Interest in the studies of the chemistry of dioxygen is one of the focal themes of current research.\textsuperscript{1,2} This is in part due to the fact that combining dioxygen with hydrocarbons is a rewarding goal, in that it provides a direct access to a number of valuable oxygenated products such as alcohols, ketones, epoxides, glycols, phenols etc. Millions of tons of oxygenated products are now produced annually all over the world by this method.\textsuperscript{3} Apart from this dioxygen plays a central role in living cells.\textsuperscript{3,4} It can either be transported by respiratory pigments, like hemoglobin, hemocyanin etc and released at the active sites, or activated in enzymatic systems called oxygenases such as cytochrome P450.\textsuperscript{4-8} At physiological temperature these oxygenases bring about important selective oxidations such as hydroxylation of hydrocarbons, epoxidation of alkenes, oxidative cleavage etc.

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 heterogeneously 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 dioxygen.\textsuperscript{1,9}
Fig. 1 Molecular orbital diagram for O₂
Owing to the importance of molecular oxygen as a reagent in biological and industrial processes, current research in this area has been directed not only towards the synthesis of metal-dioxygen complexes, but also towards understanding the bonding properties of dioxygen and its effect upon the extent to which the O=O bond of co-ordinated $O_2$ is activated.

The bonding in molecular oxygen is best described by MO theory. This theory describes the bonding as arising out of the combination of the valence orbitals of the two oxygen atoms ($2s^2 2p^4$) to give molecular orbitals, as shown in Fig. 1. The ground state is predicted to be a triplet state ($^3\Sigma^+$) with two unpaired electrons occupying a pair of degenerate $\pi^*$ anti-bonding orbitals and this also is observed to be true. The configuration and energies for the ground state and first two excited states are shown in Fig. 2. MO theory also predicts

\[
\begin{align*}
1\sum & \uparrow \downarrow \\
1\Delta & \uparrow \downarrow \\
3\sum & \uparrow \uparrow \downarrow \\
\end{align*}
\]

\[37.5 \text{ Kcal/mol}\]

Fig. 2 $\pi^*$ orbital occupancy and energies of the first two excited states of $O_2$

bond orders of 2.5, 2, 1.5 and 1 for the dioxygynyl cation $O_2^+$, molecular oxygen $O_2$, superoxide $O_2^-$, and peroxide $O_2^{2-}$, respectively. Some of the salient features for $O_2^+$, $O_2$, $O_2^-$ and $O_2^{2-}$ are summarised in Table 1.1.
Table 1.1 Some Properties of $O_2^+$, $O_2$, $O_2^-$ and $O_2^{2-}$

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond Order</th>
<th>Compound</th>
<th>$O-O$ distance (Å)</th>
<th>Bond Energy (Kcal/mol)</th>
<th>$\gamma(O-O)$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2^+$</td>
<td>2.5</td>
<td>$O_2$PtF$_6$</td>
<td>1.12</td>
<td>-</td>
<td>1905$^{11}$</td>
</tr>
<tr>
<td>$O_2$</td>
<td>2</td>
<td>$O_2$</td>
<td>1.207</td>
<td>117.2</td>
<td>1554$^{12}$</td>
</tr>
<tr>
<td>$O_2^-$</td>
<td>1.5</td>
<td>KO$_2$</td>
<td>1.28</td>
<td>-</td>
<td>1145$^{13}$</td>
</tr>
<tr>
<td>$O_2^{2-}$</td>
<td>1</td>
<td>Na$_2$O$_2$</td>
<td>1.49</td>
<td>35</td>
<td>842$^{14}$</td>
</tr>
</tbody>
</table>

Although the term molecular oxygen refers only to the free unco-ordinated $O_2$ molecule with the ground state configuration $^3\Sigma^+$, the term dioxygen has been used as the generic designation for $O_2$ moiety in any of its oxidation states and can be referred to $O_2$ in either a free or a combined state.$^{15}$ For use of this term it is essential that a covalent bond has to exist between the oxygen atoms. According to the rationalisation made by Vaska,$^{15}$ peroxo compounds involve co-valently bound dioxygen resembling $O_2^{2-}$ in peroxo configuration.

The way in which peroxo group is expected to bond to metals can range from symmetrical bidentate to a terminal monodentate position, including all the possible angles in between. The structural classification of dioxygen complexes, rationalised by Vaska$^{15}$ can be represented as shown in Fig. 3. The bridging peroxo could vary from cis-planar and trans-planar to trans-nonplanar configuration. An unusual symmetrical double
<table>
<thead>
<tr>
<th>Structural type</th>
<th>Structural designation</th>
<th>Vaska Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structural type" /></td>
<td>$\eta^2$ dioxygen</td>
<td>Type a (superoxo)</td>
</tr>
<tr>
<td><img src="image" alt="Structural type" /></td>
<td>$\eta^2$ dioxygen</td>
<td>Type IIa (peroxo)</td>
</tr>
<tr>
<td><img src="image" alt="Structural type" /></td>
<td>$\eta^1$: $\eta^1$ dioxygen</td>
<td>Type Ib (superoxo)</td>
</tr>
<tr>
<td><img src="image" alt="Structural type" /></td>
<td>$\eta^1$: $\eta^1$ dioxygen</td>
<td>Type IIb (peroxo)</td>
</tr>
<tr>
<td><img src="image" alt="Structural type" /></td>
<td>$\eta^2$: $\eta^2$ dioxygen</td>
<td>-</td>
</tr>
<tr>
<td><img src="image" alt="Structural type" /></td>
<td>$\eta^1$: $\eta^2$ dioxygen</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 3. Structural Classification of dioxygen complexes
bridging was also found,\textsuperscript{16,17} however, such examples are very rare. Deviations from the ideal symmetry are also observed very often.

In case of non-metal peroxo compounds, however, peroxo group is found to be bonded mainly in two different fashions, viz. terminal monodentate\textsuperscript{18,19} (i.e. end-on) and bridging trans-planer configuration,\textsuperscript{18,20-23} although in some cases, for example in peroxoborates, peroxo group has been shown to be bonded in a triangular bidentate manner.\textsuperscript{24} In addition peroxo group is also capable of being bonded as a hydroperoxide as observed in the cases of peroxo monocarbonate\textsuperscript{18} and peroxo-monosulphate.\textsuperscript{19}

Vibrational spectroscopy is 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} All the three IR active modes are also Raman active. The three modes are: Peroxo stretching ($A_1$) and symmetric and asymmetric M-O$_2$ stretching $A_1$ and $B_2$. The $\nu$(O-O)($A_1$) band is the most sensitive and intense one, and characteristically occurs between 800 and 950 cm$^{-1}$, but generally observed below 900 cm$^{-1}$. The frequency of this band remains fairly independent of the heteroligand environment but is effected by the mass of the central ion, indicating some degree of coupling of the $\nu$(O-O) with M-O$_2$ vibrations. For the compounds where a peroxo group (O$_2^{2-}$) is bonded in an end-on fashion, the (O-O) stretching frequency occurs at ca
900 cm\(^{-1}\), however, for complete characterisation labelling studies are generally recommended.\(^{26}\)

Simple peroxy compounds are those which contain peroxides, hydroperoxides, and water molecules. Whereas hetero ligand peroxy compounds contain one to three co-ordinated peroxy groups and one or more monodentate or polydentate ligands. Hetero ligands may vary from monodentate ions to bulky porphyrins (F\(^-\), Cl\(^-\), NH\(_3\), C\(_2\)O\(_4\)^2-, SO\(_4\)^2-, CO\(_3\)^2-, PPh\(_3\), EDTA, O-phen, Oxine, Porphyrins, Pyridine-2,6-dicarboxylic acid etc.).\(^{27}\)

Peroxy compounds can be synthesised either by activation of oxygen or by the interaction of peroxyxide with the appropriate starting material.\(^{28}\)

The stability of peroxy complexes is generally enhanced by hetero ligand environment.\(^{27}\) Many simple peroxides often explode spontaneously, some are sensitive to shock or decompose above 0°C, and several do not exist at all as stoichiometric compounds,\(^{29}\) but many hetero ligand peroxy complexes, on the other hand, survive recrystallisation from boiling aqueous solutions, heating \textit{in vacuo}, and remain unchanged for prolong periods in closed containers.\(^{27,30}\)

Peroxy complexes besides having an intrinsic interest of their own\(^{9,31-53}\) constitute an important class of reactive intermediates in catalytic oxidations\(^{54-59}\) and are involved as potential oxygen-donors in the oxygen transfer reactions to organic substrates including hydrocarbons.\(^{54}\) Moreover, the research leading to gain an insight into the roles of peroxy-
transition metal compounds in the storage and transport of
oxygen and oxidase functions in biological systems is of grow-
ing interest.\textsuperscript{28,56,60-66} The importance of neutral dioxygen
complexes in biochemistry is well known,\textsuperscript{60} but the biochemical
connection of the metal peroxy complexes with biological pro-
cesses is not very well understood. The metals Sc, Ti, V, Cr,
Y, Nb, Mo, La, Hf, Ta, W,\textsuperscript{28} and U\textsuperscript{67} form stable hetero ligand
peroxy complexes and evidences show that some of these metals
have significant biological roles.\textsuperscript{3,68-72}

It is somewhat surprising, however, that information on
the peroxy-chemistry of heavier metals and actinides are rather
scanty as opposed to a host of reports on peroxy-complexes of
lighter transition metals covering a wide range of studies,
namely synthesis, characterisation, reactivity,\textsuperscript{1-3} crystal
structure determination\textsuperscript{73-76} and some biochemical aspects.\textsuperscript{77}

A perusal of peroxy-element chemistry further reveals that
this particular aspect of non-metals did not receive due atten-
tion and comparatively a very little is reported about non-metal
peroxy compounds. Some peroxy-compounds of non-metals like
peroxodicarbonates,\textsuperscript{78} peroxyomonocarbonates \textsuperscript{78}
peroxodisulphates\textsuperscript{79,80} peroxyomonosulphates,\textsuperscript{81,82} peroxydiphosphates\textsuperscript{83} and peroxymono-
phosphoric acid\textsuperscript{83} are known and are widely used\textsuperscript{84-92} in laboratory
as well as in industry, but generally methods of their synthesis
are cumbersome.

As a case in point, phosphorus, having the atomic number
15 and the atomic weight 30.97, belongs to group V of the periodic
The elements of this group, namely nitrogen, phosphorus, arsenic, antimony and bismuth are sometimes known as pnictides. In a general sense the chemistry of phosphorus resembles that of arsenic much more closely than that of nitrogen. The stable isotope $^{31}\text{P}$ has a nuclear spin of $\frac{1}{2}$ and constitutes 100% of the naturally abundant species. There are six unstable isotopes of the element ($^{28}\text{P}, ^{29}\text{P}, ^{30}\text{P}, ^{32}\text{P}, ^{33}\text{P}, ^{34}\text{P}$) known which have very short half lives. The electronic structure of phosphorus atom is $1s^2, 2s^2, 2p^6, 3s^2, 3p^3$ with three unpaired electrons in the outer 3p orbitals which are available for chemical bonding. Phosphorus can thus be formally trivalent or pentavalent, using only three or all the five electrons, respectively, in the outer shell to form covalent linkages to other atoms.

Interestingly phosphorus is a vital element in the composition of all living matters and there is no known organism in which the chemistry of the element is not utilised. The human body contains about 1% by weight of the element with about four-fifth of this being present as hydroxyapatite in bones and teeth. Many of the most essential chemicals in life processes are phosphate esters. These include the nucleic acids like DNA and RNA, as well as adenosine monophosphate (AMP). The transfer of phosphate groups between ATP and ADP is a fundamental process in the energetics of biological systems.

Our interest in the studies of peroxo-element chemistry led us to look into the literature pertaining this aspect of phosphorus chemistry. As mentioned in passing that somewhat like carbon and sulphur, phosphorus is also known to form a few
peroxo compounds. The most well documented among them are peroxo-
monophosphoric acid\(^95\) in solution and peroxodiphosphates, \(\text{A}_4\text{P}_2\text{O}_8\),
in addition to a poorly characterised unstable peroxide, \(\text{P}_2\text{O}_6\),\(^96\)
and a diperoxophosphate.\(^95\) Between the two namely peroxomonophosphoric acid and peroxodiphosphates, the latter are rather
well characterised. Synthesis of non-metal peroxo compounds in
general and peroxophosphates in particular involves either an
electrochemical reaction\(^83\) or a complicated chemical method.\(^83\)

Although the importance of peroxomonophosphoric acid has
been highlighted in the literature,\(^97,98\) it is not very easy to
obtain. Further free peroxomonophosphoric acid does not permit
its isolation easily. Accordingly the acid is generated only in
solutions for any investigation. The first report of peroxomonophosphoric acid dates back to 1910\(^99\) and since then various
techniques for its preparation,\(^98,100\) and results of studies
of decomposition mechanism,\(^101\) and dissociation constants\(^102,103\)
have been reported. A scrutiny of the reported methods of gener-
ating the acid clearly shows that while some of the procedures
afford an impure product,\(^86\) the others are capable of producing
a pure 2\(\text{M}\) solution of peroxomonophosphoric acid.\(^98,100\) However,
the latter methods require highly concentrated hydrogen peroxide
(80-95%) that is not very commonly available thus limiting an
accessibility of the acid. It is noteworthy that no salt of the
\(\text{FO}_3\left(\text{C}_2\right)^{3-}\) ion, but for an acid salt \(\text{KH}_2\left[\text{FO}_3\left(\text{C}_2\right)^{-}\right]\) is
reported.\(^97\) The acid salt \(\text{KH}_2\left[\text{FO}_3\left(\text{C}_2\right)^{-}\right]\) has been prepared from
the interaction of \(\text{P}_4\text{C}_{10}\) with 84% \(\text{H}_2\text{O}_2\) in the presence of 43%
KOH solution\(^97\) by conducting the reaction in a perhalogenated
solvent.\(^97\)
Despite the difficulties in obtaining peroxomonophosphoric acid, it has drawn quite a lot of attention especially because of its versatile oxidising potentialities. Thus, the acid has been shown to oxidise aromatic amines to nitro compounds,\textsuperscript{89} and alkenes to epoxides.\textsuperscript{86} It is known to cause aromatic hydroxylation\textsuperscript{85} and Baeyer-Villiger reaction of acetophenone\textsuperscript{88} and diacetals.\textsuperscript{104} It has also been demonstrated that the acid is capable of oxidising inorganic species like Mn\textsuperscript{2+} \textsuperscript{99} and I\textsuperscript{-} \textsuperscript{99} to permanganate and iodine, respectively.

In addition to all that have been mentioned so far regarding peroxophosphates, there is another important aspect which deserves a due consideration. This addresses to peroxo-(fluoro)phosphates. In addition to a few fluorinated peroxides of carbon and sulphur,\textsuperscript{105} which were generally synthesised by fluorination of oxo-compounds of the corresponding elements, one also finds a mention of two peroxo-(fluoro)phosphoric acids viz., H$_2$PO$_2$(O$_2$)F and H$_2$P$_2$O$_4$(O$_2$)F$_2$ in the literature. It was reported over half-a-century ago\textsuperscript{106} that anodic oxidations of fluorophosphoric acids produced the peroxo-(fluoro)phosphoric acids H$_2$PO$_2$(O$_2$)F and H$_2$P$_2$O$_4$(O$_2$)F$_2$, only in ca.2% yields. The compounds are very poorly characterised and to our knowledge neither any salts of the acids nor any chemical syntheses of fluorinated peroxophosphate is reported until date.

\textit{In an appreciation of the interesting properties of peroxo-compounds of phosphorus,}\textsuperscript{84-92} studies of peroxo-
chemistry of the element was considered to be worthwhile and rewarding area of investigation despite the acknowledged difficulties in getting access to this field. Following selective aspects were identified as a part of the present Ph.D research:

(i) Synthesis, characterisation, and assessment of structure of alkali metal and ammonium peroxomonophosphate, \( A_3 \left[\text{PO}_3(O_2)\right] \) \( (A = \text{alkali metal or ammonium}) \), and studies of reactivities to explore their efficacy as good oxidants; and

(ii) Chemical synthesis, isolation in the solid state, and evaluation of structure and properties including reactivity of fluorinated peroxophosphate.

Accordingly, such studies were undertaken and a good amount of success achieved. Chapter 3 of the thesis presents an account of the first synthesis, characterisation, and assessment of structure and properties of sodium and ammonium peroxomonophosphate trihydrates, \( A_3 \left[\text{PO}_3(O_2)\right] \cdot 3\text{H}_2\text{O} \) \( (A = \text{Na or NH}_4) \). Sodium peroxomonophosphate trihydrate, \( \text{Na}_3 \left[\text{PO}_3(O_2)\right] \cdot 3\text{H}_2\text{O} \), was chosen as a representative example and a number of oxidation reactions have been conducted with particular emphasis on exploration of its capability as a viable substitute for the basic-\( \text{H}_2\text{C}_2 \) reagent. Also included in the same Chapter are the first chemical synthesis of a fluorinated peroxophosphate, ammonium fluoroperoxomonophosphate dihydrate, \( (\text{NH}_4)_2 \left[\text{PO}_2(O_2)\right] \cdot 2\text{H}_2\text{O} \), its characterisation, and the results of studies of reactivity as an oxidant for organic substrates.
Quite interesting was the phosphorous product isolated after working up of the oxidation product of the reactions that were conducted involving \((\text{NH}_4)_2\text{PO}_2(\text{O}_2)F_\cdot2\text{H}_2\text{O}\). This was identified as the monofluorophosphate, \(\text{PO}_3\text{F}^\text{2-}\), and the species generated interest in us particularly because of its acknowledged use as an additive in dentifrice formulations for the inhibition of dental caries. Looking back into the relevant literature, it was evident that there did not exist any simple and easily accessible route to alkali metal and ammonium monofluorophosphates, \(A_2\text{PO}_3\text{F}\) \((A = \text{alkali metal or NH}_4\)\), although they have been known for quite sometime.\(^{107-111}\) The recommended methods\(^{107-111}\) for their synthesis involve either a high temperature fusion reaction, or fluorophosphoric acid as the starting material which requires extra preparation and purification, in addition to one or more steps to remove unwanted products, inevitably formed in either of the methods, to obtain the pure products. Thus while studying the other aspects of the chemistry of phosphorous, we sought for an easy access to alkali metal and ammonium monofluorophosphate. Chapter 4 of the thesis deals with the direct synthesis of ammonium monofluorophosphate monohydrate, \((\text{NH}_4)_2\text{PO}_3\text{F}\cdot\text{H}_2\text{O}\) and potassium monofluorophosphate, \(K_2\text{PO}_3\text{F}\), their characterisation and properties, and also highlights the advantages of the new method over those previously reported.

Quite apart from the studies of chemistry of phosphorous, research involving peroxo-chemistry of transition metals has emerged out as one of the most exciting and important areas of investigation in contemporary inorganic chemistry.\(^{1-4,64-75,112}\)
A number of research groups round the world have engaged their attentions on various aspects of peroxo-metal chemistry, and consequently a remarkable amount of significant informations are now available in the literature especially on these aspects of lighter metals. Contrary to a host of reports on different aspects of peroxo-compounds of lighter transition metals, however, reports on the corresponding aspects of their heavier congeners are scanty. As a case in point, for example, although a variety of investigations have been carried out on the peroxo-titanium chemistry, peroxo-zirconium chemistry has received far less attention. Success has been achieved by other workers, of the laboratory, where the present research has been carried out, in their endeavours related to synthesis, characterisation, and evaluation of structures of a host of hetero-ligand-peroxo titanates(IV), and a good number of new compounds of this type have been prepared and newer synthetic strategies developed. The heteroligands were drawn from $F^-$, $Cl^-$, $SO_4^{2-}$ etc. It was also possible to synthesise a few molecular hetero ligand peroxo-titanium(IV) compounds like $\left[\text{Ti}(O_2)_2(L-L)\right]$ ($L-L = 1,10$-phenanthroline, $2,2'$-bipyridine), and $\left[\text{Ti}(O_2)_2(tu)\right]$ ($tu = thiourea$). To our knowledge, information on similar studies on the zirconium chemistry is only very scant.

It may be mentioned in passing the metal zirconium occurs widely on the earth's crust but not in very concentrated deposits. The major minerals are baddeleyite, $\text{ZrO}_2$ and zircon, $\text{ZrSiO}_4$. Because of the effects of lanthanide contraction both the atomic
radii of zirconium and hafnium, the radii of Zr⁴⁺ and Hf⁴⁺ ions are virtually identical, and accordingly they tend to display a similar chemistry. The chemical similarity of zirconium and hafnium is well exemplified in the context of their geochemistry. The metal of our interest at this juncture is zirconium which shows a spectrum of oxidation states ranging from zero to +4.

One of the most striking differences of the chemistry of zirconium from that of titanium is that the lower oxidation states of zirconium are of minor importance. There are few authenticated compounds of the element except those of its tetravalent ones. Zirconium(IV) oxide, ZrO₂, is more basic than TiO₂ and is virtually insoluble in an excess of base. There is, however, a more extensive aqueous chemistry of the metal because of its lower tendency towards complete hydrolysis. Nevertheless hydrolysis does occur and it is very doubtful indeed if Zr⁴⁺ aquo ions exist even in strongly acid solutions. The hydrolysed ion is often referred to as the "zirconyl" ion and written ZrO²⁺.

Our specific interest in the peroxo-zirconium chemistry led to a survey of the relevant literature. It is evident from the literature that zirconyl salts are known to form hydrated peroxides ZrO(O₂)(H₂O)ₓ¹₂⁰ and peroxo-salts K₄Zr(O₂)₄(H₂O)₆, K₄Zr₂O₁₁(H₂O)₉¹₂⁰ which have been isolated. In addition, there are claims for the existence of ZrO(O₂)₂⁻ in strong alkali and species with peroxo: Zr ratios of 1:1 and 0.5:1 in acid (2N HCl)solutions.¹²⁰ Moreover a series of products were reported in somewhat older literature¹²¹ to be obtained from zirconium sulphate-hydrogen peroxide solutions at different pH values:
$\text{Zr}_2\text{O}_3\text{S}_4\text{(H}_2\text{O})_{8-10} (\text{pH} = 0.1-0.7)$, $\text{Zr}_3\text{O}_3\text{S}_4\text{(H}_2\text{O})_{9-12} (\text{pH} = 2.0)$ and $\text{Zr}_2\text{O}_2\text{S}_4\text{(H}_2\text{O})_{3-6} (\text{pH} = 2.2)$, and cyclic structures were proposed involving two or three zirconium atoms bridged by peroxo and sulphate groups. Only a few peroxo compounds of zirconium are reported in the literature. Later on a few peroxo-fluorozirconates(IV), peroxo sulphato and peroxo oxalatozirconates(IV), and neutral peroxozirconium(IV) complexes containing organic ligands such as, picolinic acid, amino carboxylic acids etc. have been synthesised, and with these the history of peroxo-zirconium chemistry more or less ended. It is noteworthy that practically very little is known regarding reactivity of peroxo-zirconium compounds.

It is thus evident from an overview presented above that various aspects of peroxo-chemistry of zirconium not only need a great deal of work to be accomplished but also require a rather systematic approach in order to gain a clear and a deeper insight.

In view of the above and as a part of a general programme of the research group, it was imperative to undertake investigations on peroxo-zirconium chemistry. The specific aim was to evaluate conditions appropriate for the synthesis of peroxo-fluorozirconates(IV) containing both one and two peroxo groups per metal centre in addition to one or more coordinated fluoride ligands. It was also our contention to compare the results with
those of titanium,\textsuperscript{116,117} a congener of zirconium and to comment on this aspect of chemistry of the two metals.

Accordingly such work was undertaken and an interpretative account of the results of studies involving peroxyfluoro-zirconates(IV) has been presented in Chapter 5 of this thesis.

Like titanium and zirconium, actinides are known to form simple peroxides,\textsuperscript{130,131} but because of the highly complicated nature,\textsuperscript{130} peroxy-chemistry of actinides has been far less dealt with compared to that of lighter metals. As a case in point, for instance, uranium is known to form a host of simple peroxides, but its hetero-ligand-peroxy-chemistry has been practically overlooked in earlier investigations.\textsuperscript{130,131}

Uranium, the fourth element in the actinide series having ground state electronic configuration $[\text{Rn}7f^36d^17s^2]$, is the heaviest element to occur in nature, in recoverable amounts, and its isotopes are all $\alpha$-emitters, occuring in the proportions $^{238}\text{U} \ 99.28\%$, $^{235}\text{U} \ 0.71\%$ and $^{234}\text{U} \ 0.005\%$.\textsuperscript{131} The chemistry of the element shows considerable difference from the earlier actinides of the series. Stable oxidation states of the metal range progressively from $+3$ to $+6$, with the corresponding $f^n$ configuration ranging from $f^3$ to $f^0$. The most stable oxidation state of uranium is its hexavalent state, and the ligands which stabilise this particular oxidation state of the metal include halides, nitrate, carboxylates, sulphate, $\beta$-diketonates, and peroxides etc. In simple compounds the hexavalent state occurs only in hexafluoride, $\text{UF}_6$, and hexachloride, $\text{UCl}_6$,\textsuperscript{132} and the
principal chemistry of the +6 state in solid as well as in solution is that of the dioxo cation, $\text{UO}_2^{2+}$, which forms stable complexes with neutral or anionic ligands. The +5 oxidation state of the metal is stable only in dilute acidic solution and in the presence of organic complexing agents. The oxo-cation $\text{UO}_2^+$ as such is normally not stable in an aqueous solution, as it undergoes rapid disproportionation. In the tetravalent state, $\text{U}^{4+}$ ion is stable only in the absence of air or any other oxidising agents, whereas in the trivalent state $\text{U}^{3+}$ ion is produced in solutions by the action of powerful reducing agents, but is very susceptible to oxidation. The oxo ions are evidently linear in crystalline compounds as well as in solutions. The uranyl ion, $\text{UO}_2^{2+}$, characteristic of its +6 state, forms a great variety of complexes with anionic ligands and neutral molecules. Some of these complexes are important from the point of view that, they may have applications in solar energy conversion system, due to their inherent spectral properties, and may be of potential use in photogeneration of oxygen, which is of great importance for the photo cleavage of water. Structural information of the uranyl complexes based on crystallographic data shows that four, five or six atoms can lie in the equatorial plane of O–U–O group with the ligand atoms may or may not be entirely coplanar depending on the circumstances. Planar 5 and 6 co-ordination in the equatorial plane are most common and appear to give geometry more stable than the puckered hexagonal configuration. Planar 5-co-ordination best allows ratio-
lisation of a number of hydroxides and other structures, as well as the behaviour of polynuclear uranyl ion in hydrolysed solutions, and the complex ion $\text{UO}_2(\text{CH}_3\text{COO})_3^-$ represents a typical example of the planar 6-co-ordination in the equatorial plane of the O-U-O ion.

In an aqueous solution, uranyl salts give an acid reaction due to hydrolysis, and the main hydrolysed species of $\text{UO}_2^{2+}$ ion at ca. 25°C are $\text{UO}_2\text{OH}^+$, $\text{UO}_2(\text{OH})_2^{2+}$, and $\text{UO}_2(\text{OH})_5^+$, but the system is a complicated one, with the monomer being a predominant species at higher temperatures. The solubility of large amounts of $\text{UO}_3$, in $\text{UO}_2^{2+}$ solutions is also attributed to the formation of $\text{UO}_2\text{OH}^+$ and polymerised hydroxo bridged species.

Thus, it is evident from the foregoing discussion, that the chemistry of hexavalent uranium is mainly that of the uranyl ion. As mentioned earlier, peroxide ($\text{O}_2^{2-}$) acts as a stabilising ligand for uranium and the metal is known to form peroxo compounds in its highest oxidation state. The complexity involved in peroxo-uranium chemistry is an acknowledged problem, and the system is exceedingly complicated owing to the formation of a host of different peroxouranate(VI) species with a slight variation of pH of the reaction medium. Peroxouranates containing $\text{O}_2^{2-}$:U as 1:1, 1:2, 2:1, 3:1, 3:2, and 5:2 have been described in the literature in addition to a few more which were rationalised only on the basis of peroxide to uranium ratio. Among these peroxouranates, however, $\text{UO}_2(\text{O}_2)\cdot n\text{H}_2\text{O}$ (n = 2 or 4) appears to be the best characterised one. This species has been
known since 1876, and was also a subject of extensive investigations. Nevertheless its constitution was not well established for a long period, since different groups described it in different manners, e.g. true peroxide hydrate or a peroxide having the composition $U_2O_7$, a peroxy acid or an addition compound of uranium oxide, $UO_3 \cdot H_2O \cdot H_2O$. Finally Gordon and Taube showed it to be a true peroxide hydrate on the basis of their isotopic tracer studies on thermal decomposition of uranium-peroxide systems.

Albeit formation of simple peroxides of uranium as evident from the above discussion, but its heteroligand peroxy chemistry seems to be rather poorly investigated. Despite a long history of peroxy-uranium chemistry, earlier reports on heteroligand peroxouranates are rather scanty, except for some carbonato and oxalato peroxouranates, and a few fluoro peroxyuranates. In addition to these there are some reports on the studies of uranyl ion-hydrogen peroxide systems in solution containing ligands like ethylenediamintetra-acetic acid (EDTA), citric acid and fluoride etc. Relatively recent reports on heteroligand peroxouranates include a few nonelectrolytic peroxyuranates of the type $\left[ UO_2(O_2) \right]_2$ (L = Ph$_3$PO, Ph$_3$AsO, Py-N oxide or quinoline N-oxide), and a unique $\mu_2$-peroxo bridged complex benzyl-trimethyl ammonium $\mu_2$-peroxo bis $\left[ \text{trichlorodioxouranate(VI)} \right]$. The above mentioned chloroperoxo complex is one of the rare examples of a complex containing a dioxygen molecule being bonded as a $\mu_2$-peroxo group. In addition, subsequently in 1981 a few more novel mono and diperoxo
complexes of $\text{UO}_2^{2+}$ containing organic ligands have been reported.\textsuperscript{152} Apart from these, there are two more reports on the synthesis and characterisation of peroxofluoro\textsuperscript{67,153} and peroxocarbonato\textsuperscript{154} uranates(VI) from the laboratory where the present work has been carried out.

In view of the above discussion, and also taking note of some of the recent results on hetero-ligand peroxy complexes of other metals,\textsuperscript{2,116-118,154-157} it appeared that suitable chosen hetero-ligands, under appropriate experimental conditions, could impart stability to peroxy metal systems and permit their isolation in the solid state. This led us to carry out synthesis and structural assessment of some hetero-ligand peroxy-complexes of $\text{UO}_2^{2+}$ as a part of the present Ph.D. research programme. The chosen hetero-ligands include oxalate ($\text{C}_2\text{O}_4^{2-}$) and ethylenediaminetetra-acetic acid (EDTA).

While another colleague\textsuperscript{153} was engaged in the work involving dioxoperoxo(sulphato)uranates(VI) as a part of his assignment, attention of the present worker was directed to the synthesis, characterisation, and structural assessment of a molecular peroxy complex, dioxoperoxo(ethylenediaminetetra-acetic acid)Uranium(VI), $\text{UO}_2\text{(C}_2\text{O}_4\text{(EDTA))}$, to improvise a direct route to dioxoperoxo(oxalato)uranate(VI), and to rationalise the modes of bonding of $\text{O}_2^{2-}$ and $\text{C}_2\text{O}_4^{2-}$ with the $\text{UO}_2^{2+}$ centre, and to make an internal comparison of the results to correlate with that of the previously reported
Chapter 6, indeed the concluding Chapter of the thesis, deals with the studies made on complex peroxouranates.

While the present Chapter gives a non-exhaustive background information pertaining the kind of work chosen for the present Ph.D. research and highlights the scope of work in the field, Chapter 2 provides details of the methods of elemental analyses and particulars of instruments/equipment used for characterisation and structural assessment. Chapters 3 to 6 incorporate the results of studies on the chosen problems viz: peroxo-, peroxo(fluoro)- and fluorophosphates, and complex peroxozirconates and complex peroxouranates. Chapters 3 to 6 have been so designed as to make each of them a self-contained one with a brief introduction, sections on experimental and results and discussion followed by relevant bibliography. A good part of the new results has been published, while rest is under communication.
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