from the reaction of SCN$^-$ and $\text{F}^-$ with iron(III) hydroxide and hydrogen peroxide. Chapter 6, indeed the concluding Chapter of the thesis contains the results of the afore-mentioned studies.

Chapters 3 to 6 present interpretative accounts of the results of studies on peroxo- and hetero-ligand-peroxovanadates(V) and fluoro and mixed-ligand fluoro complexes of iron(III). Each of these Chapters has been so designed as to make it a self-contained one with a brief introduction, sections on experimental, and results and discussion followed by relevant bibliography. Most of the new results have been published, while the rest are under communication.
REFERENCES


43. Ref. 8, p 519.


165. Ref. 163, p. 987.

166. Ref. 163, p. 989.

167. Ref. 163, p. 1049.

168. Ref. 163, p. 1048.


172. Ref. 163, p. 1046.


