Boron is the fifth element in the Periodic Table and only non-metal of Group-III having the ground state electronic configuration $\text{He}^2 2s^2 2p$. It is the only non-metal that is 'electron deficient' and this confers a property on it leading to multicentre bonding.\(^1\) It occurs as a trace element in most soils, and is present in sea-water to the extent of a few parts per million. Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is the principal source of boron and is present in hot springs and lakes in volanic region. Natural boron has two stable isotopes $^{10}\text{B}$ and $^{11}\text{B}$, occurring in the ratio of 19.6 and 80.4, respectively. Boron is invariably present in the component of all animal tissues and plays an essential role in the nutrition of higher plants.\(^2\) While pure boron has practically no applications, its compounds find a wide range of uses. Boric acid is used as an antibacterial, and uses of borates as wood-preservatives and in the preparation of borosilicate glasses are well-known. The isotope $^{10}\text{B}$ is used as a control in nuclear reactors and also a neutron detector. Despite the $2s^2 2p$ electronic configuration, boron displays a valency of three in all its compounds. The trivalency is achieved
by promoting one of its $2s^2$ electrons to a $2p$ orbital: $1s^22s^22p \rightarrow 1s^22s2p^2$. It requires further two electrons to complete the rare gas configuration which it is ready to accept from another molecule or ion. In doing so, boron compounds behave as Lewis acids. Owing to a strong diagonal relationship, the chemistry of boron shows a close resemblance to Si than that of the other elements of the group: Al, Ga, In and Tl.

Being close to carbon in the first row of the Periodic Table, boron is also capable of forming stable bonds with those atoms which constitute most organic compounds. The chemistry of organoboron compounds started enjoying a continued interest following the discovery of the "inorganic benzene" borazine and the subsequent preparation of various organic borazine derivatives. The majority of organoboron compounds contain trigonal planar boron and a wide variety of examples within this category are supplied by orthoborates $B(OR)_3$, where $R$ can be an alkyl or aryl group. Organoboron compounds have an extensive chemistry and the research on this aspect of boron chemistry has undoubtedly opened up new horizons and this still continues to be a promising area of research. Many organoboron compounds are used as additives to lubricating oils and certain types of fuel and as components in the preparation of azo dyes. The therapeutical and industrial applications of organoboron compounds are well known. Some of them exhibit bacterial and insecticidal properties as well. However, this manifestation of boron chemistry has not been elaborated herein as our present interest pertains to studies involving non-organoboron compounds.
Unlike the other elements in the Periodic Table, the inorganic chemistry of boron has become more diverse and complex because of combination of some unique properties. The chemical properties of boron is influenced primarily by its small size and high ionisation potential (8.296 ev/atom). Thus the total energy required to produce $\text{B}^{3+}$ ions is far more than would be compensated by the lattice energies of ionic compounds. Consequently, simple electron loss to form a cation does not play any part in the chemistry of boron. Instead, covalent bond formation is of prime importance and all of its compounds are predominantly covalent. These factors coupled with the similarity in electronegativity of boron and hydrogen and a high affinity of the element for oxygen form the basis of an extensive area of research on boron chemistry. As mentioned earlier that boron never occurs as the free element and all naturally occurring boron compounds contain boron-oxygen links. Thus the B-O chemistry is the oldest branch of boron chemistry. Boron is rather inactive to attack by chemical reagents. The predominant characteristic of reagents which attack boron is their ability to form B-O bonds. As noted above, the high affinity of the element for oxygen is the basis of formation of a vast number of borates. The range of structures adopted by borates in the solid state include both trigonal planar ($\text{BO}_3$) and tetrahedral ($\text{BO}_4$) units. An interesting aspect of boron chemistry is marked by its ability to form polymeric species in which the trimeric $\text{BO}_3$ rings are fused to other units at tetrahedral boron atoms forming a complex polyanion through linking together of $\text{BO}_3$ and $\text{BO}_4$ units by shared common oxygen atoms. Amongst a number of
polyborates pentaborates form an interesting class of compounds in the field of B-O chemistry primarily because of their structural peculiarities. Potassium pentaborate dihydrate, $K\left[\text{B}_5\text{O}_6\text{(OH)}_4\right]\cdot 2\text{H}_2\text{O}$, which has enjoyed the privilege of having been attended to by several workers, $^{10-12}$ appears to be the best characterised one. This complex species has been known since 1855 $^{13}$ and has served as a subject of several investigations ever since. The reported method of its preparation requires either a drastic condition $^{13}$ or the involvement of an appreciable amount of fluoride. $^{12}$ In view of this, it was considered necessary to try for an alternative general synthetic route to potassium and ammonium pentaborate dihydrates without using any drastic conditions, and also without involving $\text{F}^-$ ions because fluoride is also a good ligand for boron. Accordingly, such studies were undertaken as a part of the research programme. Synthetic strategy was planned and potassium and ammonium compounds of the complex anion $\left[\text{B}_5\text{O}_6\text{(OH)}_4\right]^- $ were synthesised, characterised, and identity established.

The chemistry of trivalent boron is governed by the effect of the vacant $p_z$ orbital which gets involved either in intramolecular $(p-p)\Pi$ bonding or multicentre bonding or reactions with lone pairs of electrons on other molecules. One of the important points of its chemistry that deserves a special attention is the ready formation of fluoro compounds. $\text{BF}_3$ is one of the best examples of this category in which boron is so close to be coordinatively saturated that it occurs as a gas with a very low condensation temperature. Because of the donor properties of fluoride it is notable that a $\text{BF}_3$ molecule does not undergo dimerisation probably owing to formation of internal
dative \( \Pi \)-bonding of the molecule. The vacant \( p_z \) orbital of boron may interact with a filled \( p_\pi \) orbital of fluoride to give a B-F \( \Pi \) bond which would then be stabilized to monomeric form as a result of resonance. Since there are six electrons around the boron atom in the planar BF\(_3\) molecule, it shows a strong tendency to accept a pair of electrons making a total of 4 pairs of electrons, with each of them being directed from the central B atom toward the corners of a tetrahedron. BF\(_3\) is a powerful acceptor molecule and under suitable conditions reaction of the kind \( \text{BF}_3 + F^- \rightarrow \text{BF}_4^- \) occurs to afford the stable complex species, the tetrafluoroborate. It is noteworthy that tetrafluoroborate ion, BF\(_4^-\), undergoes partial hydrolysis in aqueous solution forming hydroxofluoroborate anions \( \text{BF}_n(\text{OH})_{4-n}^- \). This kind of reaction was first demonstrated by Berzelius 160 years ago. \(^{14}\) The syntheses and studies of properties of various complexes derived from the anions have engaged the attention of several groups of workers \(^{15-19}\) over the years. A survey of literature provides evidences for the existence of hydroxo(fluoro)borates, fluoro(hydroxo)oxoborates \(^{20,21}\) and oxo(hydroxo)borates \(^{10,11}\) in aqueous solutions as ascertained from the results of physico-chemical studies. In addition, investigations concerning kinetic behaviours of mixed fluoroborates and polyborates have received a considerable attention presumably again owing to their structural importance. \(^{10-12,22,23}\) In order to obtain further insight into this aspect of boron chemistry, synthesis of such compounds is the pre-requisite. In view of this and also taking note of the fact that fluoro(hydroxo)borate moiety exists in solutions \(^{20,21}\) it is quite rational to anticipate that such species can be isolated
in the solid state by proper choice of experimental conditions. This would also enable one to make an assessment of their structures and study their properties. Taking into consideration of the information gathered from the preceding discussion and also as a sequel to the efforts of other investigators\textsuperscript{24-28} of the laboratory, in which the present work was carried out, involving the studies of fluoro element chemistry, it was considered that investigations involving synthesis, characterisation, and structural assessment of newer fluoro compounds of boron would be quite rewarding. Accordingly, such studies were undertaken and hitherto unknown potassium and ammonium compounds of the complex $\left[ \text{B}_2\text{O}_2\text{F}_2(\text{OH})_2 \right]^{2-}$ ion have been prepared and characterised. The appropriate experimental conditions to isolate them in the solid state have also been worked out. Chapter 3 of the thesis presents an account of the results of these studies together with those of potassium and ammonium salts of the complex pentaborate, $\left[ \text{B}_5\text{O}_6(\text{OH})_4 \right]^{-}$ ion.

Besides oxide and fluoride, peroxide ($\text{O}_2^{2-}$) also constitutes a good ligand for boron and the chemistry of peroxoborate appears to be quite exciting although studied much less exhaustively by earlier workers. Reaction of borates with hydrogen peroxide or of boric acid with sodium peroxide is now a textbook story\textsuperscript{29} and the product obtained thereof forms an important oxidising component in many detergents because it affords hydrogen peroxide in solution which makes cleansing effect more powerful. The crystal structure of the aforesaid compound has been shown to contain the $\left[ \text{B}_2(\text{O}_2)_2(\text{OH})_4 \right]^{2-}$ anion, with two peroxo groups bridging the
tetrahedral boron atoms. It is evident from literature that the reported existence of any heteroligand peroxoborate remains unprecedented.

Simple peroxo complexes are those which contain peroxides, hydroperoxides, and water molecules. The heteroligand-peroxo complexes are mixed-ligand peroxo complexes containing one or more than one peroxo groups, one or more monodentate or polydentate ligands. Heteroligands may range from monodentate ions to bulky porphyrins. The stability of peroxo complexes is generally enhanced by specific heteroligand combinations. Many simple peroxides undergo spontaneous explosion, some are very sensitive to shock or decompose above 0°C, while several do not exist at all as stoichiometric compounds. On the other hand, many heteroligand peroxo complexes are appreciably stable so that they can be recrystallised even from boiling aqueous solutions, heated in vacuo and remain unchanged for prolong periods in closed containers. Accordingly, a considerable amount of success has been achieved in obtaining stable heteroligand peroxo compounds of metals in recent years providing scopes for further studies involving them. We were unable to discern any obvious reason as to why heteroligand peroxo compounds of boron have not been synthesised. As a case in point, for example, both fluoride (F-) and peroxide (O2^2-), independent of each other, are capable of formation of compounds with the element; thus it is quite rational to expect that under suitable experimental conditions both the aforesaid ligands can be simultaneously brought to co-ordination with boron. It is quite evident therefore that studies involving peroxofluoroborates would be a rewarding area of new
research warranting attention. In view of the above non-exhaustive
discussion, studies on peroxofluoroborate chemistry were undertaken
and a few compounds of the types \( A_2 \left[ B(O_2)F_3 \right]_7 \cdot 4H_2O \) (\( A = \text{Na or K} \))
and \((\text{NH}_4)_2 \left[ B_2(O_2)_3F_2 \right] \) have been synthesised, characterised,
and an assessment of their structures has been made. Chapter 4
of the thesis presents the results of our investigations relating
to peroxofluoroborate chemistry.

Apart from the studies of boron chemistry, investigations
concerning heteroligand-peroxo compounds of titanium in terms of
their methods of syntheses, characterisation, reactivity, and
structural elucidation constitute one of the frontier areas of
research on titanium chemistry. \(^{33-38}\)

Titanium is the first row group IVB transition metal, ninth
most abundant element and constitutes about 0.63% by weight of the
earth's crust. Besides its manifold uses in industries and in
laboratories, \(^{39}\) some of its compounds have also been used as model
systems in research related to bio-inorganic chemistry. \(^{36}\) The metal
has the ground state electronic configuration \( \left[ \text{Ar} \right] 3d^2 4s^2 \) and
exhibits oxidation states ranging from -1 to +4. Of these, +4 state
is the commonly encountered and most stable oxidation state of the
metal. Compounds in the lower oxidation states undergo ready oxidation
by air, water or other reagents to titanium(IV). The lower oxidation
states of the metal are stabilised generally by \( \Pi \)-acidic type of
ligands as it happens with other metals. The highest oxidation state
of the metal, behaving as a Lewis acid, is found in compounds which
contain strong electronegative ligands like fluoride, oxide, sulphate,
peroxide etc.
The aqueous chemistry of titanium(IV) seems to have received relatively less attention despite its continued interest. Though it has been claimed that titanium(IV) compounds in an aqueous acidic solution contain the 'titanyl', $\text{TiO}_2^+$, ion yet the question about the existence of this ion remained as a matter of prolonged dispute. However, some recent publications have confirmed the occurrence of monomeric structures of titanium(IV) compounds with terminal $\text{Ti=O}$ ('titanyl') unit. The presence of this core has also been established in aqueous acidic solutions by indirect techniques such as ion exchange, potentiometric titration, electromigration, and kinetic studies of electron-transfer and complexation reactions, and in some solid compounds by X-ray crystallographic studies. The 'titanyl' ion, $\text{TiO}_2^+$, has also been shown to form some compounds with different ligands where titanium(IV) is usually in 6- or 7-coordination. An important point about the oxotitanium(IV) complexes which also deserves a comment is that the $\text{TiO}_2^+$ group occurs not only in its monomeric form but also as a polymer with $-\text{Ti-O-Ti-}$ interactions.

It has been known for over a century that characteristic colour reactions may take place when hydrogen peroxide is added to solutions of transition metal derivatives, and some peroxo-transition metal compounds have been isolated in the solid state. Peroxo-metal compounds, besides having an intrinsic interest of their own, are of considerable and growing importance particularly in relation to the catalysis of oxidation including hydrogen peroxide itself, and the storage and transport of oxygen in biological systems. Some transition metal peroxide compounds
are also used as reagents for epoxidation of olefins, and hydroxylation of alkenes, and aromatic hydrocarbons.\textsuperscript{30,72,73}

Although the term molecular oxygen refers to the free uncombined \(O_2\) molecule with the ground state \(^3\Sigma_g^-\), the term dioxygen has been used as a characteristic designation for the \(O_2\) moiety in any of its several forms, and can refer to \(O_2\) in either a free or a combined state.\textsuperscript{74} For use of this term, the existence of a covalent bond between the two oxygen atoms is essential. Thus, a metal-dioxygen complex refers to a metal containing \(O_2\) group co-ordinated 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 coordinated dioxygen resembles a peroxide \((O_2^{2-})\) anion.\textsuperscript{70} A common characteristic of these complexes is the O-O distance, which lies between 1.40 and 1.52\(\text{Å}\) (1.49\(\text{Å}\) for \(O_2^{2-}\)), and the corresponding infrared frequency \(\nu(\text{O-O})\) which occurs between 800 and 950 cm\(^{-1}\) (802 cm\(^{-1}\) for \(O_2^{2-}\)).

As mentioned in passing while discussing the chemistry of boron, earlier in this section, that heteroligand peroxo complexes are mixed-ligand complexes and the stability of peroxo complexes is enhanced to a great extent by specific heteroligand combinations. The importance of peroxo-metal complexes in the biochemical field and its significance have been duly emphasised in the contemporary literature.\textsuperscript{30-32,35,36,71,75-78} The reactivity of peroxides,\textsuperscript{38,73} and the lability of metal-oxygen bonds in special heteroligand environments in solutions are of particular interest in biochemistry, but are not easy to assess directly.
A comparison between the peroxo and unreduced dioxygen heteroligand complexes reveals that the chemistry of the two shows a marked difference owing to the presence of two extra electrons in the antibonding $\sigma^*_{\text{PTf}}$ orbitals of the peroxide ion ($O_2^{2-}$). The electron rich $O_2^{2-}$ ion therefore preferably forms complexes with metal ions of low $d^n$ electronic configuration, while the neutral dioxygen molecule favours higher $d^n$ metal acceptors. However, these two oxygen species have at least two things in common: (i) both are stabilised by specific heteroligand spheres, and (ii) 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 still not very well understood.

Molecular oxygen is a paramagnetic molecule having a $^{3}\Sigma_g^-$ ground state, and a molecular orbital description is

$$O_2 \text{KK} (2s\sigma^g)^2 (2s\sigma_u^{-})^2 (2p\sigma^g)^2 (2p\Pi_u)^4 (2p\Pi^* g)^1 (2p\Pi^* g)^1$$

where KK term indicates that the K shells of two oxygen atoms are filled. The two unpaired electrons in the $^{3}\Sigma_g^-$ ground state occupy one each of the two degenerate antibonding $2p\Pi^* g$ orbitals, leaving $O_2$ with a formal bond order of two (Fig 1-1). The addition of one and two electrons to a neutral $O_2$ results in the formation of super-oxide ($O_2^-$) and peroxide ($O_2^{2-}$) species, respectively, leaving $O_2^-$ with a bond order of 1.5, and the $O_2^{2-}$ with a bond order of one. The way in which a peroxo group is expected to coordinate to metals
can range from a symmetrical bidentate to a terminal monodentate position, including all possible angles in between. The structural classification of dioxygen complexes can be represented as follows (Fig. 1-2) in terms of Vaska's rationalisation:74
<table>
<thead>
<tr>
<th>Structural Type</th>
<th>Structural Designation</th>
<th>Vaska Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Diagram 1]</td>
<td>(\eta^1) dioxygen</td>
<td>Type Ia (superoxo)</td>
</tr>
<tr>
<td>![Diagram 2]</td>
<td>(\eta^2) dioxygen</td>
<td>Type IIa (peroxo)</td>
</tr>
<tr>
<td>![Diagram 3]</td>
<td>(\eta^1 : \eta^1) dioxygen</td>
<td>Type Ib (superoxo)</td>
</tr>
<tr>
<td>![Diagram 4]</td>
<td>(\eta^1 : \eta^1) dioxygen</td>
<td>Type IId (peroxo)</td>
</tr>
<tr>
<td>![Diagram 5]</td>
<td>(\eta^2 : \eta^2) dioxygen</td>
<td>-</td>
</tr>
<tr>
<td>![Diagram 6]</td>
<td>(\eta^1 : \eta^2) dioxygen</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 1-2 Structural Classification of dioxygen complexes

The bridging \(\mu\)-peroxo could vary from cis-planar and trans-planar to trans-nonplanar configurations. An unusual symmetrical double bridging was also found, however, such structures are very rare. Deviations from the ideal symmetry are often encountered. In the case of
heteroligand fields the deviations are due to the inherent symmetry of different ligands. Additional ππ* electron delocalisation to the metal ion is anticipated which would therefore favour a d⁰ or a low dⁿ metal ion configuration. The stereochemical polyhedra in heteroligand peroxo complexes are often fairly predictable. The pentagonal bipyramidal arrangement is the most common for transition metal complexes, in oxo-peroxo heteroligand surroundings, usually with two coordinated peroxo groups in cis-position and the oxo group in the axial position. This kind of structures are often observed for many peroxo-vanadate(V) complexes.

Infrared spectroscopic studies are essential for the characterisation and structural assessment of peroxo-metal complexes and Raman spectroscopic studies not only complement but also augment the results of IR studies. The peroxo metal complexes involving a metal and a peroxide ligand bonded in a triangular bidentate manner would be expected to give rise to three vibrations of symmetry species (2A₁ + B₂), and these may be designated as ̅υ₁ (A₁; O=O stretching), ̅υ₂ (A₂; symmetric metal-peroxide stretch) and ̅υ₃ (B₂; asymmetric metal-peroxide stretch). All the three modes are both IR and Raman active. While the A₁ modes are polarised, the B₂ modes are depolarised. The ̅υ (O=O) band is the most sensitive and intense one and characteristically occurs between 800 and 900 cm⁻¹. The heteroligand environment does not cause any appreciable change in the frequency of this band, but is sometimes affected by the mass of the metal centre indicating coupling of the ̅υ (O=O) with M-O₂ vibrations. The co-ordination of O₂⁻ groups in a triangular bidentate
manner is by far the most common and is similar to the one proposed by Griffith \(^9^9\) for the bonding of \(O_2\) in oxyhemoglobin. It is imperative to mention here that Raman spectroscopy can also be easily applied to solutions, and the results of such studies provide further information concerning the identity and structure of a complex species in solution.

The reaction between titanium(IV) and hydrogen peroxide was first recognized in 1870 by Schoenn. \(^9^0\) It produces an intense orange colour and therefore the reaction has always served as a sensitive test for the detection of either reagent. Although some solid peroxotitanate(IV) complexes were documented in relatively older literatures, there is little agreement over their composition let alone their structures. The complexity in peroxotitanate(IV) chemistry is an acknowledged problem. \(^9^1\) and the system becomes more complicated owing to the formation of different peroxotitanate(IV) species with a variation of pH of the reaction medium. Thus the deep orange colour produced by the addition of hydrogen peroxide to an acidic titanium(IV) solution starts turning pale ultimately becoming colourless with the hike of pH of the reaction medium. A perusal of literature further reveals that heteroligand-peroxotitanium(IV) chemistry have received a relatively less attention and reports on heteroligand peroxotitanates(IV) are rather scanty, except for a few sulphato-, chloro-, and fluoro-peroxotitanates(IV). \(^9^2\) Among the fluoro-peroxotitanates(IV), however, \(A_3\left[\text{Ti}(O_2)F_5\right]\) \((A = Li, Na, K \text{ or } NH_4)^9^2\) appears to be the best characterised one and is the most often quoted example of a typical peroxotitanate(IV) compound. The procedure recommended and currently used for the preparation of alkali pentafluoro...
titanates(IV), \( A_3 \left\{ Ti(O_2)F_5 \right\} (A = Li, Na, K \text{ or } NH_4) \), requires the \( \left\{ TiF_6 \right\}^{2-} \) complex as an essential precursor, which results in an extra preparation step. In order to overcome the existing problem involved in the recommended method of synthesis, a simple and a direct general synthetic route to alkali pentafluoroperoxotitanates(IV), \( A_3 \left\{ Ti(O_2)F_5 \right\} \) appears to be highly desirable. Within the context of the chemistry of peroxotitanates(IV), to our knowledge there is no reported evidence of any diperoxotitanate(IV) complex in the solid state although some other members of the first-row transition series form a number of well-defined diperoxo compounds.\(^{82,93-96}\) Some of the rather old reports have argued for the existence of diperoxotitanate(IV) in solution.\(^ {91,97}\) We were unable to find out any convincing reason for the absence of information regarding the synthesis of any diperoxotitanate(IV) complex in the solid form. Studies in the aforementioned directions were therefore warranted. As already mentioned that the colour of titanium(IV)-hydrogen peroxide system depends heavily on the pH of the reaction solution resulting in the formation of different complex peroxotitanate(IV) species in solution. In this context it appeared quite rational to study the effect of variation of pH, keeping the heteroligand unchanged, on the composition of solid product isolated at different stages. Such studies can be envisaged at least in two different ways, viz., (1) by gradually increasing the pH of the reaction solution and isolating the product at different pH, and (2) by first raising the pH into an alkaline range followed by lowering it down to an acidic region. Accordingly, reactions among titanium(IV), hydrogen peroxide and \( F^- \) have been studied at different pH leading us to the direct
synthesis of alkali pentafluoroperoxotitanates(IV), $A_3 \sum \text{Ti}(O_2)F_5$ (A = Na, K or NH$_4$), synthesis of a new potassium monoperoxo-trifluorotitanate(IV) trihydrate, $K \sum \text{Ti}(O_2)F_3 \cdot 3H_2O$, and first synthesis of potassium and ammonium diperoxo difluorotitanates(IV), $A_2 \sum \text{Ti}(O_2)_2F_2$ (A = K or NH$_4$). A detailed account of the results of afore-mentioned investigations constitute the subject matter of Chapter 5 of the present thesis.

As a sequel to our studies on the chemistry of heteroligand peroxotitanates(IV), we were also curious to investigate the mode of binding of sulphate with titanium(IV) in the complex formed in the reaction with hydrogen peroxide in the presence of SO$_4^{2-}$. It is now an evidenced fact that the mode of binding of SO$_4^{2-}$ with transition metal in the presence of O$_2^{2-}$ ligand is not always similar — sometimes it is co-ordinated to the metal centre, either as a chelated ligand or as a bridging group, $^{98-101}$ while in a number of cases it is unable to enter into the coordination sphere and occurs as an ionic species. $^{102}$ With a view to getting an insight into the peroxotitanate(IV) chemistry, studies involving heteroligand diperoxo compounds of titanium(IV) have been identified as an aspect demanding a relatively greater attention. Strategically, this could be achieved through the synthesis, characterisation, and structural assessment of a number of compounds with varying heteroligands, viz., sulphate, N-heterocyclic ligands, and thiourea etc.
Peroxometal compounds are potential oxygen donors to organic substrates and are generally used for the epoxidation of olefines. The recent use of a peroxo compound of titanium(IV) as a catalyst in organic synthesis is an example of the utility of transition metal peroxides. In view of this, it was considered important to obtain molecular mixed-ligand diperoxo compounds of titanium(IV) in the solid state so that such compounds might serve as good candidates for studies of catalytic oxidations in terms of activation of the O-O bond of co-ordinated dioxygen.

Keeping the above in view a systematic study involving synthesis, characterisation, and structural assessment of heteroligand diperoxotitanates(IV) was undertaken as a part of the present research programme and hitherto unknown alkali diperoxomonosulphatotitanates(IV) tetrahydrates, \( A_2 \left[ \text{Ti(O}_2 \right]_2 \text{SO}_4 \text{H}_2 \text{O} \) \((A = \text{K or NH}_4)\), and three molecular mixed-ligand diperoxo compounds of titanium(IV) of the types \( \left[ \text{Ti(O}_2 \right]_2 (\text{L-L}) \text{H}_2 \text{O} \) \((\text{L-L} = 1,10\text{-phenanthroline or 2,2\text{-bipyridine}})\), and \( \left[ \text{Ti(O}_2 \right]_2 (\text{thiourea}) \text{H}_2 \text{O} \) have been synthesised. Chapter 6 of the thesis describes the results of our afore-mentioned studies.

Although solid peroxo complexes of both titanium and vanadium can be synthesised from aqueous solutions, there exists a marked difference in the types of the compounds obtained thereof. Whereas most of the reported peroxo complexes of vanadium are oxo-peroxo species, the corresponding compounds of titanium(IV) are very sparse. To our knowledge, the only
reported example of such a compound, that has been also charac-
terised crystallographically, is $K_2\left[\mathrm{Ti}_2\mathrm{O}(\mathrm{O}_2)\right]_2\left(\text{dipic}\right)_2$\(^{108}\) albeit a few non-peroxo compounds containing $\text{TiO}^{2+}$ moiety are known.\(^{54,55,109}\) Nevertheless, it appears generally accepted that oxo-titanates(IV) are quite rarely encountered. That titanium(IV) compounds in aqueous acidic solutions contain the 'titanyl' moiety and that the ion $\text{TiO}^{2+}$ is the main species of titanium present in such solutions are now certain.\(^{45,46}\) The structural unit of monomeric titanium(IV) oxo-compounds contains a $\text{Ti}=\text{O}$ ('titanyl') core,\(^{45,46,55}\) while those of polymeric complexes contains oxo-bridged ($\mu$-oxo) species through $\text{-Ti-O-Ti-}$ interactions.\(^{44,110}\) However, the question of a possibility of existence of oxo-peroxotitanate(IV) complexes containing a 'titanyl' moiety in aqueous acidic solution and isolation of any product from such solutions has not been addressed before. In view of this, it was considered important to first explore the possibility of existence of an oxo-peroxo-
titanate(IV) species in solution followed by isolation of the product and making an assessment of its structure. In order to get a further insight into the chemistry of peroxotitanate(IV) complexes, studies involving such compounds of titanium(IV) appeared to be a fascinating aspect of investigation. A planning of synthetic strategies and working out of appropriate experi-
mental conditions are important pre-requisites for this. Such studies have also been carried out as a sequel to our endeavour in this field, existence of oxo-peroxotitanate(IV) in solution has been demonstrated, and potassium oxoperoxodichlorotitanate(IV)
monohydrate, $K_2\left[\text{TiO(O}_2\text{)}\text{Cl}_2\right]_7\cdot H_2O$, has been obtained in the solid form. The structural assessment of the compound has been made by various physico-chemical techniques. The results of the above-mentioned investigations have been incorporated in Chapter 7 of the present thesis.

Interest in the field of chemistry of fluoro-containing transition metal compounds seems to be never diminishing. This field of transition metal chemistry continues to attract much attention and produces new and exciting results. Peculiarities of such compounds particularly in respect of their magnetic and structural behaviours probably make them relatively more interesting than those containing other halides. Some of the inherent properties of fluorine, e.g., its very high electronegativity and small ionic size render it suitable for stabilising higher oxidation states of metals. Applications of such compounds as insulators and semiconductors impart a further importance to the studies involving them. Consequently there has been a considerable growing interest in the research relating to the synthesis, and studies of properties, and structures of fluoro compounds of transition metals.

Like many other transition metals, titanium also forms oxofluorotitanates(IV), although information on such compounds are restricted to only a few reports. The complex $\left[\text{TiOF}_5\right]^{3-}$ is probably the most well characterised oxofluoro complex of titanium(IV) though $\left[\text{TiOF}_3\right]^{-}$ has a reported existence. In addition to these two complex species evidences concerning
oxotetrafluorotitanates(IV), $\left[ \text{TiOF}_4 \right]^{2-}$, are also documented in the literature.\textsuperscript{125-128} However, despite a number of attempts made by earlier workers\textsuperscript{125-128} synthesis of pure $\left[ \text{TiOF}_4 \right]^{2-}$ could not be successfully achieved. The complex in each case was contaminated with other products of titanium. Studies on this still appear to be continued. In a recent investigation involving a high temperature thermal decomposition of a peroxo complex $K_2 \left[ \text{Ti}(O_2)F_4 \right]$, $K_2 \left[ \text{TiOF}_4 \right]$ has been obtained as one of the main products. Here again, contamination of the product stood in the way of obtaining a pure compound. This drew our attention and it was considered imperative to develop a suitable synthetic route to pure oxotetrafluorotitanate(IV), $\left[ \text{TiOF}_4 \right]^{2-}$, complex. Investigation of the spectroscopic properties of such compounds is expected to yield some valuable information regarding their structures. In view of the preceding discussion, studies on oxotetrafluorotitanates(IV) were undertaken and a new synthetic route to pure $A_2 \left[ \text{TiOF}_4 \right]$ ($A = K$, Cs or $\text{NH}_4$), has been developed. The compounds have been characterised and an assessment of their structure made. Chapter 8 of thesis contains the results of the afore-mentioned studies.

The new results reported in the present thesis have been broadly divided into two parts viz., Part A and Part B. While Part A of the thesis, consisting of Chapters 3 and 4, presents the work on boron chemistry, Part B, comprising of Chapters 5, 6, 7 and 8, deals with the results of studies involving the chosen aspects of titanium chemistry. 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. Some of the new results have been published, some are now in press, while the rest are under communication.
References


14. Ref 9, p 886.
29. Ref. 9, p 887.


56. (a) Ref 39, p 811.


91. Ref 57, p 286.
92. Ref 58, p 378.


CHAPTER 2
Methods of Elemental Analyses and Particulars of Instruments/Equipment Used for Characterisation and Structural Assessment of Compounds

The methods employed for the quantitative determination of various constituents, and the relevant particulars of the instruments/equipment used for the characterisation and structural assessment of the newly synthesised compounds are given in this Chapter.

Elemental Analyses

Boron

(i) Determination of boron gravimetrically as nitron tetrafluoroborate

In a typical procedure, an accurately weighed amount of the boron compound was dissolved in water and the solution was treated with 20-25 cm$^3$ of 0.1N NaOH solution in order to decompose the compound. The mixture was heated for ca 10 to 15 min on a steam-bath to ensure complete decomposition. The solution was filtered, and the filtrate was collected in a polyethylene beaker. The filtrate was diluted to about 60 cm$^3$ with distilled water and acidified with dilute (5N) sulphuric acid using methyl red as the indicator. To it was added 15 cm$^3$ of 10% nitron reagent followed
by the addition of 2 cm$^3$ 48% hydrofluoric acid with stirring until the precipitate ceased to appear. The solution was allowed to stand overnight and then cooled in an ice-bath for ca. 2h. The precipitate was filtered on a weighed porcelain crucible and washed well (5 to 6 times) with saturated nitron tetrafluoroborate solution, and finally dried to constant weight by heating at 105-110°C. The precipitate was weighed as C$_{20}$H$_{16}$N$_4$·HBF$_4$.

The above mentioned method was used for the estimation of boron in alkali-metal and ammonium peroxofluoroborate complexes.

(ii) Determination of boron as boric acid$^{1b}$

An accurately weighed amount of the boron compound was transferred quantitatively to a 250 cm$^3$ volumetric flask, and the volume was made up to the mark. An amount of 25 cm$^3$ of this solution was titrated with standard 0.1(N) hydrochloric acid using methyl orange as indicator. To another amount of 25 cm$^3$ of the solution was added the quantity of standard hydrochloric acid determined in the previous titration followed by the addition of 2g of mannitol and shaken well until dissolved, and a few drops of phenolphthalein was also added. It was then titrated with standard sodium hydroxide solution until a faint but permanent pink colour appeared.

1 cm$^3$ 1N NaOH solution $\equiv$ 0.06184g of $\text{H}_3\text{BO}_3$
The method described above was used for the determination of boron contents in pentaborate and fluoro(hydroxo)oxoborate compounds.

Titanium

Titanium was estimated gravimetrically as titanium dioxide.

In a representative procedure, an accurately weighed amount of the titanium compound was dissolved in a minimum volume of dilute (2N) hydrochloric acid and from which titanium was precipitated out as hydrated titanium oxide by the addition of a dilute sodium hydroxide solution. The precipitate was separated by filtration, washed several times with water to make it free from alkali, and then dissolved in 3(N) hydrochloric acid. To the clear solution thus obtained was added a slight excess of a freshly prepared 6% aqueous solution of cupferron with stirring until the curdy precipitate ceased to appear. The precipitate was then filtered off on a filter paper. The precipitate along with the filter paper was transferred in a large crucible and was cautiously ignited with a gradual increase in temperature to constant weight. Titanium was finally weighed as TiO₂.

Active Oxygen (Peroxo Oxygen)³⁻⁵

(i) Permanganometry³

An accurately weighed amount of the peroxo-boron or the peroxo-titanium(IV) compound was dissolved in 7(N) sulphuric acid containing ca 4g of boric acid. Boric acid was used to
prevent any loss of active oxygen through the formation of peroxoboric acid. The resulting solution was then titrated with a standard potassium permanganate solution.

\[
1 \text{ cm}^3 \text{ of } 1\text{N KMnO}_4 \equiv 0.01701g \text{ of } H_2O_2
\]

This method is suitable for the determination of peroxide contents of peroxo-boron as well as of peroxo-titanium(IV) compounds.

(ii) Iodometry\textsuperscript{4}

In a freshly prepared 2(N) sulphuric acid solution, containing an appropriate amount of potassium iodide (ca 1g in 100 cm\textsuperscript{3}), was added an accurately weighed amount of the peroxo-boron or peroxo-titanium(IV) compound with continuous stirring. The mixture was allowed to stand for ca 10 min in CO\textsubscript{2} atmosphere in the dark. The liberated iodine was then titrated with a standard sodium thiosulphate solution, adding 2 cm\textsuperscript{3} of freshly prepared starch solution when the colour of the iodine was nearly discharged.

\[
1 \text{ cm}^3 \text{ of } 1\text{N Na}_2S_2O_3 \equiv 0.01701g \text{ of } H_2O_2
\]

(iii) Determination of Peroxide (O\textsuperscript{2−}) by Titration with a standard Ce\textsuperscript{4+} solution\textsuperscript{5}

An accurately weighed amount of the peroxo-titanium(IV) compound was dissolved in a 2(N) sulphuric acid solution in the presence of an excess of boric acid (ca 5g). Peroxide was then determined by titrating with a standard Ce\textsuperscript{4+} solution.
Fluoride

An accurately weighed amount of a fluoroborate or a fluorotitanate(IV) compound was dissolved in water and the solution was treated with alkali (e.g. sodium hydroxide) in order to decompose the compound. The mixture was heated over a steam-bath for ca 10 min to ensure complete decomposition. Titanium in a fluorotitanate was precipitated as hydrated titanium oxide, and separated out by filtration, and washed several times with water. The filtrate and washings were collected for fluoride estimation. In the case of boron compounds, the solution was straightway used for the estimation of fluoride. To the combined filtrate and washings in the case of titanium compounds and to the solution in place of boron compounds, 2 to 3 drops of bromophenol blue indicator and 3 cm$^3$ of 10% sodium chloride solution were added and the whole was diluted to about 250 cm$^3$. Dilute nitric acid was added to it until colour changed to just yellow, followed by the addition of dilute sodium hydroxide solution until the colour ultimately just changed to blue. The mixture was subsequently treated with 1 cm$^3$ of concentrated hydrochloric acid and 5.0g of lead nitrate, and heated on a steam-bath. After all the lead nitrate had dissolved, 5.0g of crystallised sodium acetate was added to the solution and the solution was digested on a steam-bath for about half an hour with occasional stirring. The whole was allowed to stand overnight.
For the gravimetric estimation, the precipitate lead chloride fluoride, PbClF, was filtered through a weighed Gooch crucible (grade 4) and weighed as PbClF after drying at 140-150°C to constant weight. In the volumetric estimation, the precipitate PbClF was quantitatively collected by filtration through a Whatman 542 filter paper and washed once with cold water, then 3 to 4 times with saturated solution of lead chloride fluoride, and finally once more with cold water. The precipitate was dissolved in 100 cm$^3$ of 5% (v/v) nitric acid by heating over a steam-bath for 4-5 min. A known excess of saturated 0.1N silver nitrate solution was added to it, followed by digestion on a steam-bath for 30 min, and then cooled at room temperature in the absence of light. The precipitated silver chloride was filtered through a sintered glass crucible and washed with cold water. The unreacted silver nitrate in the filtrate and washings was titrated with a saturated 0.1N potassium thiocyanate solution using 1 cm$^3$ of ferric ion indicator solution until one drop of thiocyanate solution produced a permanent faint brown colour. The amount of silver nitrate in the filtrate, thus found, was subtracted from that originally added, and the content of fluoride was calculated from the amount of silver nitrate consumed.

1 cm$^3$ of 1N AgNO$_3$ $\equiv$ 0.0190g of F
Chloride

An accurately weighed amount of the chlorotitanate(IV) compound was treated with 25 cm$^3$ of water and was dissolved completely by the addition of a few drops of dilute nitric acid solution. The clear solution thus obtained, was treated with dilute sodium hydroxide solution followed by heating the mixture over a steam-bath for ca 15 min for complete decomposition. Titanium in the compound was precipitated as hydrated titanium oxide which was separated out by filtration and washed several times with water. The filtrate and washings were collected for chloride estimation. To the combined filtrate and washings 5 cm$^3$ of 6N nitric acid and a known excess of saturated 0.1N silver nitrate solution were added, and the whole was stirred well until the coagulation of the precipitate was complete. The precipitated silver chloride was filtered through a sintered glass crucible and washed thoroughly with very dilute nitric acid (1:100). The unreacted silver nitrate in the filtrate and washings was titrated with a saturated 0.1N potassium thiocyanate solution using 1 cm$^3$ of ferric alum indicator until one drop of the thiocyanate solution produced a permanent faint brown colour. The amount of silver nitrate in the filtrate, thus found, was subtracted from that originally added, and the content of chloride was then calculated from the amount of silver nitrate consumed.

$$1 \text{ cm}^3 \text{ of } 1\text{N } \text{AgNO}_3 \equiv 0.03546\text{g of Cl}$$
A known amount of the sulphotitanate(IV) compound was treated with 25 cm$^3$ of water and was dissolved completely by the addition of a few drops of dilute HNO$_3$ solution. A 30% solution of sodium hydroxide was added to the above solution slowly with stirring and the mixture was heated over a steam-bath for ca 30 min. The precipitated hydrated titanium oxide was separated by filtration and carefully washed 2-3 times with cold water. The combined filtrate and washings was concentrated by boiling and neutralised with dilute nitric acid (volume of the solution was ca 230 cm$^3$). This was acidified by the addition of 0.3-0.6 cm$^3$ of concentrated HCl solution and heated to boiling. A warm solution (10-12 cm$^3$) of 5% barium chloride (5g BaCl$_2$·2H$_2$O in 100 cm$^3$ of water) was added from a burette or a pipette drop by drop with continuous stirring, and the resultant precipitate was allowed to settle for ca 2 min. The supernatant liquid was tested for complete precipitation by adding a few drops of barium chloride solution. The process was repeated until a slight excess of barium chloride was present in the mixture to ensure complete precipitation. The mixture was kept covered over a steam-bath for 1h in order to allow time for complete precipitation of BaSO$_4$. The precipitated barium sulphate was filtered through a previously weighed sintered glass crucible (grade 4) using gentle suction. The precipitate was washed with warm water until the filtrate gave no precipitate with a few drops of silver nitrate solution. The crucible with its content was dried at ca 110°C and heated for
10-15 min at a higher temperature (ca 600°C) followed by cooling in a desiccator. The ignition process was continued until constant weight was attained.

The sulphate content of the sample was finally weighed as BaSO₄.

**Sodium and Potassium**

Sodium and potassium contents were determined by flame photometry. A solution containing sodium or potassium ions was acidified with hydrochloric acid. The acidified solution thus obtained was then used for flame photometry.

**Carbon, Hydrogen, and Nitrogen**

Carbon, hydrogen, and nitrogen were estimated by micro analytical methods. The results of analyses were obtained from Amdel Australian Micro Analytical Service, Port Melbourne, Victoria 3207, Australia, and also from Micro Analytical Laboratories, Regional Sophisticated Instrumentation Centre, NEHU, Shillong 793003.

**Particulars of Instruments/Equipment Used**

**pH Measurement**

The pH of the reaction solutions, whenever required, were measured by using a Systronics Type 335 digital pH meter (and also by BDH indicator paper).
Molar Conductance

Molar conductance measurements were made using a Philips PR 9500 conductivity bridge and also by a Systronics Type 304 digital conductivity bridge.

Magnetic Susceptibility

The Gouy method was used to measure the magnetic susceptibility of the complexes. The compound Hg[Co(NCS)$_4$]$_2$ was used as the standard for calibration.

Infrared Spectra

Infrared spectra were recorded on the following spectrophotometers:
(a) Perkin-Elmer Model 297
(b) Perkin-Elmer Model 983

Laser Raman Spectra

Laser Raman (IR) spectra were recorded on a SPEX Ramalog Model 1403 Raman Spectrometer. The 4880ÂÅ or 5145ÂÅ laser line from Spectra-Physics Model 165 Argon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube, followed by photon-count processing system.

The sample was held either in a quartz capillary or in the form of a pressed pellet. In some cases solution spectra were also recorded. The recording was done at ambient temperatures.
ESR Spectra

ESR spectra of polycrystalline solid compounds were recorded using a Varian E109, X-band ESR spectrometer with 100K modulator.
References


2. Ref 1, p 544.

3. Ref 1, p 295

4. Ref 1, p 363.

5. Ref 1, p 325.

6. (a) Ref 1, p 569.
   (b) Ref 1, p 269.

7. Ref 1, p 266.

8. Ref 1, p 463.
CHAPTER 3
A New Route to Potassium and Ammonium Pentaborate Dihydrates,
\[ A \left[ B_5O_6(OH)_4 \right] \cdot 2H_2O \ (A = \text{K or NH}_4), \] and Synthesis and Structural Assessment of New Fluoro(hydroxo)oxoborate Dihydrates,
\[ A_2 \left[ B_2O_2F_2(OH)_2 \right] \cdot 2H_2O \ (A = \text{K or NH}_4) \]

The tetrafluoroborate, \( BF_4^- \), and its hydroxy derivatives have a long history and syntheses and studies of properties of various complexes derived from the anions have received a considerable attention over the years.\(^1\)\(^-\)\(^6\) Interest in the studies involving polyborates and mixed fluoroborates has been highlighted in Chapter 1. Potassium pentaborate dihydrate, \( K \left[ B_5O_6(OH)_4 \right] \cdot 2H_2O \), an interesting species in the field of B-O chemistry, is an example of an unusual structure in which the structural unit has one tetrahedrally co-ordinated B atom. The compound has been known for over a century and the literature methods of synthesis of this compound involve either a drastic condition\(^7\) or the use of an appreciable amount of fluoride.\(^8\) Our contention was to develop a new and general synthetic route to potassium and ammonium pentaborate dihydrates, \( A \left[ B_5O_6(OH)_4 \right] \cdot 2H_2O \ (A = \text{K or NH}_4) \), using a mild condition without involving fluoride.

*The results described in this Chapter have been published: J. Chem. Soc., Dalton Trans., 1987, 0000.*
The present Chapter of the thesis deals with the details of a new method of synthesis, and characterisation of potassium and ammonium salts of the complex \( \left[ B_5O_6(OH)_4 \right]^- \) ion.

Although there are physico-chemical evidences for the existence of various fluoro(hydroxo)borates and fluoro(hydroxo)oxoborates, and oxo(hydroxo)borates in aqueous solution, report on solid polyborates or oxoborates containing fluoride as one of the ligands seems unprecedented. In view of a considerable interest in the chemistry of fluoroborates and also considering the fact that fluoro(hydroxo)borate moiety exists in solution, it was expected that such species will be capable of being synthesised under suitable experimental conditions and isolated in the solid state. Accordingly, such investigations were undertaken.

The present Chapter also describes the first synthesis, characterisation, and structural assessment of potassium and ammonium fluoro(hydroxo)oxoborate dihydrates, \( A_2 \left[ B_2O_2F_2(OH)_2 \right] \cdot 2H_2O \) (\( A = K \) or \( NH_4 \)).

**Experimental**

The chemicals used were all reagent grade products (B.D.H., E. Merck, S.D's, Loba-Chemie, and IDPL).
Synthesis of Potassium and Ammonium Pentaborate Dihydrates,

\[ \text{A} \left[ \text{B}_5\text{O}_6(\text{OH})_4 \right] \cdot 2\text{H}_2\text{O} (\text{A} = \text{K or NH}_4) \]

A typical procedure

To a suspension of 1.0g (16.17 mmol) of boric acid in ca 5 cm\(^3\) of water was added a 20% solution of potassium hydroxide or 25% aqueous ammonia (sp.gr. 0.9) in the case of NH\(_4^+\) salt, under constant magnetic stirring first to dissolve the boric acid and then to raise the pH of the medium to 9. An amount of 6 cm\(^3\) of acetylacetone was then added to the reaction mixture and the whole was stirred for ca 30 min. While the potassium salt was spontaneously precipitated from the reaction mixture at ambient temperatures, the corresponding ammonium salt was obtained by concentrating the content of the reaction vessel until a white product began to appear. The compounds were washed twice with ethanol and finally dried in vacuo over concentrated sulphuric acid. The yields of K\[ \text{B}_5\text{O}_6(\text{OH})_4 \right] \cdot 2\text{H}_2\text{O} and NH_4[ \text{B}_5\text{O}_6(\text{OH})_4 \right] \cdot 2\text{H}_2\text{O} were 1.6g (34%) and 1.4g (32%), respectively.

Synthesis of Potassium and Ammonium Fluoro(hydroxo)oxoborate Dihydrates, \( \text{A}_2 \left[ \text{B}_2\text{O}_2\text{F}_2(\text{OH})_2 \right] \cdot 2\text{H}_2\text{O} (\text{A} = \text{K or NH}_4) \)

Since the methods of syntheses of alkali fluoro(hydroxo)-oxoborates are similar only a representative method is described.
An amount of 2.0g (32.34 mmol) of boric acid was mixed well with the corresponding alkali fluoride, AF (A = K or NH₄), in a polythene beaker, with the maintenance of the ratio of B:AF at 1:2.5. To this was added 8 cm³ (192 mmol) of 48% HF to obtain a clear solution. This was then heated for ca 30 min over a steam-bath keeping the beaker uncovered in a ventilated hood. The volume of the reaction solution was reduced in this process, and the potassium or ammonium fluoro(hydroxo)oxoborate dihydrate was precipitated in a high yield. The product thus obtained was separated by filtration, washed three times with ethanol, and finally dried in vacuo over concentrated sulphuric acid. The specific gram amounts of reagents used and the yields of $A_2 \left[ B_2O_2F_2(OH)_2 \right]_2 \cdot 2H_2O$ (A = K or NH₄) are shown in Table 3-1.

**Elemental Analyses**

Estimations of boron, fluoride, potassium, nitrogen, and hydrogen were performed by the methods described in Chapter 2 of the thesis. The results of elemental analyses of $A_2 \left[ B_5O_6(OH)_4 \right]_2 \cdot 2H_2O$ (A = K or NH₄) are given in Table 3-2, while those of $A_2 \left[ B_2O_2F_2(OH)_2 \right]_2 \cdot 2H_2O$ (A = K or NH₄) are reported in Table 3-3.

**Results and Discussion**

It is known from the chemistry of boron that a high affinity of boron for oxygen is a dominant factor for the formation of a vast number of borates. The borates consist mainly of $B_2O_3$ moieties.
Table 3-1. Amounts of Reagents Used for the Synthesis and the Yields of $A_2 \overset{\mathcal{B}_2\mathcal{O}_2\mathcal{F}_2(\text{OH})_2}{\mathcal{H}_2\mathcal{O}}$ (A = K or NH$_4$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield g (%)</th>
<th>Amount of boric acid g (mmol)</th>
<th>Amount of AF g (mmol)</th>
<th>Amount of 48% HF cm$^3$ (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2 \overset{\mathcal{B}_2\mathcal{O}_2\mathcal{F}_2(\text{OH})_2}{\mathcal{H}_2\mathcal{O}}$</td>
<td>4.5 (58)</td>
<td>2.0 (32.34)</td>
<td>4.7 (81.04)</td>
<td>8.0 (192)</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2 \overset{\mathcal{B}_2\mathcal{O}_2\mathcal{F}_2(\text{OH})_2}{\mathcal{H}_2\mathcal{O}}$</td>
<td>4.2 (66)</td>
<td>2.0 (32.34)</td>
<td>3.0 (81.08)</td>
<td>8.0 (192)</td>
</tr>
</tbody>
</table>
Table 3-2. Analytical Data of A $\left[\text{B}_5\text{O}_6\text{(OH)}_4\right]_2\cdot 2\text{H}_2\text{O}$ (A = K or NH$_4$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found % (Calcd. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K or N</td>
</tr>
<tr>
<td>$\text{K}\left[\text{B}_5\text{O}_6\text{(OH)}_4\right]_2\cdot 2\text{H}_2\text{O}$</td>
<td>13.1 (13.26)</td>
</tr>
<tr>
<td>$\text{NH}_4\left[\text{B}_5\text{O}_6\text{(OH)}_4\right]_2\cdot 2\text{H}_2\text{O}$</td>
<td>5.04 (5.12)</td>
</tr>
</tbody>
</table>
Table 3-3. Analytical Data of $A_2 [B_2O_2F_2(OH)]_2 \cdot 2H_2O$

(A = K or NH$_4$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found % (Calcd. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K or N</td>
</tr>
<tr>
<td>$K_2 [B_2O_2F_2(OH)]_2 \cdot 2H_2O$</td>
<td>32.62</td>
</tr>
<tr>
<td></td>
<td>(32.50)</td>
</tr>
<tr>
<td>$(NH_4)_2 [B_2O_2F_2(OH)]_2 \cdot 2H_2O$</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td>(14.14)</td>
</tr>
</tbody>
</table>
with the occasional occurrence of $B_2O_4$ units. An interesting aspect of boron chemistry is marked by its ability to form polymeric species.\(^{12}\) Alkali-metal borates have been the subject of much studies and the structural elucidation of polyborates have evoked a considerable interest.\(^8,10,11\) One such example is potassium pentaborate dihydrate, $K[B_5O_6(OH)_4]_2H_2O$, which has drawn the attention of several workers\(^8,10,11\) probably because of its structural peculiarities. This compound was first reported in 1855 and was prepared by boiling a solution of KOH dissolved in a saturated solution of boric acid keeping the K:B ratio at ca 1:5. Recently in 1983, Emsley et al.\(^8\) have also reported the synthesis of this salt from boric acid partly dissolved in water and their procedure involves an appreciable amount of potassium fluoride. It was emphasised\(^8\) that the fluoride ions have an important role as a catalyst in bringing about the polymerisation of boric acid leading to the formation of pentaborate species, $\left[B_5O_6(OH)_4\right]^{-}$. Our concern in this context was to develope an alternative general method for the synthesis of potassium and ammonium pentaborate dihydrates, $A[B_5O_6(OH)_4]_2H_2O$ ($A =$ K or $NH_4$), without using any drastic conditions, and also avoiding $F^-$ ions, unlike the earlier methods,\(^8\) because fluoride is also a good ligand for boron. Strategically, it was thought that simply by proper adjustment of pH by the addition of potassium hydroxide or aqueous ammonia, which would also act as the source of counter-cations, the complex species might be generated in solutions and then isolated in the
solid state. The strategy seems to have worked. Thus the present method involves the reaction between a suspension of boric acid in water and the corresponding alkali hydroxide at room temperatures followed by the addition of acetylacetone. It is imperative to mention that a slow addition of alkali has to be continued until the medium attains pH 9. Addition of the stipulated amount of acetylacetone (vide Experimental) brings down the pH to 8 owing to its weak acidity. Acetylacetone apparently played two roles viz., (i) it helped in controlling the appropriate pH of the medium, and (ii) it facilitated precipitation of the desired compound from the reaction solution. The new method is easy to manipulate and in this way $\text{A} [\text{B}_5\text{O}_6(\text{OH})_4]_{\text{2H}_2\text{O}}$ (A = K or NH$_4$) compounds can be synthesised without making use of F$^-$ ions.

The compounds are white microcrystalline products, soluble in water at room temperatures. They permit molar conductance measurements and the values are found to lie between 120 and 130 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ showing that the compounds are 1:1 electrolytes. Molar conductances of the solutions of the compounds recorded at the intervals of 7, 15 and 30 days indicated no apparent change in the $\Delta_M$ values attesting to their stabilities also in solutions. In order to further establish their identity, the IR and laser Raman (IR) spectra of the compounds were recorded. While the IR spectra were recorded in the solid state, the IR spectra were recorded both on solids as well as on their solutions. The spectral features are identical to those reported
in the literature\textsuperscript{10,13} for the salts of the complex $\left[\text{B}_5\text{O}_6(\text{OH})_4\right]^{-}$ ion. These results and those of chemical analyses are in excellent agreement with the formulas of the compounds suggesting that the compounds are the same as those reported earlier in the literature.\textsuperscript{8,10,11,13}

In view of the physico-chemical evidences concerning the existence of fluoro(hydroxo)borates in solutions,\textsuperscript{9} it was expected that similar species could be isolated in the solid state by proper adjustment of experimental conditions. It has been found that a reaction of a mixture of boric acid and potassium or ammonium fluoride, $\text{AF} (A=\text{K or NH}_4)$, in the ratio of $\text{H}_3\text{BO}_3:\text{AF}$ as 1:2.5, with 48\% HF at a steam-bath temperature leads to the synthesis of hitherto unknown potassium or ammonium fluoro(hydroxo)oxoborate dihydrate, $A_2[\text{B}_2\text{O}_2\text{F}_2(\text{OH})_2]^{-}.2\text{H}_2\text{O} (A=\text{K or NH}_4)$. The pH of the solution, immediately after the formation of the compound, was found to be 2. The reaction was facile and the yields of the products were also high. The spontaneous separation of the compound from the reaction solution is an advantage of the method. It is necessary to carry out the reactions at a steam-bath temperature as this probably facilitates the reaction, and more so the volume is reduced considerably allowing the compound to be thwarted out of the reaction medium.

The compounds, $A_2[\text{B}_2\text{O}_2\text{F}_2(\text{OH})_2]^{-}.2\text{H}_2\text{O} (A=\text{K or NH}_4)$, are white microcrystalline products and insoluble in organic solvents. They decompose in water, thus precluding their molar conductance measurements. They do not melt upto 250°C. The results of elemental
analyses of the $K^+$ and $\text{NH}_4^+$ salts suggest the stoichiometry of $K:2:2:2$ and $N:2:2:2$ as $1:1:1:3$ and $1:1:1:7$, respectively. Accordingly, the compounds have been tentatively formulated as $A_2\left[B_2O_2F_2(OH)\right]_2\cdot2H_2O$ ($A = K$ or $\text{NH}_4$). Strong desiccation of the compounds over concentrated sulphuric acid did not remove the water of crystallisation. Owing to a pronounced tendency of boron to form a tetrahedral structure, a dimeric formula over a monomeric one is preferred which has been augmented by the results of spectroscopic studies.

The $B-F$ and $B-O$ vibrations are important spectroscopic probes for molecular structure assessment, and are amenable to a direct study by IR and $\nu$RF spectroscopy (Table 3-4). The IR spectra showed bands at $\nu c a$ 596, $\nu c a$ 746, and $\nu c a$ 1300 cm$^{-1}$, and a broad absorption at $\nu c a$ 1060 cm$^{-1}$, the broadening of which is probably because of overlap of $B-O$ and $B-F$ vibrational modes. The band at $\nu c a$ 596 cm$^{-1}$ has been assigned to $\nu (B-OH)$, those at $\nu c a$ 746 and $\nu c a$ 1300 cm$^{-1}$ have been attributed to $\nu (B-O-B)$ and $\nu (B-O-B)$ modes, respectively. In addition the spectra show two extra bands at $\nu c a$ 1640 and $\nu c a$ 3450 cm$^{-1}$ typical for $\delta (H-O-H)$ and $\nu (O-H)$ of uncoordinated water. The absorptions at 3157, 3040, and 1400 cm$^{-1}$ in the spectrum of the $\text{NH}_4^+$ salt have been attributed to $\nu_3$, $\nu_1$ and $\nu_4$ modes of $\text{NH}_4^+$. The IR spectra of both the compounds were recorded only on solids as they decompose in water even at room temperatures. The characteristic features of IR spectra are the peaks at $\nu c a$ 775, $\nu c a$ 820, and $\nu c a$ 595 cm$^{-1}$. The peaks at $\nu c a$ 775 and $\nu c a$ 595 cm$^{-1}$ have been
assigned to \( \nu (B-F)^{20} \) and \( \nu (B-OH)^{16} \) modes, respectively, originating from the presence of co-ordinated fluoride and OH and compare very well with those observed for some other complex species of boron. The signal at ca 820 cm\(^{-1}\) has been assigned to \( \nu (B-O)^{16} \) (of the B-O-B framework). However, a corresponding band in the IR spectra could not be precisely identified probably owing to its overlap with the B-OH vibration. Thus, it may be inferred from the results of IR and 1R spectroscopic studies that the complex species contains two tetrahedral boron atoms with a B<>B linkage, in addition to one F\(^-\) and one OH\(^-\) being terminally bonded to each of the two boron atoms, and accordingly the complex ion has been formulated as \( \left[ \text{B}_2\text{O}_2\text{F}_2(\text{OH})_2 \right]^{2-} \).

Thus it is evident from the present studies that the classic oft-quoted pentaborate, \( \text{A}\left[\text{B}_5\text{O}_6(\text{OH})_4\right]_2\text{H}_2\text{O} \) (\( \text{A}=\text{K} \) or \( \text{NH}_4 \)), can be synthesised rather easily, directly from the reaction of boric acid with potassium hydroxide or aqueous ammonia at pH 9 without using any drastic conditions or fluoride ions. The white crystalline \( \text{A}\left[\text{B}_5\text{O}_6(\text{OH})_4\right]_2\text{H}_2\text{O} \) compounds are stable and do not decompose in water.

Potassium and ammonium fluoro(hydroxo)oxoborate dihydrates, \( \text{A}_2\left[\text{B}_2\text{O}_2\text{F}_2(\text{OH})_2\right]_2\text{H}_2\text{O} \) (\( \text{A}=\text{K} \) or \( \text{NH}_4 \)), can be obtained from the reaction of a solution of boric acid with AF and 48\% hydrofluoric acid. The compounds do not melt up to 250\(^\circ\)C. Unlike the \( \text{A}\left[\text{B}_5\text{O}_6(\text{OH})_4\right]_2\text{H}_2\text{O} \) compounds, they decompose in water. The complex
Table 3-4. Structurally Significant IR and laser Raman (lR) Bands of $A_2 \left[ B_2O_2F_2(OH)_2 \right]_2\cdot 2H_2O$ (A = K or $NH_4$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR cm$^{-1}$</th>
<th>Raman cm$^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2 \left[ B_2O_2F_2(OH)_2 \right]_2\cdot 2H_2O$</td>
<td>596w</td>
<td>595</td>
<td>$\nu$ (B-OH)</td>
</tr>
<tr>
<td></td>
<td>746m</td>
<td></td>
<td>$\nu_s$ (B-O-B)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>775</td>
<td>$\nu$ (B-F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>825</td>
<td>$\nu$ (B-O) (of the B-O-B framework)</td>
</tr>
<tr>
<td></td>
<td>1065br</td>
<td></td>
<td>$\nu$ (B-O) + $\nu$ (B-F)</td>
</tr>
<tr>
<td></td>
<td>1300w</td>
<td></td>
<td>$\nu_{as}$ (B-O-B)</td>
</tr>
<tr>
<td></td>
<td>1640m</td>
<td></td>
<td>$\delta$ (H-O-H)</td>
</tr>
<tr>
<td></td>
<td>3450m</td>
<td></td>
<td>$\nu$ (O-H)</td>
</tr>
<tr>
<td>$\left[ B_2O_2F_2(OH)_2 \right]_2\cdot 2H_2O$</td>
<td>598w</td>
<td>595</td>
<td>$\nu$ (B-OH)</td>
</tr>
<tr>
<td></td>
<td>749m</td>
<td></td>
<td>$\nu_s$ (B-O-B)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>778</td>
<td>$\nu$ (B-F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>820</td>
<td>$\nu$ (B-O) (of the B-O-B framework)</td>
</tr>
<tr>
<td></td>
<td>1060br</td>
<td></td>
<td>$\nu$ (B-O) + $\nu$ (B-F)</td>
</tr>
<tr>
<td>$\left[ B_2O_2F_2(OH)_2 \right]_2\cdot 2H_2O$</td>
<td>1305w</td>
<td></td>
<td>$\nu_{as}$ (B-O-B)</td>
</tr>
<tr>
<td></td>
<td>1640m</td>
<td></td>
<td>$\delta$ (H-O-H)</td>
</tr>
<tr>
<td></td>
<td>3455m</td>
<td></td>
<td>$\nu$ (O-H)</td>
</tr>
<tr>
<td></td>
<td>3157m</td>
<td></td>
<td>$\nu_3$</td>
</tr>
<tr>
<td></td>
<td>3040s</td>
<td></td>
<td>$\nu_1$ N-H</td>
</tr>
<tr>
<td></td>
<td>1400s</td>
<td></td>
<td>$\nu_4$</td>
</tr>
</tbody>
</table>
\((\text{NH}_4)_2\left[\text{B}_2\text{O}_2\text{F}_2\text{OH}_2\right]\cdot2\text{H}_2\text{O}\)
$K_2[B_2O_2F_2(OH)_2].2H_2O$
\[ B_2O_2F_2(OH)_2 \] species contains two tetrahedral boron atoms with a B\( \sigma \)B linkage, in addition to one F\(^-\) and one OH\(^-\) being terminally bonded to each of the two boron atoms.
References


CHAPTER 4
Alkali-Metal and Ammonium Peroxofluoroborates, $A_2 \left[ B(O_2)F_3 \right] \cdot 4H_2O$ ($A = \text{Na or K}$), and $(NH_4)_2 \left[ B_2(O_2)F_2 \right]$. First Synthesis of Peroxofluoroborate Complexes*

The reaction of borates with hydrogen peroxide leads to products which probably contain the complex $\left[ B_2(O_2)_{2}(OH)_{4} \right]^{2-}$ ion and the alkali-metal salts of this anion constitute an important oxidising component in many detergents. The commercially most important compound in this context is $Na_2 \left[ B_2(O_2)_{2}(OH)_{4} \right] \cdot 6H_2O$. No heteroligand peroxo complex of boron is known to our knowledge, although many reported examples of such compounds of metals are documented in the literature.\textsuperscript{2-9} Interestingly, introduction of specific heteroligands in the coordination sphere seems to increase the stability of peroxo complexes of elements and permits isolation in the solid form thus providing a scope of studying their properties and making an assessment of their structures. In view of a considerable amount of success that has been achieved in obtaining stable heteroligand peroxo compounds of metals in recent years,\textsuperscript{7-9} it was expected that similar species of boron could also be isolated in the solid state and the results obtained would provide

*The subject matter of this Chapter has been published: Inorg. Chem., 1985, 24, 2580.
internally consistent data regarding the effect of heteroligands on the stability of peroxoborate systems.

Chapter 4 of the thesis deals with the first synthesis, characterisation, and assessment of structures of the title compounds.

Synthesis of Alkali-metal and Ammonium Peroxofluoroborates, 
\[ A_2 \{B(O_2)F_3\}_7 \cdot 4H_2O \text{ (A = Na or K), and (NH}_4\}_2 \{B_2(O_2)_3F_2\}_7 \]

As the methods of synthesis of the afore-mentioned compounds are similar, only a typical procedure is described below.

To a suspension of 2.0g (32.34 mmol) of boric acid in ca 15 cm\(^3\) of water was added alkali-metal hydroxide, AOH (A = Na or K), or aqueous ammonia solution, under constant magnetic stirring, first to completely dissolve the boric acid and then to raise the pH of the medium to 9. While sodium hydroxide or potassium hydroxide was added as a 20% solution, the aqueous ammonia was added as its 25% solution (sp.gr. 0.9). An amount of 6.0 cm\(^3\) (120 mmol) of 40% HF solution was added and the resultant mixture was stirred for ca 5 min. The pH of the resultant solution was adjusted to 9 by a careful addition of the corresponding alkali-metal hydroxide solution or aqueous ammonia, and the mixture was cooled in an ice-water bath for ca 15 min followed by the addition of 14 cm\(^3\) (123.4 mmol) of 30% hydrogen peroxide. The solution was cooled in an ice-water bath for ca 10 min under slow magnetic stirring and the pH of the
solution was raised once again to 9 by adding the corresponding alkali. Addition of a nearly equal volume of ethanol to the above solution produced white crystalline alkali-metal or ammonium peroxofluoroborate in a very high yield. The compound thus obtained was separated by filtration, washed three times with ethanol, and finally dried in vacuo over concentrated sulphuric acid. The amounts of reagents used for the synthesis and the yields of $\text{A}_2 \left\langle \text{B(O}_2\text{)}\text{F}_3 \right\rangle \cdot 4\text{H}_2\text{O} \ (\text{A} = \text{Na or K})$ and $(\text{NH}_4)_2 \left\langle \text{B}_2\text{(O}_2\text{)}_3\text{F}_2 \right\rangle$ are reported in Table 4-1.

Elemental Analyses

Estimations of boron, fluoride, peroxide, sodium, potassium, and nitrogen were accomplished by the methods already described in Chapter 2 of the thesis. The results of elemental analyses of the newly synthesised compounds are given in Table 4-2.

Results and Discussion

The reaction of orthoboric acid with hydrogen peroxide produces the peroxoborate species $\left\langle \text{B}_2\text{(O}_2\text{)}_2\text{(OH)}_4 \right\rangle^{2-}$ in solution and the alkali-metal salts of this complex ion are prepared from the reaction of borates with hydrogen peroxide. The sodium salt can also be prepared from the reaction of boric acid with sodium peroxide. Further it is well-known from the familiar chemistry of boron that fluoride reacts with trivalent boron rather easily. Thus it was expected that under the appropriate conditions both peroxide ($\text{O}_2^{2-}$) and fluoride ($\text{F}^{-}$) ligands might be made to coordinate
Table 4-1. Amounts of Reagents Used for the Synthesis and the Yields of $A_2 \left[ B(O_2)_3 F_3 \right] \cdot 4H_2 O$ ($A = \text{Na or K}$) and $(\text{NH}_4)_2 \left[ B_2 (O_2)_3 F_2 \right]\n
<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield g (%)</th>
<th>Amount of boric acid g (mmol)</th>
<th>Amount of 40% HF cm$^3$ (mmol)</th>
<th>Amount of 30% H$_2$O$_2$ cm$^3$ (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2 \left[ B(O_2)_3 F_3 \right] \cdot 4H_2 O$</td>
<td>6.5 (92)</td>
<td>2.0 (32.34)</td>
<td>6 (120)</td>
<td>14 (123.4)</td>
</tr>
<tr>
<td>K$_2 \left[ B(O_2)_3 F_3 \right] \cdot 4H_2 O$</td>
<td>6 (74)</td>
<td>2.0 (32.34)</td>
<td>6 (120)</td>
<td>14 (123.4)</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2 \left[ B_2 (O_2)_3 F_2 \right]$</td>
<td>4.5 (72)</td>
<td>2.0 (32.34)</td>
<td>6 (120)</td>
<td>14 (123.4)</td>
</tr>
</tbody>
</table>
Table 4-2. Analytical Data of $A_2 \left\{ B\left(O_2\right)F_3 \right\} \cdot 4H_2O$ ($A = Na$ or $K$) and $(NH_4)_2 \left\{ B_2\left(O_2\right)_3F_2 \right\}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found % (Calcd. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A or N</td>
</tr>
<tr>
<td>$Na_2 \left{ B\left(O_2\right)F_3 \right} \cdot 4H_2O$</td>
<td>45.35</td>
</tr>
<tr>
<td></td>
<td>(45.98)</td>
</tr>
<tr>
<td>$K_2 \left{ B\left(O_2\right)F_3 \right} \cdot 4H_2O$</td>
<td>31.54</td>
</tr>
<tr>
<td></td>
<td>(31.27)</td>
</tr>
<tr>
<td>$(NH_4)_2 \left{ B_2\left(O_2\right)_3F_2 \right}$</td>
<td>14.47</td>
</tr>
<tr>
<td></td>
<td>(14.62)</td>
</tr>
</tbody>
</table>

$^a$ Peroxo-oxygen
with boron in the presence of each other to produce heteroligand peroxoborate complexes.

Strategically most important was the evaluation of a suitable pH of the reaction medium to enable formation of the desired complexes. Accordingly, the reactions of boric acid with alkali-metal hydroxide, AOH, or aqueous ammonia, 40% HF, and 30% H₂O₂ solution were performed at pH 9 which gave rise to the formation of the complex ion \( \Sigma \text{B}(O₂,F₃)⁻ \) in the case where the alkali-metal hydroxide was either NaOH or KOH, and \( \Sigma \text{B}_₂(O₂,F₂)⁻ \) in the case of aqueous ammonia. The complex ions were isolated as \( \text{Na}_2 \Sigma \text{B}(O₂,F₃).4\text{H}_₂\text{O} \), \( \text{K}_2 \Sigma \text{B}(O₂,F₃).4\text{H}_₂\text{O} \), and \( \text{(NH₄)}_2 \Sigma \text{B}_₂(O₂,F₂) \) in very high yields by the addition of ethanol which facilitated precipitation. The peroxofluoroborate formation reactions are best monitored through peroxo-oxygen estimation. This is accomplished by isolating a small amount of the sample from the reaction mixture followed immediately by the estimation of active oxygen. It must be emphasised that maintenance of pH of the reaction medium at 9 is very vital for the formation and hence successful isolation of the compounds. It has been observed by carrying out similar reactions at pH 3-4 that the products obtained thereof contain very low level of peroxide suggesting thereby that acidic condition of the reaction medium is not conducive to the formation of peroxofluoroborate species.

The synthetic reactions were monitored by IR spectroscopy. The appearance of a strong band at ca 860 cm⁻¹ due to \( \Sigma \) (O-O), and
a band at ca 1050 cm$^{-1}$ owing to $\nu (B-F)$ in the IR spectrum of a small amount of the sample isolated from the reaction solutions indicated the formation of peroxofluoroborates.

Characterisation and Assessment of Structure

The newly synthesised alkali-metal and ammonium peroxofluoroborate complexes are all white crystalline stable products and can be stored in sealed polyethylene bags. Their stabilities can be ascertained by periodic estimation of peroxide. The peroxide content in each of the compounds was estimated by titration with a standard potassium permanganate solution and also with a standard Ce$^{4+}$ solution, in the presence of boric acid to prevent any loss of active oxygen. The results obtained thereof and those of the analyses of other constituents of the compounds suggest the stoichiometry of B:O$_2$F$^{-}$ as 1:1:3 in each of the Na$^+$ and K$^+$ salts, and 2:3:2 in the NH$_4^+$ salt. Accordingly, the compounds have been formulated as Na$_2$B$_2$(O$_2$)F$_3$.7H$_2$O, K$_2$B$_2$(O$_2$)F$_3$.4H$_2$O, and (NH$_4$)$_2$B$_2$(O$_2$)$_3$F$_2$.7H$_2$O. The peroxofluoroborates do not melt up to 300°C, however, the (NH$_4$)$_2$B$_2$(O$_2$)$_3$F$_2$.7H$_2$O compounds volatilises at about 165°C. Pyrolytic studies reveal that while all the compounds start losing peroxo oxygen at ca 130°C, the Na$^+$ and K$^+$ salts also start expelling water at nearly the same temperature. The compounds are stable and permit molar conductance measurements. The molar conductances of the compounds have been found to lie between 230 and 270 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ (at 22°C in water) in very good agreement with their formulas. A slightly higher value in the
case of the Na⁺ salt might be due to the presence of a trace of impurity, presumably sodium fluoride, arising from its low solubility.

The infrared spectra of peroxofluoroborates are quite characteristic. The most significant feature of IR spectra of the compounds are the absorptions (Table 4-3) at ca 1050 and ca 860 cm⁻¹ which have been assigned to the ν (B-F)¹¹ and ν (O-O)¹² modes, respectively, originating from the presence of coordinated fluoride and peroxide ligands. The position of ν (O-O) suggests a strong possibility of the O₂²⁻ ligand being bonded to the boron centre in a triangular bidentate (C₂ᵥ) manner, and the complex anion [B(O₂)F₃]²⁻ may be a pentacoordinated monomer, however, the possibility that the complex ion is tetrahedral with a terminal O=O group can not be ruled out. The IR spectrum of the complex anion [B₂(O₂)₃F₂]²⁻ shows a pattern generally similar to that of [B(O₂)F₃]²⁻ species, except for much greater broadening of the band at 1050 cm⁻¹. Thus it is believed that the stereochemistry of boron in the [B₂(O₂)₃F₂]²⁻ ion is tetrahedral, which is attained through coordination of one peroxide (O₂²⁻) ligand in a triangular bidentate fashion, one terminal fluoride (F⁻) ligand, and one end of a bridging O=O ligand. An alternate structure of the dimer, similar to that found for Na₂B₄O₉·4H₂O, with two O=O bridges connecting the two boron atoms (i.e. a six membered B₂O₄ ring), is also possible irrespective of the mode of coordination of the third peroxide group. In view of the structural study of the complex anion [B₂(O₂)₂(OH)₄]²⁻, the latter
Table 4-3. Molar Conductance Values and Structurally Significant IR Bands of $A_2 [B(O_2)F_3]_{2} \cdot 4H_2O$ (A = Na or K) and $(NH_4)_2 [B_2(O_2)_3F_2]$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar Conductance $\Omega^{-1} cm^2 mol^{-1}$</th>
<th>IR cm$^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Na_2 [B(O_2)F_3]_{2} \cdot 4H_2O$</td>
<td>270</td>
<td>1060s</td>
<td>$\gamma$ (B-F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>860m</td>
<td>$\gamma$ (O-O)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3450m</td>
<td>$\gamma$ (O-H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1640m</td>
<td>$\delta$ (H-O-H)</td>
</tr>
<tr>
<td>$K_2 [B(O_2)F_3]_{2} \cdot 4H_2O$</td>
<td>255</td>
<td>1050s</td>
<td>$\gamma$ (B-F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>860m</td>
<td>$\gamma$ (O-O)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3450m</td>
<td>$\gamma$ (O-H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1640m</td>
<td>$\delta$ (H-O-H)</td>
</tr>
<tr>
<td>$(NH_4)_2 [B_2(O_2)_3F_2]$</td>
<td>234</td>
<td>1050 (s, br)</td>
<td>$\gamma$ (B-F)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>850m</td>
<td>$\gamma$ (O-O)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3155m</td>
<td>$\gamma_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3045s</td>
<td>$\gamma_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1400s</td>
<td>$\gamma_4$</td>
</tr>
</tbody>
</table>

N-H
$\text{Na}_2\text{B}_2\text{O}_4\text{F}_3\cdot 4\text{H}_2\text{O}$

Transmittance (arbitrary scale)
$K_2[B(O_2)F_3] \cdot 4H_2O$

Transmittance (arbitrary scale)
structure appears more likely. The additional bands at ca 3450 and ca 1640 cm⁻¹ in the case of Na⁺ and K⁺ salts, resemble in their shapes and positions those arise from ν (O-H) and δ(H-O-H) modes, respectively, of uncoordinated water.¹³,¹⁴ The broad nature of the ν (O-H) band in each case indicates a fair possibility of hydrogen bonding through F—H—F interactions. The bands at 1400, 3045, and 3155 cm⁻¹ in the spectrum of (NH₄)₂B₂O₅F₇ have been attributed to the ν₄, ν₁ and ν₃ modes of NH₄⁺.¹⁵

Thus, it may be inferred from the results of studies described in the present Chapter that the hitherto unknown peroxofluoroborates, A₂[B(O₂)F₃]₄H₂O (A = Na or K), and (NH₄)₂[B₂(O₂)₃F₂] can be synthesised under the appropriate experimental conditions and pH. 9 has been found to be conducive to the synthesis of such compounds. The complexes are comparatively more stable than the simple peroxoborates. The results of IR spectra suggest that while the complex [B(O₂)F₃]⁻ ion contains a peroxide group bonded to the boron centre in a triangular bidentate fashion in addition to the coordinated fluoride ligands, the complex [B₂(O₂)₃F₂]⁻ species contains two boron atoms each of which is tetrahedrally linked to one end of a bridging O-O ligand, one coordinated triangularly bonded peroxide group, and a terminal fluoride ligand.

The results of the present investigations may have an impact on the chemistry of peroxo-boron compounds and it is expected that further research in this area will generate more information pertaining to peroxo-boron chemistry.
References


10. Ref 1, p 956.


