SOME CONTRIBUTIONS TO OXO, FLUORO, AND PEROXO CHEMISTRY OF BORON AND TITANIUM

ABSTRACT

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DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES

A THESIS
SUBMITTED
IN
FULFILMENT OF THE REQUIREMENT OF THE DEGREE OF

DOCTOR OF PHILOSOPHY

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG
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Thesis.

"Some Contributions to Oxo, Fluoro, and Peroxo Chemistry of Boron and Titanium"

Abstract

The above mentioned thesis is based on the results of studies involving syntheses and assessment of structures of some oxo, oxofluoro and heteroligand-peroxo compounds of boron, and syntheses and physico-chemical studies of heteroligand-peroxo complexes of titanium(IV). Further, the thesis also contains a direct synthesis of alkali oxotetrafluorotitanates(IV). The subject matter of the thesis has been distributed over eight Chapters. The results described in Chapters 3-8 have been grouped into two parts, viz., Part A and Part B. While Part A, consisting of Chapters 3 and 4, deals with the studies on the above mentioned aspects of boron chemistry, Part B, which includes Chapters 5-8, contains the results of studies on titanium(IV) chemistry.

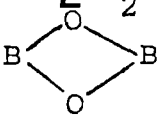
Chapter 1 presents a brief introduction pertaining to the research embodied in the thesis. It highlights (i) the importance of and the interest in the studies of peroxo-element chemistry in general, and heteroligand peroxoborate and heteroligand peroxotitanate(IV) compounds in particular, and (ii) problems associated with the reported methods of syntheses of oxo-compounds of boron, alkali pentafluoroperoxotitanates(IV), and alkali

oxotetrafluorotitanates(IV). Another piece of a problem, as emphasised in this Chapter, is the lack of evidence regarding the existence of complex diperoxotitanate(IV) species in the solid state. This Chapter also projects the scope of work on the chosen aspects of boron and titanium chemistry.

Details of the methods of elemental analyses and the instruments/equipment used for the characterisation and structural assessment of the newly synthesised compounds constitute the basis of Chapter 2.

PART A

Chapter 3 of the thesis describes a new route to the synthesis of potassium and ammonium pentaborate dihydrates, $A[B_5O_6(OH)_4].2H_2O$ (A = K or NH_4), and synthesis and structural assessment of new fluoro(hydroxo)oxoborate dihydrates, $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = K or NH_4). The synthesis of $A[B_5O_6(OH)_4].2H_2O$ (A = K or NH_4) has been achieved from the reaction of a suspension of boric acid in water with potassium hydroxide or aqueous ammonia at pH 9. Compounds were precipitated with acetylacetone. The identity of the compounds have been established on the basis of the results of elemental analyses, IR and laser Raman (lR) spectroscopic studies. The molar conductances of $A[B_5O_6(OH)_4].2H_2O$, recorded at 23°C, were found to be in order (ca 120 $\Omega^{-1}cm^2mol^{-1}$), and time dependent molar conductivity studies of the compounds suggest that they do not undergo decomposition in water at ambient temperatures.

White microcrystalline $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = K or NH_4) compounds have been synthesised from the reaction of a solution of boric acid and the corresponding alkali fluoride, AF (A = K or NH_4), in 48% HF in the molar ratio of B:AF as 1:2.5, followed by warming at a steam-bath temperature. Characterisation of the compounds were made from the results of elemental analyses, IR and 1R spectroscopic studies. The compounds decompose in water at ambient temperatures thus precluding their molar conductance measurements. The results of IR and 1R spectroscopic studies suggest that the complex species $[B_2O_2F_2(OH)_2]^{2-}$ contains two tetrahedral boron atoms with a  linkage.

Chapter 4 of the thesis provides an account of the first reported synthesis of peroxofluoroborate complexes, $A_2[B(O_2)F_3].4H_2O$ (A = Na or K), and $(NH_4)_2[B_2(O_2)_3F_2]$, their characterisation, and assessment of structures. The complexes $A_2[B(O_2)F_3].4H_2O$ (A = Na or K), and $(NH_4)_2[B_2(O_2)_3F_2]$ have been synthesised from the reaction of boric acid with aqueous hydrofluoric acid and hydrogen peroxide at pH 9, maintained by the addition of alkali hydroxide or aqueous ammonia. Precipitation of the compounds from the reaction solutions was achieved by the addition of ethanol. The new compounds have been characterised on the basis of the results of chemical analyses, molar conductance measurements, pyrolysis at 130°C, and IR spectroscopic studies. The complexes are stable at room temperatures, however, they start decomposing at 130°C. An analysis of the results of IR spectra suggests that while the complex

$[B(O_2)F_3]^{2-}$ ion contains a peroxide group bonded to the boron centre in a triangular bidentate (C_{2v}) fashion in addition to the coordinated fluoride ligands, the complex $[B_2(O_2)_3F_2]^{2-}$ 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.

PART B

Reported in Chapter 5 are a direct synthesis of alkali-metal and ammonium pentafluoroperoxotitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4), first synthesis and structural assessment of potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3].3H_2O$, and potassium and ammonium difluorodiperoxotitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4). In view of the difficulties encountered in the synthesis of $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4) using the literature reported method, a direct procedure has been developed for the synthesis of $A_3[Ti(O_2)F_5]$. The new method involves a reaction among freshly prepared TiO_2, aqueous hydrofluoric acid, and hydrogen peroxide at pH 6, adjusted by the addition of alkali hydroxide or aqueous ammonia. The compounds were characterised, and their identity established from the results of chemical analyses, conductance and magnetic susceptibility measurements, and IR and laser Raman (lR) spectroscopic studies. The advantages of the new method has also been accentuated.

It has been shown that the reaction of a solution of freshly prepared TiO_2 in 40% HF with an excess of aqueous hydrogen peroxide and KOH, followed by the addition of hydrofluoric acid to adjust the pH of the reaction solution between 8 and 9, affords the yellow microcrystalline potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3].3H_2O$, in a high yield. The compound has been characterised by elemental analyses, magnetic susceptibility measurement and IR and lR spectroscopic studies. IR and lR spectral results show that the peroxide group isbonded to the titanium(IV) centre in a triangular bidentate (C_{2v}) manner. The compound is stable in the absence of moisture. $K[Ti(O_2)F_3].3H_2O$, which decomposes in water at ambient temperatures precluding molar conductance measurement, is diamagnetic.

The synthesis of light-yellow potassium and ammonium difluorodiperoxotitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4), has been accomplished from the reaction of a solution of freshly prepared TiO_2 in 40% HF with 30% hydrogen peroxide at pH 9 maintained by the addition of potassium hydroxide or aqueous ammonia until a faint yellow colouration was developed; the compounds were precipitated from the reaction solution by adding ethanol in a nearly quantitative yield. The identity of the compounds, $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4), has been ascertained on the basis of the results of chemical analyses, molar conductance and magnetic susceptibility measurements, and IR and lR spectroscopic studies. The molar conductances of $A_2[Ti(O_2)_2F_2]$

recorded at ambient temperatures have been found to lie in the range 220-240 $\Omega^{-1}cm^2mol^{-1}$ in conformity with their formulas. The results of magnetic susceptibility measurements of the compounds provide evidences for their diamagnetic nature, and lend support to the occurence of titanium(IV) in each of them. IR and lR spectral results provide an unequivocal evidence for the occurence of triangularly bonded peroxide (O_2^{2-}) groups. The spectroscopic results also show that $\tilde{\nu}$ (O-O) decreases with an increase in the number of coordinated peroxide groups. Further, the results of lR spectroscopic studies in solution suggest that the complex species $[Ti(O_2)_2F_2]^{2-}$ retains its structural identity.

Chapter 6 of the thesis describes the synthesis and physico-chemical studies of potassium and ammonium diperoxo-(sulphato)titanate(IV) tetrahydrates, $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4), and molecular mixed-ligand peroxo complexes of titanium(IV) of the types $[Ti(O_2)_2(L\text{-}L)]$ (L-L = 1,10-phenanthroline (o-phen) or 2,2′-bipyridine (bipy), and $[Ti(O_2)_2(thiourea)].H_2O$. The synthesis of $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4) complexes was achieved from the reaction of freshly prepared TiO_2 with 7.65M H_2SO_4 and 30% H_2O_2 at pH 2.5-3, maintained by the addition of KOH or aqueous ammonia. The yellow diperoxo(sulphato)titanates(IV), which were obtained in very high yields, were characterised and their identity established from the results of elemental analyses, magnetic susceptibility measurements, and IR, lR, and EPR spectral studies. The $A_2[Ti(O_2)_2SO_4].4H_2O$ compounds are practically insoluble in

water and stable upto 120°C. The complex peroxo(sulphato)-titanates(IV), $A_2[Ti(O_2)_2SO_4].4H_2O$, are diamagnetic in nature and are EPR silent in conformity with the occurence of titanium(IV) in each of them. The presence of triangular bidentate peroxide (O_2^{2-}) and chelated sulphate (SO_4^{2-}) ligands in the complex $[Ti(O_2)_2SO_4]^{2-}$ ion has been ascertained from IR and lR spectroscopic studies.

Syntheses of molecular mixed-ligand peroxo complexes of titanium(IV) of the types $[Ti(O_2)_2(L\text{-}L)]$ (L-L = o-phen or bipy) and $[Ti(O_2)_2(thiourea)].H_2O$ were accomplished from the reaction of a solution of freshly prepared TiO_2 in 40% HF with an ethanolic solution of 1,10-phenanthroline, an ethanolic solution of 2,2'-bipyridine, an aqueous solution of thiourea, respectively, and 30% H_2O_2 at pH 7 maintained by the addition of aqueous ammonia. They are stable for a prolonged period. The compounds are insoluble in water as well as in common organic solvents. The IR and lR spectra provide evidence for the occurence of triangular bidentate peroxides (O_2^{2-}) in each of the complexes. While o-phen and bipy occur as bidentate ligands in the respective compounds, thiourea in $[Ti(O_2)_2(thiourea)].H_2O$ acts as a monodentate ligand. The compounds are all diamagnetic in nature in accord with the presence of titanium(IV).

Laser Raman spectroscopic evidence for the existence of oxoperoxotitanate(IV) containing 'titanyl' moiety in aqueous solution and synthesis of an unusual example of peroxotitanate(IV) complex potassium oxoperoxodichlorotitanate(IV) monohydrate, $K_2[TiO(O_2)Cl_2].H_2O$, constitute the subject matter of Chapter 7.

Laser Raman (lR) spectrum of an yellow solution obtained from the reaction of a freshly prepared TiO_2 with potassium chloride, hydrogen peroxide and hydrochloric acid at pH 6, adjusted by a careful addition of KOH solution showed —— in addition to the expected modes of peroxide (O_2^{2-}) ——— a distinct polarised signal characteristic of $\tilde{\nu}$ (Ti=O). The yellow solution as obtained above on being treated with ethanol, to initiate precipitation, afforded light-yellow microcrystalline $K_2[TiO(O_2)Cl_2].H_2O$ compound in a very high yield. The compound, which is insoluble both in water and common organic solvents at ambient temperatures precluding molar conductance measurement, is diamagnetic. An analysis of the results of spectroscopic studies suggests that a monomeric oxoperoxotitanate(IV) species formed in solution undergoes polymerisation in the process of its isolation in the solid form via μ-oxo bridges in the crystal lattice. The results also provide evidences for the occurence of a triangularly bonded peroxide (O_2^{2-}) group. Further the spectra suggests that the complex species $[TiO(O_2)Cl_2]^{2-}$ has a distorted octahedral structure through -Ti-O-Ti- interactions.

Chapter 8, indeed the concluding Chapter of the thesis, contains the results of studies involving the synthesis, characterisation, and assessment of structure of alkali-metal and ammonium oxotetrafluorotitanates(IV), $A_2[TiOF_4]$ (A = K, Cs or NH_4). In view of the problems encountered in the synthesis of pure $[TiOF_4]^{2-}$ by the literature methods, a new procedure has been developed for the synthesis of pure $A_2[TiOF_4]$ (A = K, Cs

or NH_4). The new method of synthesis is based on the reaction of freshly precipitated TiO_2 with 4M sulphuric acid and an aqueous solution of the corresponding AF (A = K or NH_4) with the molar ratio of Ti:AF being maintained at 1:7. While the potassium salt was spontaneously precipitated from the reaction solution, precipitation of ammonium salt required the addition of ethanol. The corresponding Cs^+ salt has been prepared from the ammonium salt, $(NH_4)_2[TiOF_4]$, by metathesis. The $A_2[TiOF_4]$ compounds are all white products and decompose in water at ambient temperatures. That, the titanium occurs in its +4 oxidation state (d^o) in each of the compounds is evidenced by the results of magnetic susceptibility measurements. They are also EPR silent. The IR and lR spectra provide evidence for a distorted octahedral structure of the complex $[TiOF_4]^{2-}$ ion with -Ti-O-Ti- interactions.

The results of research described in Chapters 3, 4 and 5 have been published, and those described in Chapter 8 is now in press, while the work described in Chapters 6 and 7 have been communicated for publication.

Chapter 3

J. Chem. Soc., Dalton Trans., 1987, 000.

Chapter 4

Inorg. Chem., 1985, 24, 2580.

Chapter 5

Polyhedron, 1985, 4, 1449; Inorg. Chem., 1986, 25, 168.

Chapter 8

Ind. J. Chem., 1987, in press (IC 5439/87).

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Thesis

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Dr. Mihir K. Chaudhuri
Professor of Chemistry
Department of Chemistry

I certify that the thesis entitled "SOME CONTRIBUTIONS TO OXO, FLUORO, AND PEROXO CHEMISTRY OF BORON AND TITANIUM", submitted by Mr. Bimalendu Das for the Degree of Doctor of Philosophy of the North Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

Date: February 26, 1988.

Place: Shillong

Mihir Kanti Chaudhuri

Signature of the Supervisor

C O N T E N T S

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I shall be failing in my duty if I do not express my deep sense of indebtedness to my fellow research scholars - Dr. M.N. Bhattacharjee, Dr. S.K. Ghosh, Dr. Z. Hiese, Dr. R.N. Dutta Purkayastha, Miss N.S. Islam, Mrs. M. Devi, Mr. S. Purkayastha, Mr. M. Bhattacharjee, Mr. C.R. Bhattacharjee and Mr. P. Paul for their goodwill, cooperation and ungrudging help.

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I choose to refrain from expressing my gratitude to my parents, wife, brothers, sister and other members of my family, the quality of whose interest in my academic pursuits is beyond compare.

(B. Das)

ABSTRACT

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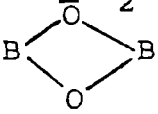
White microcrystalline $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = K or NH_4) compounds have been synthesised from the reaction of a solution of boric acid and the corresponding alkali fluoride, AF (A = K or NH_4), in 48% HF in the molar ratio of B:AF as 1:2.5, followed by warming at a steam-bath temperature. Characterisation of the compounds were made from the results of elemental analyses, IR and 1R spectroscopic studies. The compounds decompose in water at ambient temperatures thus precluding their molar conductance measurements. The results of IR and 1R spectroscopic studies suggest that the complex species $[B_2O_2F_2(OH)_2]^{2-}$ contains two tetrahedral boron atoms with a  linkage.

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PART B

Reported in Chapter 5 are a direct synthesis of alkali-metal and ammonium pentafluoroperoxotitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4), first synthesis and structural assessment of potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3].3H_2O$, and potassium and ammonium difluorodiperoxotitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4). In view of the difficulties encountered in the synthesis of $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4) using the literature reported method, a direct procedure has been developed for the synthesis of $A_3[Ti(O_2)F_5]$. The new method involves a reaction among freshly prepared TiO_2, aqueous hydrofluoric acid, and hydrogen peroxide at pH 6, adjusted by the addition of alkali hydroxide or aqueous ammonia. The compounds were characterised, and their identity established from the results of chemical analyses, conductance and magnetic susceptibility measurements, and IR and laser Raman (lR) spectroscopic studies. The advantages of the new method has also been accentuated.

It has been shown that the reaction of a solution of freshly prepared TiO_2 in 40% HF with an excess of aqueous hydrogen peroxide and KOH, followed by the addition of hydrofluoric acid to adjust the pH of the reaction solution between 8 and 9, affords the yellow microcrystalline potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3].3H_2O$, in a high yield. The compound has been characterised by elemental analyses, magnetic susceptibility measurement and IR and lR spectroscopic studies. IR and lR spectral results show that the peroxide group isbonded to the titanium(IV) centre in a triangular bidentate (C_{2v}) manner. The compound is stable in the absence of moisture. $K[Ti(O_2)F_3].3H_2O$, which decomposes in water at ambient temperatures precluding molar conductance measurement, is diamagnetic.

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Syntheses of molecular mixed-ligand peroxo complexes of titanium(IV) of the types $[Ti(O_2)_2(L-L)]$ (L-L = o-phen or bipy) and $[Ti(O_2)_2(thiourea)].H_2O$ were accomplished from the reaction of a solution of freshly prepared TiO_2 in 40% HF with an ethanolic solution of 1,10-phenanthroline, an ethanolic solution of 2,2'-bipyridine, an aqueous solution of thiourea, respectively, and 30% H_2O_2 at pH 7 maintained by the addition of aqueous ammonia. They are stable for a prolonged period. The compounds are insoluble in water as well as in common organic solvents. The IR and lR spectra provide evidence for the occurence of triangular bidentate peroxides (O_2^{2-}) in each of the complexes. While o-phen and bipy occur as bidentate ligands in the respective compounds, thiourea in $[Ti(O_2)_2(thiourea)].H_2O$ acts as a monodentate ligand. The compounds are all diamagnetic in nature in accord with the presence of titanium(IV).

Laser Raman spectroscopic evidence for the existence of oxoperoxotitanate(IV) containing 'titanyl' moiety in aqueous solution and synthesis of an unusual example of peroxotitanate(IV) complex potassium oxoperoxodichlorotitanate(IV) monohydrate, $K_2[TiO(O_2)Cl_2].H_2O$, constitute the subject matter of Chapter 7.

Laser Raman (lR) spectrum of an yellow solution obtained from the reaction of a freshly prepared TiO_2 with potassium chloride, hydrogen peroxide and hydrochloric acid at pH 6, adjusted by a careful addition of KOH solution showed —— in addition to the expected modes of peroxide (O_2^{2-}) ——— a distinct polarised signal characteristic of $\tilde{\nu}$ (Ti=O). The yellow solution as obtained above on being treated with ethanol, to initiate precipitation, afforded light-yellow microcrystalline $K_2[TiO(O_2)Cl_2].H_2O$ compound in a very high yield. The compound, which is insoluble both in water and common organic solvents at ambient temperatures precluding molar conductance measurement, is diamagnetic. An analysis of the results of spectroscopic studies suggests that a monomeric oxoperoxotitanate(IV) species formed in solution undergoes polymerisation in the process of its isolation in the solid form via μ-oxo bridges in the crystal lattice. The results also provide evidences for the occurence of a triangularly bonded peroxide (O_2^{2-}) group. Further the spectra suggests that the complex species $[TiO(O_2)Cl_2]^{2-}$ has a distorted octahedral structure through -Ti-O-Ti- interactions.

Chapter 8, indeed the concluding Chapter of the thesis, contains the results of studies involving the synthesis, characterisation, and assessment of structure of alkali-metal and ammonium oxotetrafluorotitanates(IV), $A_2[TiOF_4]$ (A = K, Cs or NH_4). In view of the problems encountered in the synthesis of pure $[TiOF_4]^{2-}$ by the literature methods, a new procedure has been developed for the synthesis of pure $A_2[TiOF_4]$ (A = K, Cs

or NH_4). The new method of synthesis is based on the reaction of freshly precipitated TiO_2 with 4M sulphuric acid and an aqueous solution of the corresponding AF (A = K or NH_4) with the molar ratio of Ti:AF being maintained at 1:7. While the potassium salt was spontaneously precipitated from the reaction solution, precipitation of ammonium salt required the addition of ethanol. The corresponding Cs^+ salt has been prepared from the ammonium salt, $(NH_4)_2[TiOF_4]$, by metathesis. The $A_2[TiOF_4]$ compounds are all white products and decompose in water at ambient temperatures. That, the titanium occurs in its +4 oxidation state (d^o) in each of the compounds is evidenced by the results of magnetic susceptibility measurements. They are also EPR silent. The IR and 1R spectra provide evidence for a distorted octahedral structure of the complex $[TiOF_4]^{2-}$ ion with -Ti-O-Ti- interactions.

The results of research described in Chapters 3, 4 and 5 have been published, and those described in Chapter 8 is now in press, while the work described in Chapters 6 and 7 have been communicated for publication.

Chapter 3

J. Chem. Soc., Dalton Trans., 1987, 0000.

Chapter 4

Inorg. Chem., 1985, 24, 2580.

Chapter 5

Polyhedron, 1985, 4, 1449; Inorg. Chem., 1986, 25, 168.

Chapter 8

Ind. J. Chem., 1987, in press (IC 5439/87).

CHAPTER 1

Chapter 1

INTRODUCTION

Boron is the fifth element in the Periodic Table and only non-metal of Group-III having the ground state electronic configuration $[He]2s^2 2p$. 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, $Na_2B_4O_7.10H_2O$, is the principal source of boron and is present in hot springs and lakes in volanic region. Natural boron has two stable isotopes ^{10}B and ^{11}B, occuring 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}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 : $1s^2 2s^2 2p \longrightarrow 1s^2 2s 2p^2$. 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[3-5] 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.[6-8] 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 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 occuring 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 (BO_3) and tetrahedral (BO_4) units. An interesting aspect of boron chemistry is marked by its ability to form polymeric species[9] in which the trimeric BO_3 rings are fused to other units at tetrahedral boron atoms forming a complex polyanion through linking together of BO_3 and 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, $K[B_5O_6(OH)_4].2H_2O$, 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 eversince. 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 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 $[B_5O_6(OH)_4]^-$ 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)π 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. 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 BF_3 molecule does not undergo dimerisation probably owing to formation of internal

dative π-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 π 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 $BF_3 + F^- \longrightarrow BF_4^-$ 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[14] $[BF_n(OH)_{4-n}]^-$. 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[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 $[B_2O_2F_2(OH)_2]^{2-}$ 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, $[B_5O_6(OH)_4]^-$ ion.

Besides oxide and fluoride, peroxide (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 text book story[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 $[B_2(O_2)_2(OH)_4]^{2-}$ 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[30-32] 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 (O_2^{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 $A_2[B(O_2)F_3].4H_2O$ (A = Na or K) and $(NH_4)_2[B_2(O_2)_3F_2]$ 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 $[Ar]3d^2 4s^2$ 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 π-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.[40] Though it has been claimed that titanium(IV) compounds in an aqueous acidic solution contains the 'titanyl', TiO^{2+}, ion yet the question about the existence of this ion remained as a matter of prolonged dispute.[41-44] However, some recent publications[45,46] have confirmed the occurence of monomeric structures of titanium(IV) compounds with terminal Ti=O ('titanyl') unit. The presence of this core has also been established in aqueous acidic solutions by indirect techniques such as ion exchange,[47] potentiometric titration,[41] electromigration,[48] and kinetic studies of electron-transfer and complexation reactions,[42,43,49-53] and in some solid compounds by X-ray crystallographic studies.[54,55] The 'titanyl' ion, TiO^{2+}, has also been shown to form some compounds with different ligands where titanium(IV) is usually in 6- or 7-coordination.[56] An important point about the oxotitanium(IV) complexes which also deserves a comment is that the TiO^{2+} group occurs not only in its monomeric form but also as a polymer with -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,[57,58] and some peroxo-transition metal compounds have been isolated in the solid state. Peroxo-metal compounds, besides having an intrinsic interest of their own,[59-68] are of considerable and growing importance particularly in relation to the catalysis of oxidation[69] including hydrogen peroxide itself,[30] and the storage and transport of oxygen in biological systems.[70,71] Some transition metal peroxide compounds

are also used as reagents for epoxidation of olefines, and hydroxylation of alkenes, and aromatic hydrocarbons.[30,72,73]

Although the term molecular oxygen refers to the free uncombined O_2 molecule with the ground state $^3\sum_g^-$, 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.[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.[70] A common characteristic of these complexes is the O-O distance, which lies between 1.40 and 1.52Å (1.49Å for O_2^{2-}), and the corresponding infrared frequency $\tilde{\nu}$ (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.[30-32,35,36,71,75-78] The reactivity of peroxides,[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 O-Pπ^* 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,[70] 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 $^3\sum_g^-$ ground state, and a molecular orbital description is

$$O_2 \quad KK\ (2s\sigma_g)^2\ (2s\sigma_u^*)^2\ (2p\sigma_g)^2\ (2p\pi_u)^4\ (2p\pi_g^*)^1\ (2p\pi_g^*)^1$$

where KK term indicates that the K shells of two oxygen atoms are filled. The two unpaired electrons in the $^3\sum_g^-$ 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

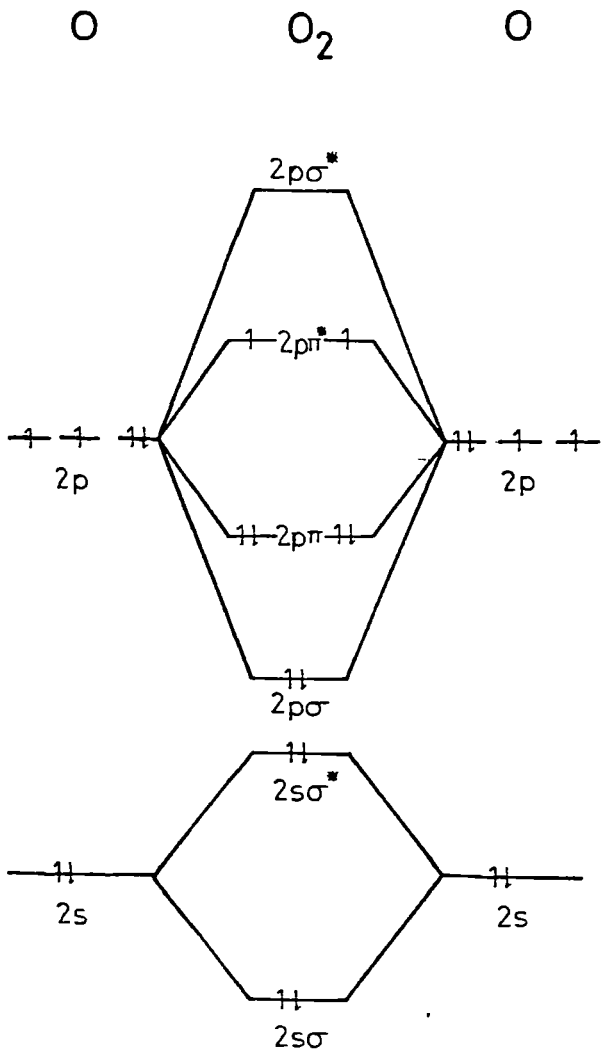


Fig 1-1.Molecular orbital diagram for O_2

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]

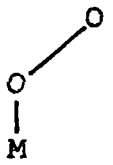
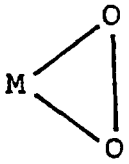
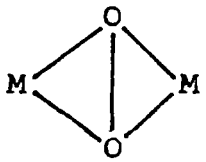
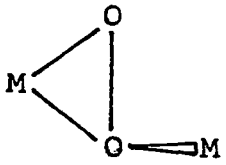
Structural Type	Structural Designation	Vaska Classification
	η^1 dioxygen	Type Ia (superoxo)
	η^2 dioxygen	Type IIa (peroxo)
	$\eta^1 : \eta^1$ dioxygen	Type Ib (superoxo)
	$\eta^1 : \eta^1$ dioxygen	Type IIb (peroxo)
	$\eta^2 : \eta^2$ dioxygen	-
	$\eta^1 : \eta^2$ dioxygen	-

Fig. 1-2 Structural Classification of dioxygen complexes

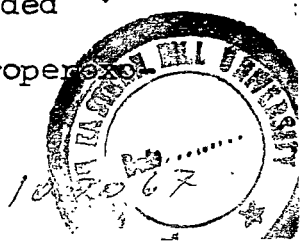
The bridging μ-peroxo could vary from cis-planar and trans-planar to trans-nonplanar configurations. An unusual symmetrical double bridging was also found,[79-81] however, such structures are very rare. Deviations from the ideal symmetry are often encountered. In the case of

heteroligand fields the deviations are due to the inherent symmetry of different ligands. Additional $p\pi^*$ electron delocalisation to the metal ion is anticipated which would therefore favour a d^o or a low d^n metal ion configuration. The stereochemical polyhedra in heteroligand peroxo complexes are often fairly predictable. The pentagonal bipyramidal arrangement is the most common[82,83] 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.[34,84-88] The peroxo metal complexes involving a metal and a peroxide ligand bonded in a triangular bidentate manner would be expected[85] to give rise to three vibrations of symmetry species $(2A_1 + B_2)$, and these may be designated as $\tilde{\nu}_1$ (A_1; O-O stretching); $\tilde{\nu}_2$ (A_2; symmetric metal-peroxide stretch) and ν_3 (B_2; asymmetric metal-peroxide stretch). All the three modes are both IR and Raman active. While the A_1 modes are polarised, the B_2 modes are depolarised. The $\tilde{\nu}$ (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 $\tilde{\nu}$ (O-O) with M-O_2 vibrations. The co-ordination of O_2^{2-} groups in a triangular bidentate

manner is by far the most common and is similar to the one proposed by Griffith[89] 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.[90] 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,[91] 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 peroxo-titanates(IV) are rather scanty, except for a few sulphato-, chloro-, and fluoro-peroxotitanates(IV).[92] Among the fluoro-peroxotitanates(IV), however, $A_3[Ti(O_2)F_5]$ (A = Li, Na, K or NH_4)[92] appears to be the best characterised one and is the most often quoted example of a typical peroxotitanate(IV) compound. The procedure recommended[91,92] and currently used for the preparation of alkali pentafluoroperoxo-



titanates(IV), $A_3[Ti(O_2)F_5]$ (A = Li, Na, K or NH_4), requires the $[TiF_6]^{2-}$ 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), $A_3[Ti(O_2)F_5]$ 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 to 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), $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4), synthesis of a new potassium monoperoxo-trifluorotitanate(IV) trihydrate, $K[Ti(O_2)F_3].3H_2O$, and first synthesis of potassium and ammonium diperoxodifluorotitanates(IV), $A_2[Ti(O_2)_2F_2]$ (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 hetero-ligand 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.[30] The recent use of a peroxo compound of titanium(IV) as a catalyst in organic synthesis[38] 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, $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4), and three molecular mixed-ligand diperoxo compounds of titanium(IV) of the types $[Ti(O_2)_2(L\text{-}L)]$ (L-L = 1,10-phenanthroline or 2,2′-bipyridine), and $[Ti(O_2)_2(thiourea)].H_2O$ 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,[82,93,103-107] the corresponding compounds of titanium(IV) are very sparse. To our knowledge, the only

reported example of such a compound, that has been also characterised crystallographically, is $K_2[Ti_2O(O_2)_2(dipic)_2]$ (dipic = dipicoline)[108] albeit a few non-peroxo compounds containing 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 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 Ti=O ('titanyl') core,[45,46,55] while those of polymeric complexes contains oxo-bridged (μ-oxo) species through -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 experimental 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, $K_2[TiO(O_2)Cl_2].H_2O$, 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.[111-118] This field of transition metal chemistry continues to attract much attention and produces new and exciting results.[119-122] 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[123] 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 $[TiOF_5]^{3-}$ [55] is probably the most well characterised oxofluoro complex of titanium(IV) though $[TiOF_3]^-$ has a reported existence.[124] In addition to these two complex species evidences concerning

oxotetrafluorotitanates(IV), $[TiOF_4]^{2-}$, are also documented in the literature.[125-128] However, despite a number of attempts made by earlier workers[125-128] synthesis of pure $[TiOF_4]^{2-}$ 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[129] involving a high temperature thermal decomposition of a peroxo complex $K_2[Ti(O_2)F_4]$, $K_2[TiOF_4]$ 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 develope a suitable synthetic route to pure oxotetrafluorotitanate(IV), $[TiOF_4]^{2-}$, 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 $A_2[TiOF_4]$ (A = K, Cs or 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.

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CHAPTER 2

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[1]

(i) Determination of boron gravimetrically as nitron tetrafluoroborate[1a]

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 $C_{20}H_{16}N_4 \cdot HBF_4$.

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.

$$1\ cm^3\ 1\underline{N}\ NaOH\ solution \equiv 0.06184g\ of\ H_3BO_3$$

The method described above was used for the determination of boron contents in pentaborate and fluoro(hydroxo)oxoborate compounds.

Titanium[2]

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 form 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 alongwith 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 TiO_2.

Active Oxygen (Peroxo Oxygen)[3-5]

(i) Permanganometry[3]

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.

$$1\ cm^3 \text{ of } 1\underline{N}\ KMnO_4 \equiv 0.01701g \text{ of } H_2O_2$$

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

(ii) Iodometry[4]

In a freshly prepared 2(N) sulphuric acid solution, containing an appropriate amount of potassium iodide (ca 1g in 100 cm^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_2 atmosphere in the dark. The liberated iodine was then titrated with a standard sodium thiosulphate solution, adding 2 cm^3 of freshly prepared starch solution when the colour of the iodine was nearly discharged.

$$1\ cm^3 \text{ of } 1\underline{N}\ Na_2S_2O_3 \equiv 0.01701g \text{ of } H_2O_2$$

(iii) Determination of Peroxide (O_2^{2-}) by Titration with a standard Ce^{4+} solution[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^{4+} solution.

Fluoride[6]

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,[6a] 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,[6b] 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 1$\underline{N}$ $AgNO_3 \equiv$ 0.0190g of F

Chloride[7]

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.

$$1\ cm^3 \text{ of } 1\underline{N}\ AgNO_3 \equiv 0.03546g \text{ of } Cl$$

Sulphate[8]

A known amount of the sulphatotitanate(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 $BaCl_2.2H_2O$ 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 $BaSO_4$.

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 $Hg[Co(NCS)_4]$ 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 (lR) spectra were recorded on a SPEX Ramalog Model 1403 Raman Spectrometer. The 4880Å or 5145Å 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 $100K_c$ modulator.

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   (b) Ref 1, p 269.

7. Ref 1, p 266.

8. Ref 1, p 463.

CHAPTER 3

Chapter 3

A New Route to Potassium and Ammonium Pentaborate Dihydrates, $A[B_5O_6(OH)_4]\cdot 2H_2O$ (A = K or NH_4), and Synthesis and Structural Assessment of New Fluoro(hydroxo)oxoborate Dihydrates, $A_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ (A = K or NH_4)*

The tetrafluoroborate, BF_4^-, and its hydroxy derivatives $[BF_n(OH)_{4-n}]^-$ 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, $K[B_5O_6(OH)_4]\cdot 2H_2O$, 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 develope a new and general synthetic route to potassium and ammonium pentaborate dihydrates, $A[B_5O_6(OH)_4]\cdot 2H_2O$ (A = K or NH_4), using a mild condition without involving fluoride.

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*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 $[B_5O_6(OH)_4]^-$ ion.

Although there are physico-chemical evidences for the existence of various fluoro(hydroxo)borates and fluoro(hydroxo)-oxoborates,[9] and oxo(hydroxo)borates[10,11] 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, $A_2[B_2O_2F_2(OH)_2].2H_2O$ (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, $A[B_5O_6(OH)_4].2H_2O$ (A = 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 $K[B_5O_6(OH)_4].2H_2O$ and $NH_4[B_5O_6(OH)_4].2H_2O$ were 1.6g (34%) and 1.4g (32%), respectively.

Synthesis of Potassium and Ammonium Fluoro(hydroxo)oxoborate Dihydrates, $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = 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 NH_4), in a polythene beaker, with the maintenance of the ratio of B:AF at 1:2.5. To this was added 8 cm^3 (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 $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = K or NH_4) 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 $A[B_5O_6(OH)_4].2H_2O$ (A = K or NH_4) are given in Table 3-2, while those of $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = K or NH_4) 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 BO_3 moieties

Table 3-1. Amounts of Reagents Used for the Synthesis and the Yields of $A_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ (A = K or NH_4)

Compound	Yield g (%)	Amount of boric acid g (mmol)	Amount of AF g (mmol)	Amount of 48% HF cm^3 (mmol)
$K_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$	4.5 (58)	2.0 (32.34)	4.7 (81.04)	8.0 (192)
$(NH_4)_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$	4.2 (66)	2.0 (32.34)	3.0 (81.08)	8.0 (192)

Table 3-2. Analytical Data of A $[B_5O_6(OH)_4]\cdot 2H_2O$ (A = K or NH_4)

Compound	Found % (Calcd. %)		
	K or N	B	H
$K[B_5O_6(OH)_4]\cdot 2H_2O$	13.1 (13.26)	18.58 (18.70)	2.54 (2.72)
$NH_4[B_5O_6(OH)_4]\cdot 2H_2O$	5.04 (5.12)	19.89 (20.14)	4.24 (4.39)

Table 3-3. Analytical Data of $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = K or NH_4)

Compound	Found % (Calcd. %)			
	K or N	B	F	H
$K_2[B_2O_2F_2(OH)_2].2H_2O$	32.62 (32.50)	9.1 (9.16)	15.78 (15.83)	2.35 (2.50)
$(NH_4)_2[B_2O_2F_2(OH)_2].2H_2O$	14.1 (14.14)	11.05 (11.11)	19.0 (19.19)	7.1 (7.07)

with the occassional occurence of BO_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, $[B_5O_6(OH)_4]^-$. 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 A $[B_5O_6(OH)_4].2H_2O$ (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 $\Omega^{-1}cm^2mol^{-1}$ 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 Λ_M values attesting to their stabilities also in solutions. In order to further establish their identity, the IR and laser Raman (lR) spectra of the compounds were recorded. While the IR spectra were recorded in the solid state, the lR spectra were recorded both on solids as well as on their solutions. The spectral features are identical to those reported

in the literature[10,13] for the salts of the complex $[B_5O_6(OH)_4]^-$ 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.[8,10,11,13]

In view of the physico-chemical evidences concerning the existence of fluoro(hydroxo)borates in solutions,[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, AF (A = K or NH_4), in the ratio of H_3BO_3: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, $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = 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, $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = 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 NH_4^+ salts suggest the stoichiometry of K:B:F:H and N:B:F:H as 1:1:1:3 and 1:1:1:7, respectively. Accordingly, the compounds have been tentatively formulated as $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = K or 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 lR spectroscopy (Table 3-4). The IR spectra showed bands at ca 596, ca 746, and ca 1300 cm^{-1}, and a broad absorption at ca 1060 cm^{-1}, the broadening of which is probably because of overlap of B-O[14] and B-F[15] vibrational modes. The band at ca 596 cm^{-1} has been assigned to ν (B-OH),[16] those at ca 746 and ca 1300 cm^{-1} have been attributed to ν_s(B-O-B) and ν_{as}(B-O-B) modes, respectively.[17] In addition the spectra show two extra bands at ca 1640 and ca 3450 cm^{-1} typical for δ(H-O-H) and ν (O-H) of uncoordinated water.[18] The absorptions at 3157, 3040, and 1400 cm^{-1} in the spectrum of the NH_4^+ salt have been attributed to ν_3, ν_1 and ν_4 modes of NH_4^+.[19] The lR spectra of both the compounds were recorded only on solids as they decompose in water even at room temperatures. The characteristic features of lR spectra are the peaks at ca 775, ca 820, and ca 595 cm^{-1}. The peaks at ca 775 and ca 595 cm^{-1} have been

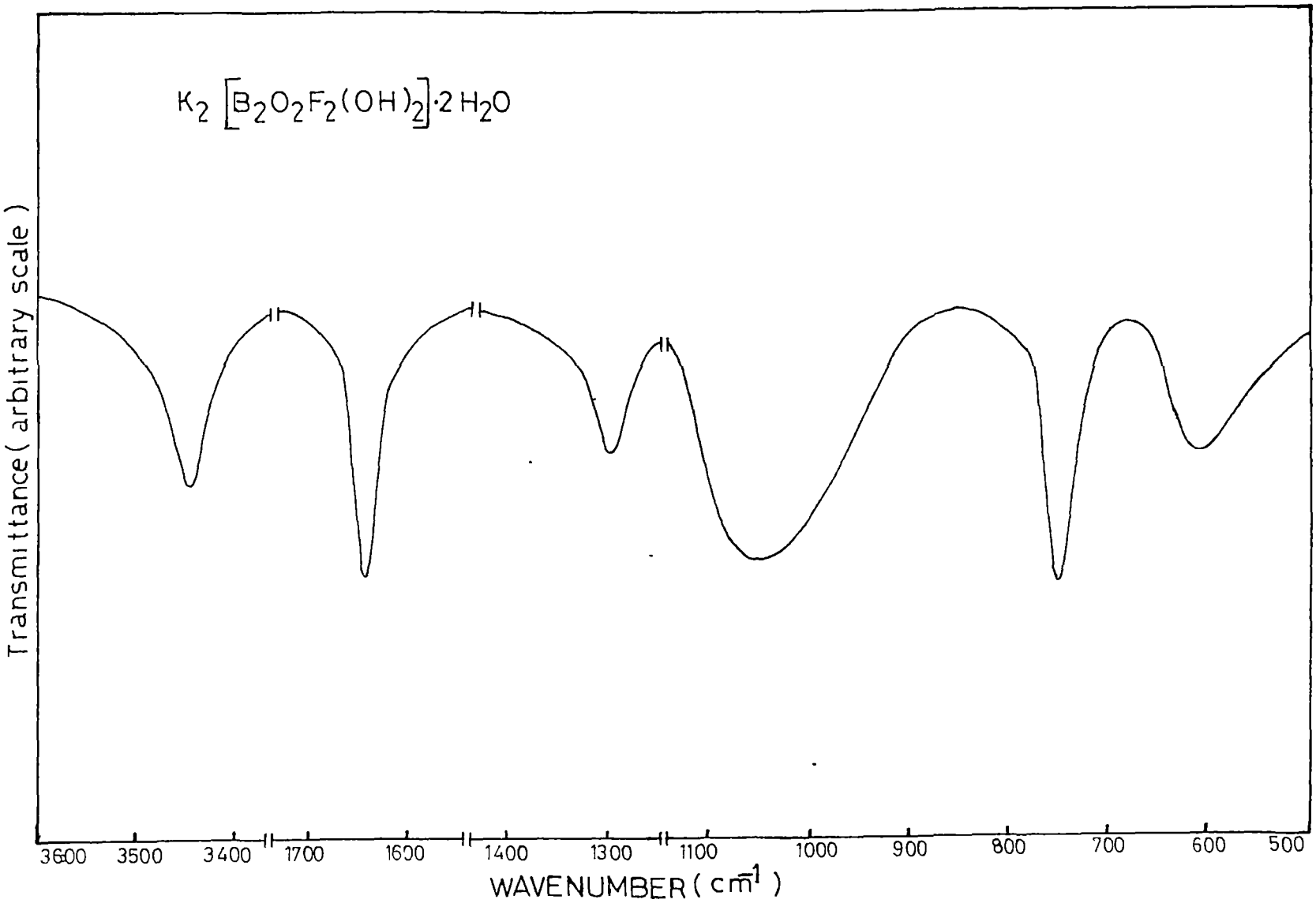
assigned to ν (B-F)[20] and ν (B-OH)[16] modes, respectively, originating from the presence of co-ordinated fluoride and OH and compare very well with those observed for some other complex species of boron. The signal at ca 820 cm^{-1} has been assigned to ν (B-O)[16] (of the B-O-B frame work). However, 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<O>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 $[B_2O_2F_2(OH)_2]^{2-}$.

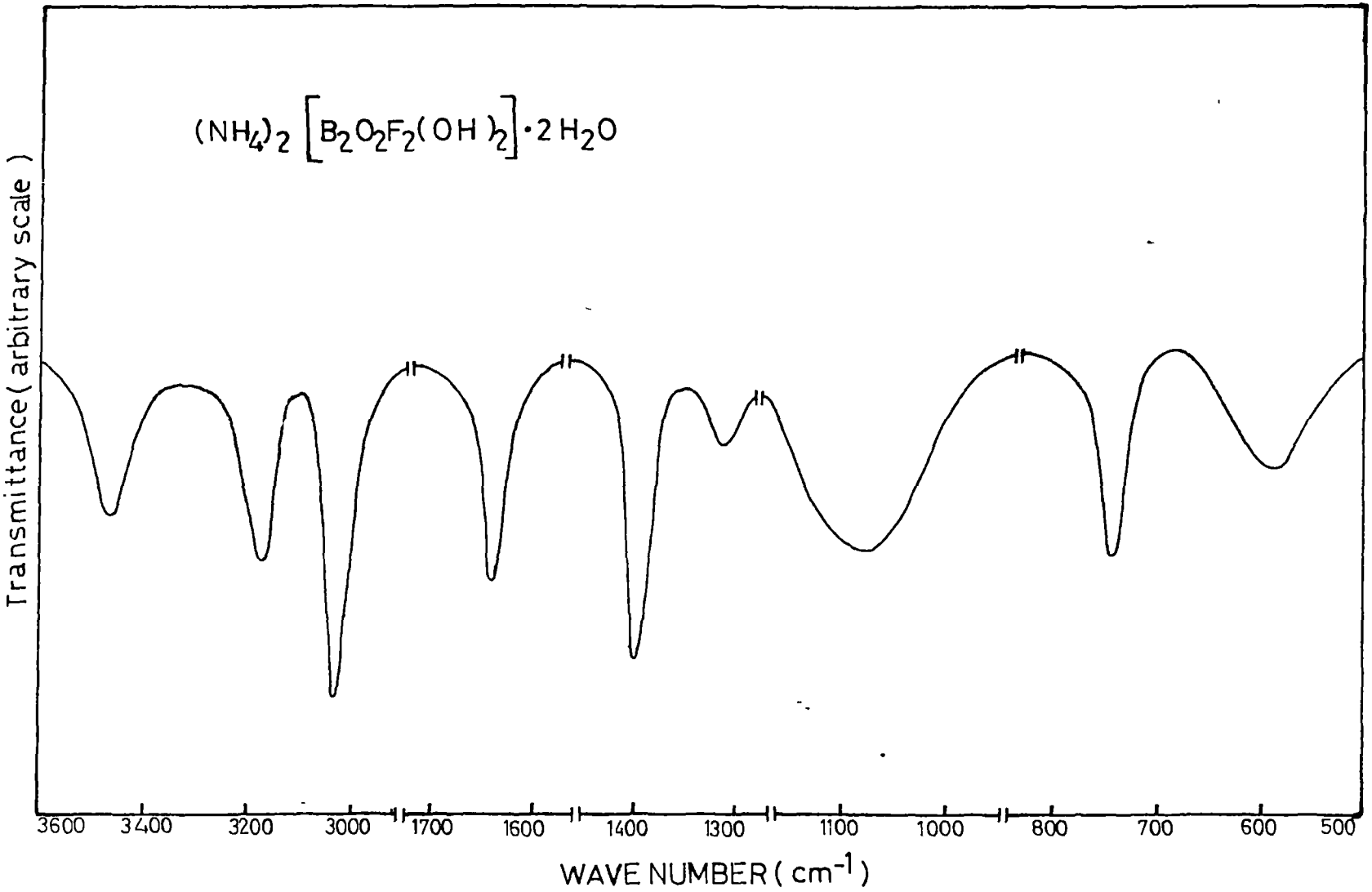
Thus it is evident from the present studies that the classic oft-quoted pentaborate, $A[B_5O_6(OH)_4].2H_2O$ (A = K or NH_4), can be synthesised rather easily, directly from the reaction of boric acid with potassium hydroxide or aqueous ammonia at pH 9 without using any drastic conditions or fluoride ions. The white crystalline $A[B_5O_6(OH)_4].2H_2O$ compounds are stable and do not decompose in water.

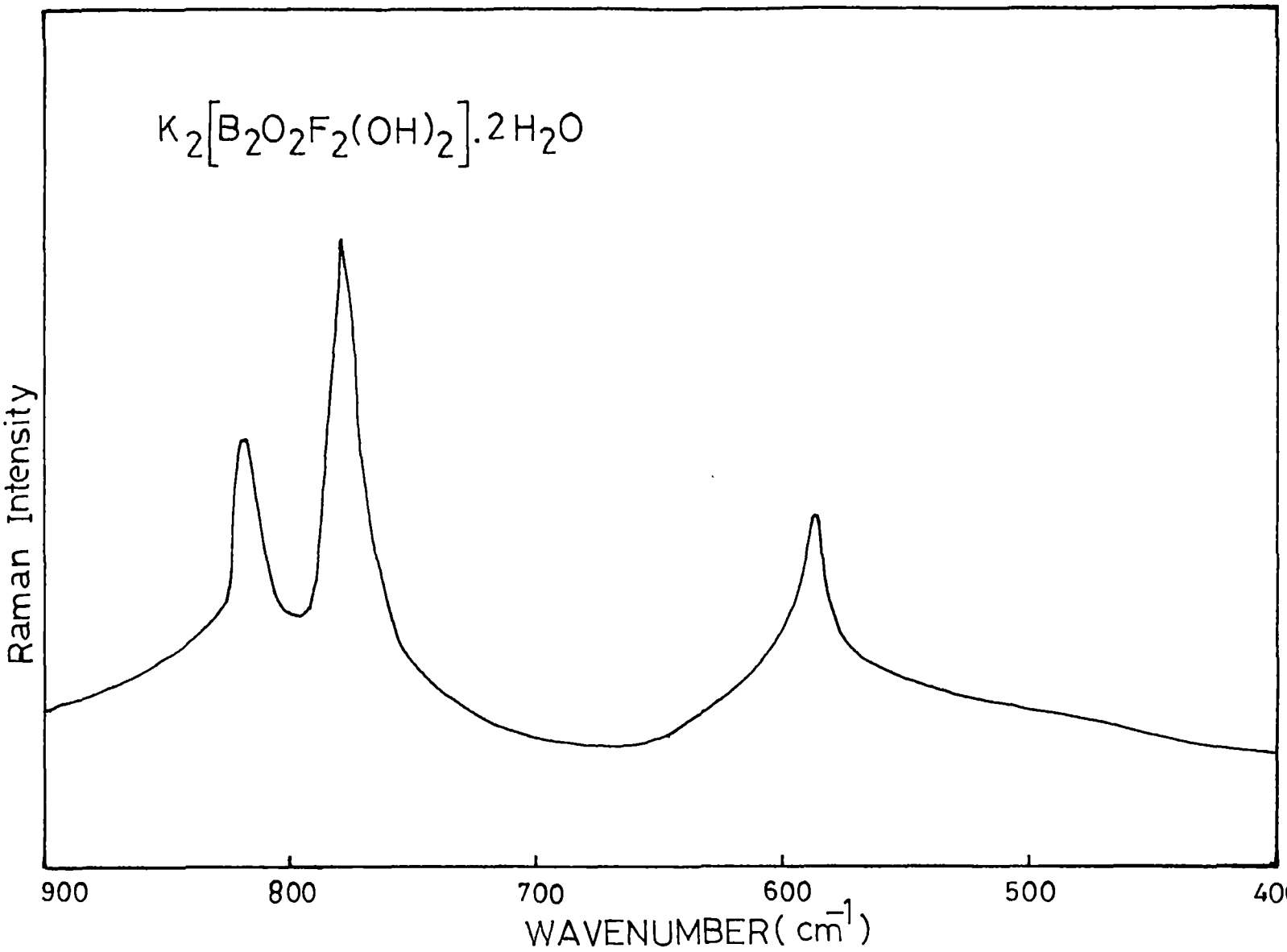
Potassium and ammonium fluoro(hydroxo)oxoborate dihydrates, $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = K or NH_4), can be obtained from the reaction of a solution of boric acid with AF and 48% hydrofluoric acid. The compounds do not melt upto 250°C. Unlike the $A[B_5O_6(OH)_4].2H_2O$ compounds, they decompose in water. The complex

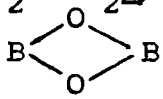
Table 3-4. Structurally Significant IR and laser Raman (lR) Bands of $A_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ (A = K or NH_4)

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$K_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$	596w	595	ν (B-OH)
	746m		ν_s (B-O-B)
		775	ν (B-F)
		825	ν (B-O) (of the B-O-B framework)
	1065br		ν (B-O) + ν (B-F)
	1300w		ν_{as} (B-O-B)
	1640m		δ (H-O-H)
	3450m		ν (O-H)
$(NH_4)_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$	598w	595	ν (B-OH)
	749m		ν_s (B-O-B)
		778	ν (B-F)
		820	ν (B-O) (of the B-O-B framework)
	1060br		ν (B-O) + ν (B-F)
	1305w		ν_{as} (B-O-B)
	1640m		δ (H-O-H)
	3455m		ν (O-H)
	3157m		ν_3 N-H
	3040s		ν_1 N-H
	1400s		ν_4 N-H


$K_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$
Transmittance (arbitrary scale)
3600
3500
3400
1700
1600
1400
1300
1100
1000
900
800
700
600
500
WAVENUMBER (cm^{-1})


$(NH_4)_2\left[B_2O_2F_2(OH)_2\right]\cdot 2H_2O$
Transmittance (arbitrary scale)
3600
3400
3200
3000
1700
1600
1400
1300
1100
1000
800
700
600
500
WAVE NUMBER (cm^{-1})


$K_2[B_2O_2F_2(OH)_2].2H_2O$
Raman Intensity
900
800
700
600
500
400
WAVENUMBER(cm^{-1})

$[B_2O_2F_2(OH)_2]^{2-}$ species contains two tetrahedral boron atoms with a  linkage, in addition to one F^- and one OH^- being terminally bonded to each of the two boron atoms.

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CHAPTER 4

Chapter 4

Alkali-Metal and Ammonium Peroxofluoroborates, $A_2[B(O_2)F_3].4H_2O$ (A = Na or K), and $(NH_4)_2[B_2(O_2)_3F_2]$. First Synthesis of Peroxofluoroborate Complexes*

The reaction of borates with hydrogen peroxide leads to products which probably contain the complex $[B_2(O_2)_2(OH)_4]^{2-}$ 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 $Na_2[B_2(O_2)_2(OH)_4].6H_2O$. 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.[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,[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, $A_2[B(O_2)F_3].4H_2O$ (A = Na or K), and $(NH_4)_2[B_2(O_2)_3F_2]$

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 $A_2[B(O_2)F_3].4H_2O$ (A = Na or K) and $(NH_4)_2[B_2(O_2)_3F_2]$ 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 $[B_2(O_2)_2(OH)_4]^{2-}$ in solution[1] 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.[10] Thus it was expected that under the appropriate conditions both peroxide (O_2^{2-}) and fluoride (F^-) ligands might be made to coordinate

Table 4-1. Amounts of Reagents Used for the Synthesis and the Yields of $A_2[B(O_2)F_3] \cdot 4H_2O$ (A = Na or K) and $(NH_4)_2[B_2(O_2)_3F_2]$

Compound	Yield g (%)	Amount of boric acid g (mmol)	Amount of 40% HF cm^3 (mmol)	Amount of 30% H_2O_2 cm^3 (mmol)
$Na_2[B(O_2)F_3] \cdot 4H_2O$	6.5 (92)	2.0 (32.34)	6 (120)	14 (123.4)
$K_2[B(O_2)F_3] \cdot 4H_2O$	6 (74)	2.0 (32.34)	6 (120)	14 (123.4)
$(NH_4)_2[B_2(O_2)_3F_2]$	4.5 (72)	2.0 (32.34)	6 (120)	14 (123.4)

Table 4-2. Analytical Data of $A_2[B(O_2)F_3] \cdot 4H_2O$ (A = Na or K) and $(NH_4)_2[B_2(O_2)_3F_2]$

Compound	Found % (Calcd. %)			
	A or N	B	O[a]	F
$Na_2[B(O_2)F_3] \cdot 4H_2O$	45.35 (45.98)	5.21 (4.96)	14.8 (14.69)	27.11 (26.16)
$K_2[B(O_2)F_3] \cdot 4H_2O$	31.54 (31.27)	4.52 (4.32)	13.2 (12.8)	23.12 (22.79)
$(NH_4)_2[B_2(O_2)_3F_2]$	14.47 (14.62)	11.64 (11.28)	51.2 (50.07)	19.75 (19.82)

[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% H_2O_2 solution were performed at pH 9 which gave rise to the formation of the complex ion $[B(O_2)F_3]^{2-}$ in the case where the alkali-metal hydroxide was either NaOH or KOH, and $[B_2(O_2)_3F_2]^{2-}$ in the case of aqueous ammonia. The complex ions were isolated as $Na_2[B(O_2)F_3].4H_2O$, $K_2[B(O_2)F_3].4H_2O$, and $(NH_4)_2[B_2(O_2)_3F_2]$ 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 thence 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 $\tilde{\nu}$ (O-O), and

a band at ca 1050 cm^{-1} owing to ν (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

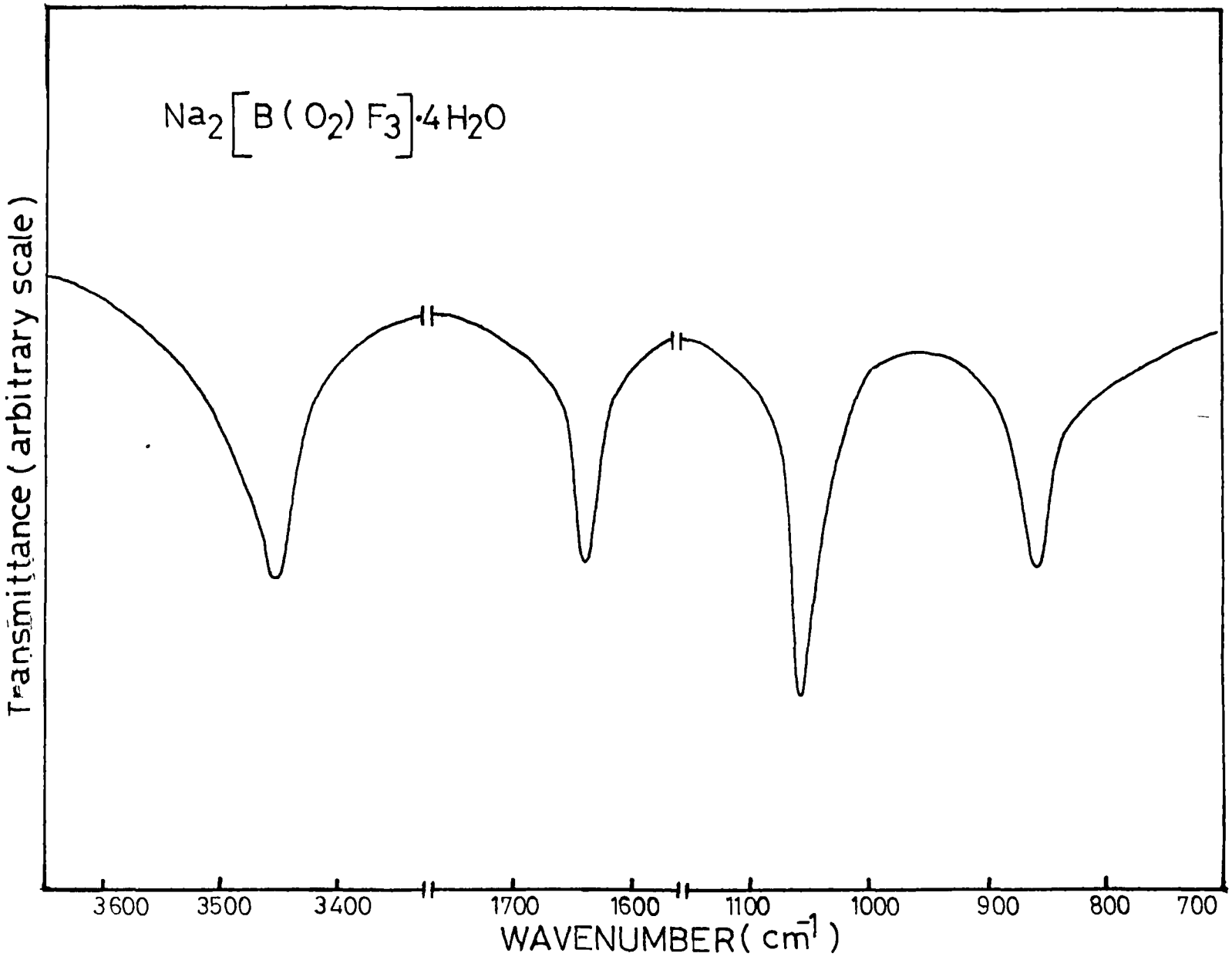
The newly synthesised alkali-metal and ammonium peroxofluoroborate complexes are all white crystalline stable products and can be stored in sealed polyethylene bags. Their stabilities can be ascertained by periodic estimation of peroxide. The peroxide content in each of the compounds was estimated by 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 $B:O_2^{2-}:F^-$ 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 $Na_2[B(O_2)F_3].4H_2O$, $K_2[B(O_2)F_3].4H_2O$, and $(NH_4)_2[B_2(O_2)_3F_2]$. The peroxofluoroborates do not melt upto 300°C, however, the $(NH_4)_2[B_2(O_2)_3F_2]$ 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 $\Omega^{-1}cm^2mol^{-1}$ (at 22°C in water) in very good agreement with their formulas. A slightly higher value in the

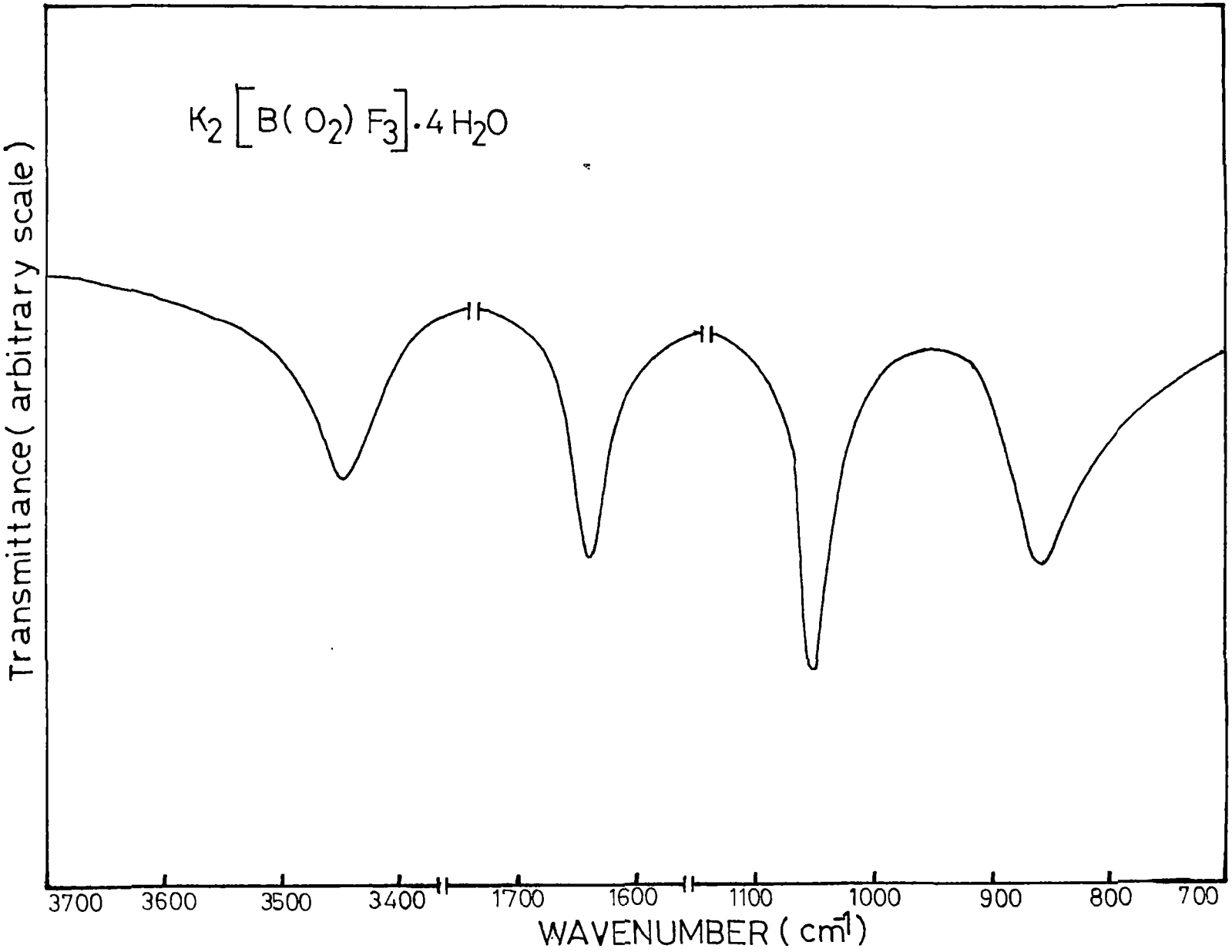
case of the Na^+ salt might be due to the presence of a trace of impurity, presumably sodium fluoride, arising from its low solubility.

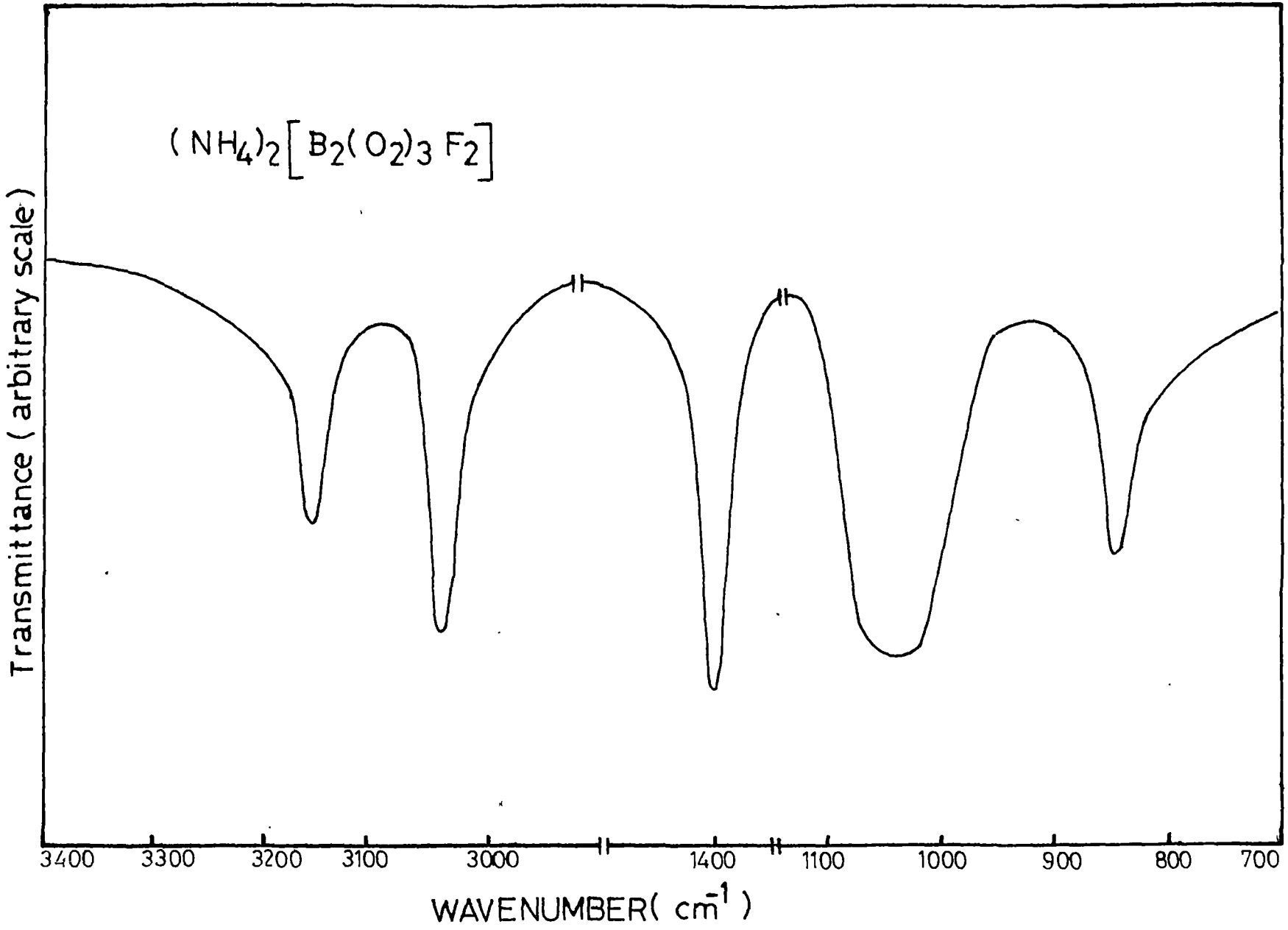
The infrared spectra of peroxofluoroborates are quite characteristic. The most significant feature of IR spectra of the compounds are the absorptions (Table 4-3) at ca 1050 and ca 860 cm^{-1} which have been assigned to the ν (B-F)[11] and ν (O-O)[12] modes, respectively, originating from the presence of coordinated fluoride and peroxide ligands. The position of ν (O-O) suggests a strong possibility of the O_2^{2-} ligand being bonded to the boron centre in a triangular bidentate (C_{2v}) manner, and the complex anion $[B(O_2)F_3]^{2-}$ 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 $[B_2(O_2)_3F_2]^{2-}$ shows a pattern generally similar to that of $[B(O_2)F_3]^{2-}$ species, except for much greater broadening of the band at 1050 cm^{-1}. Thus it is believed that the stereochemistry of boron in the $[B_2(O_2)_3F_2]^{2-}$ ion is tetrahedral, which is attained through coordination of one peroxide (O_2^{2-}) 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 $NaBO_3 \cdot 4H_2O$, with two O-O bridges connecting the two boron atoms (i.e. a six membered B_2O_4 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 $[B_2(O_2)_2(OH)_4]^{2-}$, the latter

Table 4-3. Molar Conductance Values and Structurally Significant IR Bands of $A_2[B(O_2)F_3].4H_2O$ (A = Na or K) and $(NH_4)_2[B_2(O_2)_3F_2]$

Compound	Molar conductance $\Omega^{-1}cm^2mol^{-1}$	IR cm^{-1}	Assignment
$Na_2[B(O_2)F_3].4H_2O$	270	1060s	ν (B-F)
		860m	ν (O-O)
		3450m	ν (O-H)
		1640m	δ (H-O-H)
$K_2[B(O_2)F_3].4H_2O$	255	1050s	ν (B-F)
		860m	ν (O-O)
		3450m	ν (O-H)
		1640m	δ (H-O-H)
$(NH_4)_2[B_2(O_2)_3F_2]$	234	1050 (s,br)	ν (B-F)
		850m	ν (O-O)
		3155m	ν_3 N-H
		3045s	ν_1 N-H
		1400s	ν_4 N-H


$Na_2[B(O_2)F_3]\cdot 4H_2O$
Transmittance (arbitrary scale)
3600
3500
3400
1700
1600
1100
1000
900
800
700
WAVENUMBER (cm^{-1})


$K_2[B(O_2)F_3]\cdot 4H_2O$
Transmittance (arbitrary scale)
3700
3600
3500
3400
1700
1600
1100
1000
900
800
700
WAVENUMBER (cm^{-1})


$(NH_4)_2[B_2(O_2)_3F_2]$
Transmittance (arbitrary scale)
3400
3300
3200
3100
3000
1400
1100
1000
900
800
700
WAVENUMBER(cm^{-1})

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 $(NH_4)_2[B_2(O_2)_3F_2]$ have been attributed to the ν_4, ν_1 and ν_3 modes of NH_4^+.[15]

Thus, it may be inferred from the results of studies described in the present Chapter that the hitherto unknown peroxofluoroborates, $A_2[B(O_2)F_3].4H_2O$ (A = Na or K), and $(NH_4)_2[B_2(O_2)_3F_2]$, 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 $[B(O_2)F_3]^{2-}$ ion contains a peroxide group bonded to the boron centre in a triangular bidentate fashion in addition to the coordinated fluoride ligands, the complex $[B_2(O_2)_3F_2]^{2-}$ 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.

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PART B

CHAPTER 5

Chapter 5

Direct Synthesis of Alkali-Metal and Ammonium Pentafluoroperoxotitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4), and First Synthesis and Structural Assessment of Potassium and Ammonium Difluorodiperoxotitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4), and Potassium Trifluoroperoxotitanate(IV) Trihydrate, $K[Ti(O_2)F_3].3H_2O$*

The importance of and the interests in peroxo transition metal compounds, which rendered them the focus of one of the active areas of contemporary research, have been emphasised in the literature[1-7] and highlighted in Chapter 1. Many transition metals, of which titanium is not an exception, give colour reactions with hydrogen peroxide owing to the formation of complex peroxo-metal species in solution. Although the chemistry of peroxotitanate(IV) complexes has a rather long history, only a limited number of heteroligand-peroxotitanates(IV) have a reported existence —— of which sulphato- and fluoro-peroxotitanates(IV) are the frequently quoted ones.[8] The only fluoro-peroxotitanate(IV) known[8] to our knowledge is $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4). The literature method of synthesis of $A_3[Ti(O_2)F_5]$ requires $[TiF_6]^{2-}$ as an

*The work described in this Chapter has been published: Polyhedron, 1985, 4, 1449; Inorg. Chem., 1986, 26, 168.

essential precursor which involves an extra preparation step. Within the context of the chemistry of peroxotitanates(IV), there is no reported existence of any diperoxotitanate(IV) complex in the solid state although evidences concerning the occurence of such complex species in solutions are documented in the literature.[9] We were unable to think of any obvious reason for the lack of information regarding the synthesis of diperoxotitanate(IV) complexes in the solid form.

It was, however, expected that diperoxo complexes of titanium(IV) would be capable of being synthesised under suitable experimental conditions. In view of this as well as the intrinsic importance of peroxo-metal compounds,[1-7] a systematic study involving synthesis, studies of properties, and structural assessment of peroxotitanate(IV) compounds was undertaken. This has now led to the synthesis of a series of novel fluoroperoxotitanate(IV) of the types $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4) and $K[Ti(O_2)F_3].3H_2O$.

The present Chapter reports a direct method for the synthesis of $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4), and first syntheses, characterisation, and assessment of structures of potassium and ammonium difluorodiperoxotitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4), and potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3].3H_2O$. Characterisation and structural assessment of the newly synthesised compounds have been made by various physicochemical studies including laser Raman (1R) spectroscopy.

Experimental

Reagent grade chemicals were used for the present studies (E. Merck, S.D's, B.D.H., and Loba-Chemie).

Synthesis of Alkali-Metal and Ammonium Pentafluoroperoxotitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4)

In a typical reaction, to a stirred cold solution of 2.0g (25 mmol) of TiO_2 in 20 cm^3 (400 mmol) of 40% hydrofluoric acid obtained by heating the mixture for ca 20 min, was added 20 cm^3 (176.4 mmol) of 30% H_2O_2 at ca 20°C. After the solution was stirred for ca 10 min at 20°C the corresponding alkali-metal hydroxide, AOH (A = Na or K), or aqueous ammonia was added in small portions with slow stirring until the pH of the solution was raised to 6 whereupon yellow microcrystalline alkali-metal or ammonium pentafluoroperoxotitanate(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4), was precipitated in a very high yield. While sodium or potassium hydroxide was added in the form of powder, aqueous ammonia was added as its concentrated solution (sp.gr. 0.9). The cooling bath was removed and the compound was separated by centrifugation, washed three times with ethanol, and finally dried in vacuo over concentrated sulphuric acid.

The specific amounts of reagents used for the synthesis and the yields of $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4) are reported in Table 5-1.

Table 5-1. Amounts of Reagents Used for the Synthesis and the Yields of $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4)

Compound	Yield g (%)	Amount of TiO_2 in g (mmol)	Amount of 40% HF cm^3 (mmol)	Amount of 30% H_2O_2 cm^3 (mmol)
$Na_3[Ti(O_2)F_5]$	5.5 (90)	2.0 (25)	20 (400)	20 (176.4)
$K_3[Ti(O_2)F_5]$	6.5 (89)	2.0 (25)	20 (400)	20 (176.4)
$(NH_4)_3[Ti(O_2)F_5]$	5.5 (96)	2.0 (25)	20 (400)	20 (176.4)

Synthesis of Potassium and Ammonium Difluorodiperoxotitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4)

Since the method of synthesis of potassium or ammonium difluorodiperoxotitanate(IV), is a general one, only a representative procedure is described below.

In a typical synthesis, 1.0g (12.5 mmol) of TiO_2 was dissolved in 10 cm^3 (200 mmol) of 40% HF by warming over a steam-bath for ca 20 min. The clear solution was cooled to ca 20°C followed by the addition of 20 cm^3 (176.4 mmol) of 30% H_2O_2 with stirring. To the solution was added in small portions powdered potassium hydroxide

or aqueous ammonia (sp.gr. 0.9) in the case of NH_4^+ salt, with slow stirring until the pH of the reaction solution was raised to 9. The colour of the solution first turned red and then yellow giving a yellow precipitate at pH ca 6, which slowly went into solution with simultaneous decrease in the intensity of colour, with the progress of addition of alkaline medium. The ultimate colour of the solution at pH 9 was very faint yellow. Addition of ethanol to this solution afforded a very faint yellowish white microcrystalline potassium or ammonium difluorodiperoxotitanate(IV) compound , $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4), in a nearly quantitative yield. Each of the compounds was allowed to settle for ca 20 min, separated by centrifugation, and purified by washing 3-4 times with ethanol. The product thus obtained was dried in vacuo over concentrated sulphuric acid. The amounts of reagents used for the synthesis and the yields of $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4) are shown in Table 5-2.

Synthesis of Potassium Trifluoroperoxotitanate(IV), Trihydrate, $K[Ti(O_2)F_3].3H_2O$

An amount of 1.0g (12.5 mmol) of TiO_2 was dissolved in 10 cm^3 (200 mmol) of 40% HF by heating for ca 10 min over a steam-bath. The clear solution was cooled to 20°C and 20 cm^3 (176.4 mmol) of 30% H_2O_2 was added under stirring, followed by the addition of 17.5g (311.9 mmol) of powdered potassium hydroxide. The colourless solution thus obtained was maintained at ca 20°C for 15 min. Dropwise addition of 40% HF to the solution until the pH of the

medium was reduced to 8-9, changed the colour of the reaction solution to yellow and afforded yellow microcrystalline potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3].3H_2O$. Addition of hydrofluoric acid was stopped at this stage and the product was isolated by centrifugation, washed 3-4 times with ethanol, and finally dried in vacuo over concentrated sulphuric acid.

The yield of $K[Ti(O_2)F_3].3H_2O$ was 2g (69%).

Table 5-2. Amounts of Reagents Used for the Synthesis and the Yields of $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4)

Compound	Yield g (%)	Amount of TiO_2 in g (mmol)	Amount of 40% HF cm^3 (mmol)	Amount of 30% H_2O_2 cm^3 (mmol)
$K_2[Ti(O_2)_2F_2]$	2.6 (91)	1.0 (12.5)	10 (200)	20 (176.4)
$(NH_4)_2[Ti(O_2)_2F_2]$	2.2 (94)	1.0 (12.5)	10 (200)	20 (176.4)

Elemental Analyses

Quantitative estimations of titanium, peroxide, fluoride, sodium, potassium, and nitrogen contents of the compounds have been made by the methods already described in Chapter 2.

The analytical data of $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4), and $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4), and $K[Ti(O_2)F_3].3H_2O$ are set out in Table 5-3.

Table 5-3. Analytical Data of $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4), $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4), and $K[Ti(O_2)F_3].3H_2O$

Compound	Found % (Calcd. %)			
	A or N	Ti	O[a]	F
$Na_3[Ti(O_2)F_5]$	28.1 (28.28)	19.3 (19.64)	13.6 (13.12)	38.4 (38.96)
$K_3[Ti(O_2)F_5]$	39.8 (40.14)	16.7 (16.39)	11.2 (10.95)	32.9 (32.51)
$(NH_4)_3[Ti(O_2)F_5]$	18.51 (18.35)	21.2 (20.9)	14.2 (13.97)	41.8 (41.48)
$K_2[Ti(O_2)_2F_2]$	34.7 (34.28)	21.3 (21)	28.4 (28.06)	16.3 (16.66)
$(NH_4)_2[Ti(O_2)_2F_2]$	15.21 (15.06)	25.3 (25.75)	34.8 (34.4)	20.8 (20.43)
$K[Ti(O_2)F_3].3H_2O$	17.3 (17.0)	20.45 (20.82)	14.2 (13.91)	24.3 (24.78)

[a]Peroxo-oxygen

Results and Discussion

It is well known that titanium(IV) produces a characteristic colour with hydrogen peroxide solution and it serves as a very good test reaction for the detection of the metal.[9] Reactions of titanium(IV) with hydrogen peroxide are, however, complicated and different types of complex peroxo-titanate species are formed with a small variation of acidity/alkalinity of the reaction media. This is probably one of the main reasons why not much is known about peroxotitanates(IV). Pentafluoroperoxotitanate(IV), $[Ti(O_2)F_5]^{3-}$, is the most often quoted example of a typical peroxotitanate(IV) compound albeit a few more also have been reported.[10,11] However, no direct method of and the optimum pH required for the synthesis of the complex are known to date. The procedure recommended and generally used for the purpose requires the $[TiF_6]^{2-}$ complex as the essential precursor, which results in an extra preparation step. In order to circumvent the existing difficulties a search for the direct synthetic route to such compounds was therefore required. Considering that the reaction of hydrogen peroxide with titanium(IV) leading to a complex peroxo-titanate(IV) of a definite composition is highly dependent on the pH of the reaction medium and also that fluoride is known to form complexes with titanium(IV), it was expected that pentafluoro-peroxotitanate(IV) complexes could be synthesised directly from TiO_2 by proper adjustment of pH of the reaction solution. Thus, evaluation of an appropriate pH for successful synthesis of pentafluoroperoxotitanate(IV) complexes is emphasised to be an important pre-requisite. In the present case, the suitable pH for the synthesis was found to be 6. The strategy of the reaction

was that TiO_2 would dissolve in aqueous HF forming a fluorotitanate(IV), *in situ*, which without isolation would then be made to react with H_2O_2, at pH 6 of the reaction medium to afford the complex $[Ti(O_2)F_5]^{3-}$. The reaction took place accordingly and afforded yellow microcrystalline alkali-metal and ammonium pentafluoroperoxotitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4), in very high yields. The procedure is straightforward and simple and the spontaneous separation of the compound from the reaction solution at pH 6 is an additional advantage of the method.

In order to synthesise hitherto unknown fluoroperoxotitanate(IV) complexes containing two peroxo groups bonded per titanium(IV) centre, the reaction of a solution of TiO_2 in 40% HF was conducted at a much higher concentration of the alkaline medium (pH 9) with the anticipation that an increased pH would favour and facilitate introduction of more than one O_2^{2-} group into the coordination sphere of titanium(IV) at the expense of some F^- ligands already bonded to the metal. Thus, in accord with the strategy synthesis of difluorodiperoxotitanate(IV) complexes, $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4), was achieved at pH 9. That pH 9 is conducive to the synthesis was obtained from the facts that $A_3[Ti(O_2)F_5]$ which formed at pH 6 started dissolving with the progress of hike of pH, that the colour of the reaction solution started becoming pale and ultimately very pale at pH 9, and that the product isolated at pH 9 showed a clear shift of the ν (O-O) mode in the IR spectrum to a relatively lower frequency *ca* 860 cm^{-1}

in contrast to ca 900 cm^{-1} typically observed for the monoperoxotitanate(IV) complexes, $A_3[Ti(O_2)F_5]$ (Table 5-4). The product isolated at pH values between 6 and 8 showed two ν (O-O) modes at ca 900 and ca 860 cm^{-1}, suggesting thereby that the peroxide uptake process is in progress but is not complete until pH 9. A plausible mechanism, in view of the compounds isolated at pH 6 and 9 as $A_3[Ti(O_2)F_5]$ and $A_2[Ti(O_2)_2F_2]$, respectively, and also taking into consideration of the reported method of synthesis of $[Ti(O_2)F_5]^{3-}$ [9,12] complex, is that a fluorotitanate(IV) complex is first formed from the reaction of TiO_2 with 40% HF, which subsequently undergoes stepwise peroxogenation to afford $[Ti(O_2)F_5]^{3-}$ and $[Ti(O_2)_2F_2]^{2-}$. This certainly indicates that O_2^{2-} can displace some of F^- around a titanium(IV) centre at higher pH values even in the presence of a high concentration of fluoride ions. It is quite reasonable to assume that other heteroligand-peroxo complexes of titanium could be obtained directly from TiO_2.

Considering the importance of pH in the syntheses of fluoroperoxotitanate(IV) complexes, we were also interested to study the effect of variation of pH to the reaction among titanium(IV), O_2^{2-} and F^-, by first raising the pH to an alkaline region followed by bringing it down to an acidic range. Accordingly, the reaction of a solution of TiO_2 in 40% hydrofluoric acid with hydrogen peroxide was conducted at a highly alkaline condition followed by adjustment of pH of the reaction medium between 8 and 9 by a careful addition of 40% HF which led to the successful synthesis and isolation of a novel complex peroxotitanate(IV), potassium

trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3].3H_2O$, in a high yield. It is believed, here again, that TiO_2 dissolves in aqueous hydrofluoric acid to give a fluorotitanate(IV) species, which in the presence of an excess of hydrogen peroxide undergoes peroxogenation, facilitated by the addition of alkali. A practically colourless solution obtained at this stage indicates the eventual formation of a highly peroxogenated titanium species which might not be containing any coordinated fluoride. However, since the contention was to investigate the effect of lowering of the pH of the reaction medium, alkalinity of the reaction solution was reduced using 40% HF, which ultimately led to success in synthesis of the complex $[Ti(O_2)F_3]^-$ ion at pH 8-9. In an attempt to evaluate the effect of further lowering of pH on the composition of fluoroperoxotitanates(IV), pH of the reaction solution was adjusted to 6, and the compound isolated therefrom exhibited all the properties of already known complex $K_3[Ti(O_2)F_5]$.

The compounds $A_3[Ti(O_2)F_5]$ are yellow and $A_2[Ti(O_2)_2F_2]$ and $K[Ti(O_2)F_3].3H_2O$ are very light yellowish-white microcrystalline products. While $A_3[Ti(O_2)F_5]$ and $A_2[Ti(O_2)_2F_2]$ are soluble in water at room temperatures and do not exhibit any noticeable tendency for hydrolysis, $K[Ti(O_2)F_3].3H_2O$ is stable in the absence of moisture, and in water it decomposes slowly. The $A_3[Ti(O_2)F_5]$ and $A_2[Ti(O_2)_2F_2]$ compounds permit molar conductance measurements and the conductances of $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4), and $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4) have been found to lie in the range 350-370 and 220-240 $\Omega^{-1}cm^2mol^{-1}$, respectively, in conformity with their formulas. The room temperature

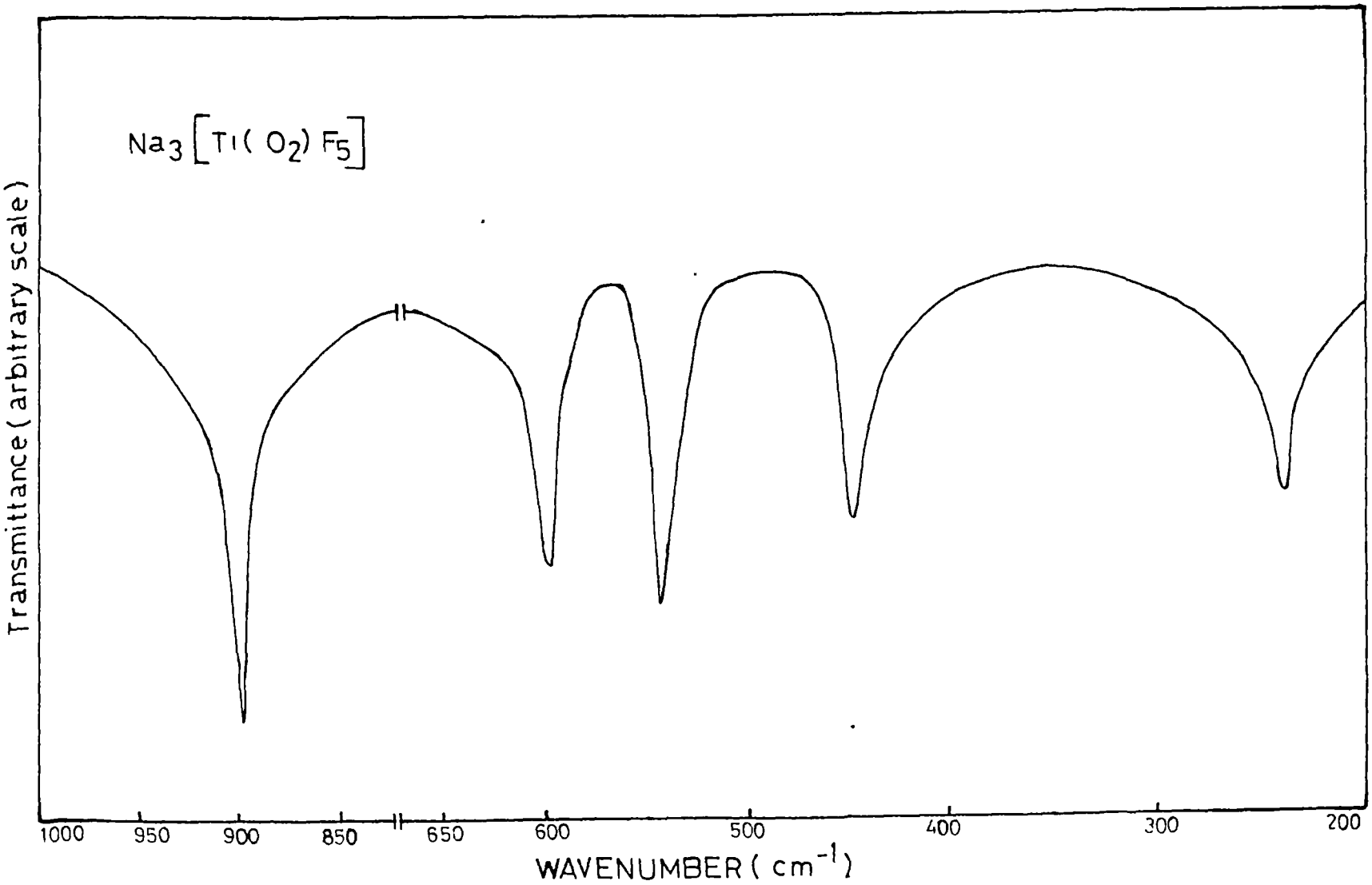
molar conductance of $K[Ti(O_2)F_3].3H_2O$ was higher than the expected value. Due to their instability many peroxometalate compounds do not permit molar conductance measurements. Thus the higher value in the case of $K[Ti(O_2)F_3].3H_2O$ is not too surprising. The diamagnetic nature of the compounds, as evidenced by the results of magnetic susceptibility measurements, support the view that titanium occurs in its +4 oxidation state in each of the newly synthesised compounds. The determination of peroxide content, considered to be extremely important, to ascertain the number of peroxide groups bonded to titanium(IV) centre, was accomplished by redox titrations with a standard Ce^{4+} solution and also with standard $KMnO_4$ solution in the presence of boric acid to prevent any loss of active oxygen. The results of which conspicuously suggested the presence of one peroxide group coordinated to titanium(IV) centre in each of the $A_3[Ti(O_2)F_5]$ and $K[Ti(O_2)F_3].3H_2O$, and two peroxide groups in $A_2[Ti(O_2)_2F_2]$ compounds.

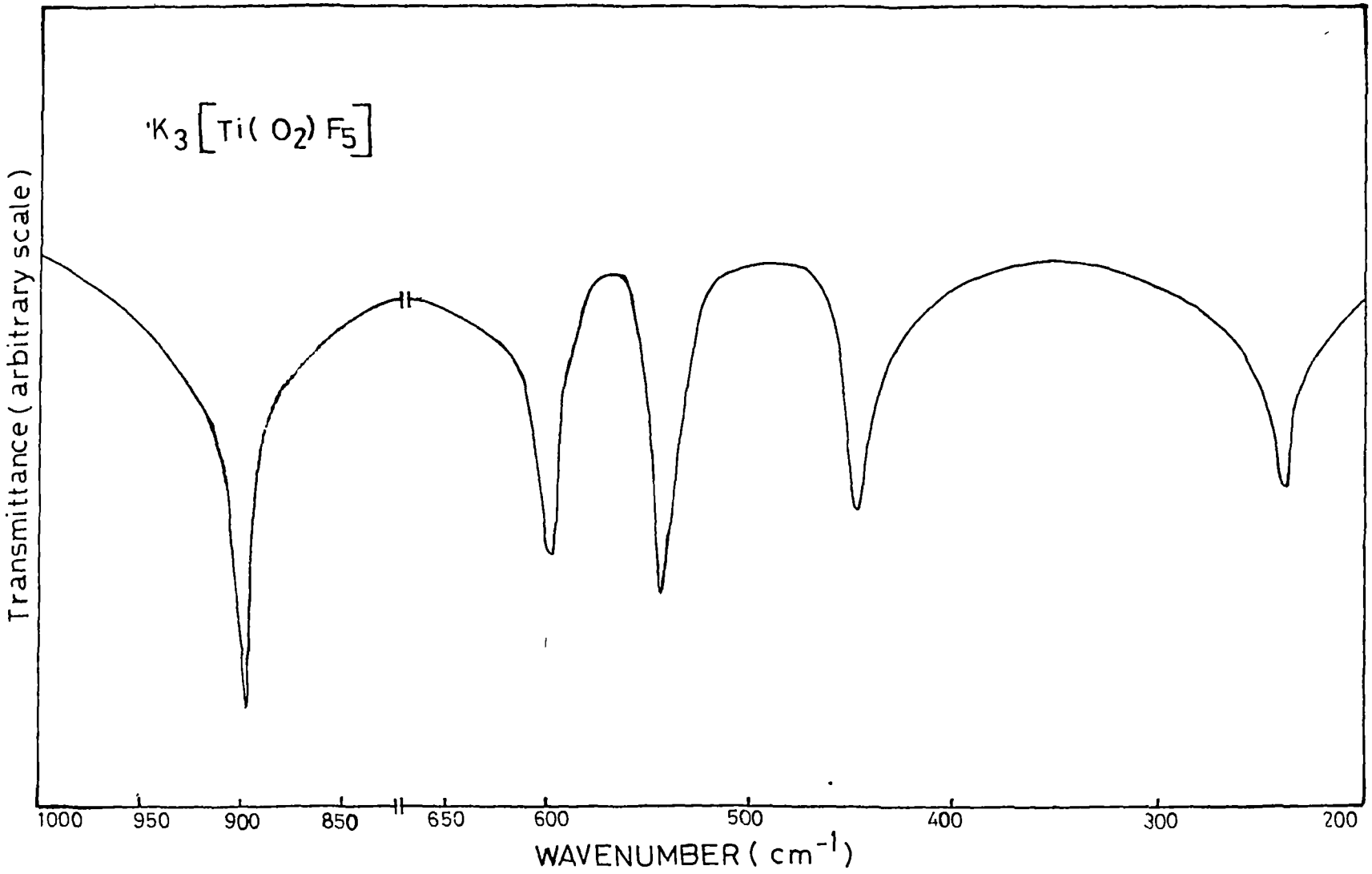
The O-O and metal-O_2 vibrations of peroxometal compounds are important spectroscopic probes for molecular structure assessment in such systems and are amenable to direct study by IR and Raman spectroscopy. Typically the IR and laser Raman spectra of the $A_3[Ti(O_2)F_5]$ compounds exhibit peaks (Table 5-4) at ca 900, ca 600 and ca 530 cm^{-1}. The peak at ca 900 cm^{-1} has been assigned to ν (O-O) ν_1, while the ones at ca 600 and at ca 530 cm^{-1} have been attributed to ν (Ti-O_2) ν_3 and ν (Ti-O_2) ν_2 modes, respectively.[12,13] The IR and lR spectra of the

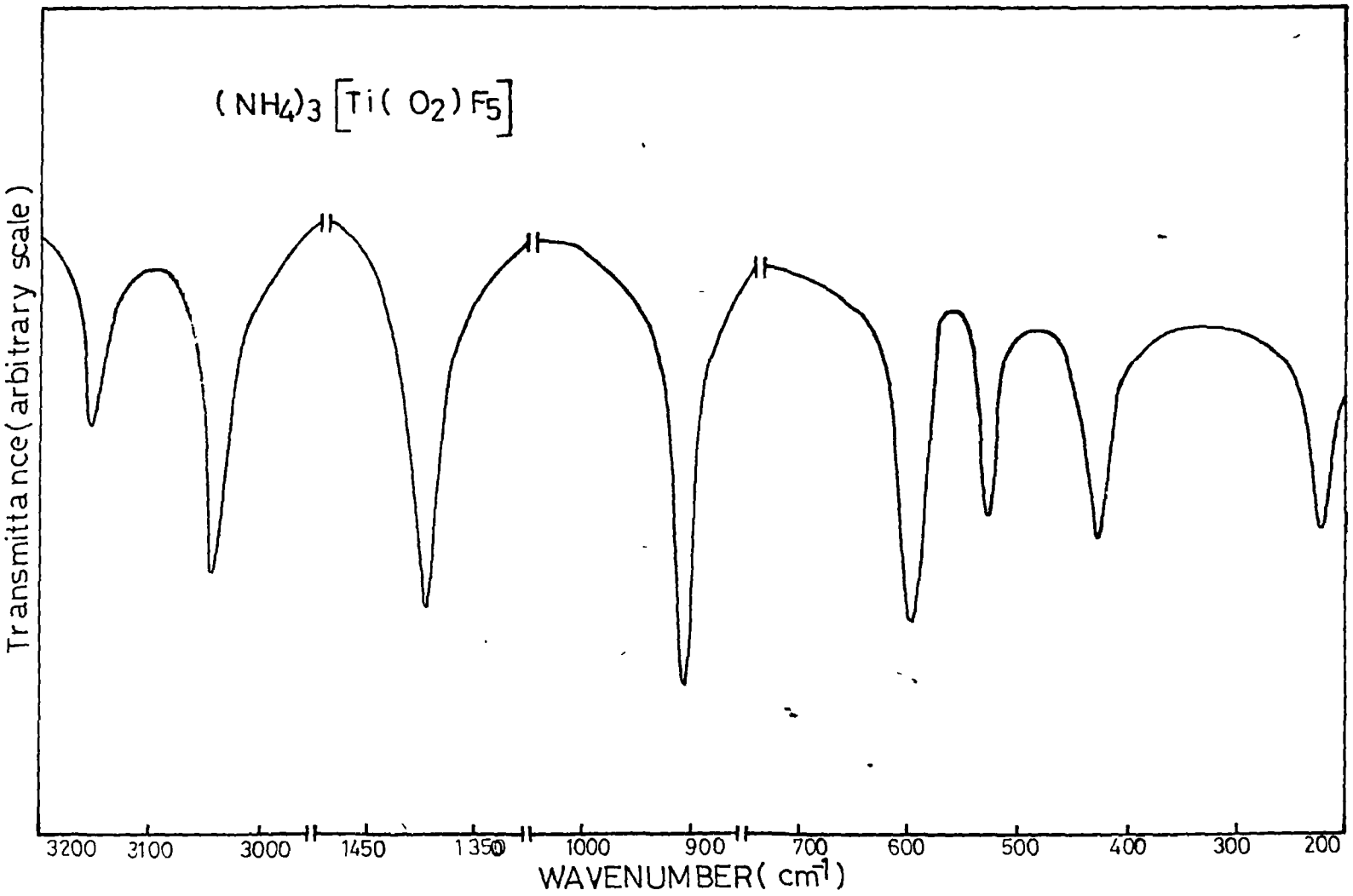
Table 5-4. Molar Conductance Values and Structurally Significant Infrared and laser Raman Bands of $A_3[Ti(O_2)F_5]$ (A = Na, K or NH_4)

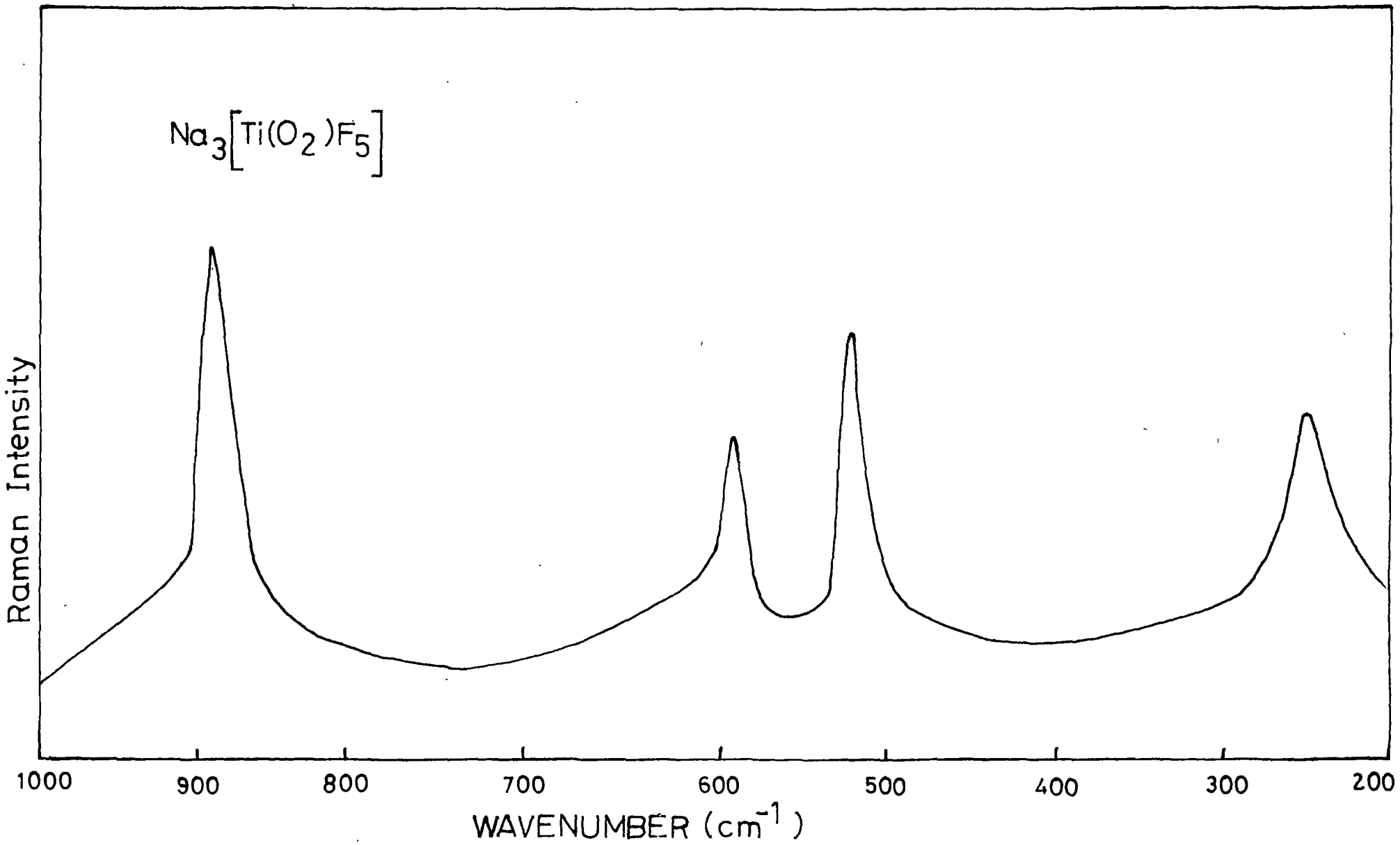
Compound	Molar Conductance $\Omega^{-1}cm^2mol^{-1}$	IR cm^{-1}	Raman[a] cm^{-1}	Assignment
$Na_3[Ti(O_2)F_5]$	350	900vs	900s (p)	ν (O-O) ν_1
		600s	600m (dp)	ν (Ti-O_2) ν_3
		549s	525s (p)	ν (Ti-O_2) ν_2
		450m		ν (Ti-F)
		240m	250m	Ti-F def
$K_3[Ti(O_2)F_5]$	370	900vs	900s (p)	ν (O-O) ν_1
		600s	600m (dp)	ν (Ti-O_2) ν_3
		530s	520s (p)	ν (Ti-O_2) ν_2
		430m		ν (Ti-F)
		230m	270m	Ti-F def
$(NH_4)_3[Ti(O_2)F_5]$	365	905vs	900s (p)	ν (O-O) ν_1
		600s	590m (dp)	ν (Ti-O_2) ν_3
		530s	530s (p)	ν (Ti-O_2) ν_2
		430m		ν (Ti-F)
		225m	270m	Ti-F def

[a]Abbreviations: p, polarised band; dp, depolarised band


$Na_3[Ti(O_2)F_5]$
Transmittance (arbitrary scale)
1000
950
900
850
650
600
500
400
300
200
WAVENUMBER (cm^{-1})


$K_3[Ti(O_2)F_5]$
Transmittance (arbitrary scale)
1000
950
900
850
650
600
500
400
300
200
WAVENUMBER (cm^{-1})


$(NH_4)_3[Ti(O_2)F_5]$
Transmittance (arbitrary scale)
3200
3100
3000
1450
1350
1000
900
700
600
500
400
300
200
WAVENUMBER (cm^{-1})


$Na_3[Ti(O_2)F_5]$
Raman Intensity
1000
900
800
700
600
500
400
300
200
WAVENUMBER (cm^{-1})

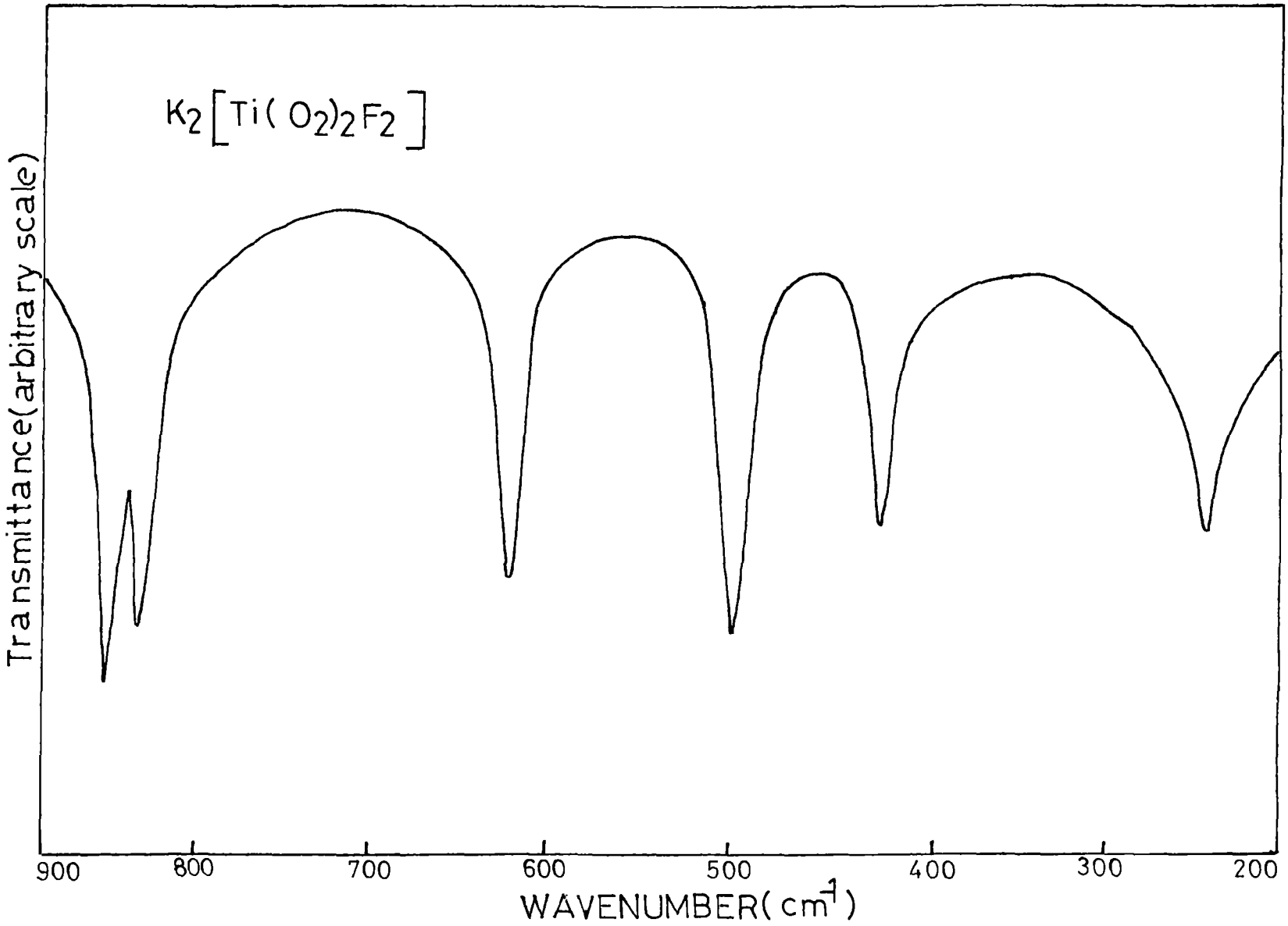
$A_2[Ti(O_2)_2F_2]$ compounds bear a very strong resemblance with each other (Table 5-5) and show absorptions at ca 860 and 830, ca 610, and ca 520 cm^{-1} representative of ν (O-O) ν_1 and ν (Ti-O_2) ν_2 and ν_3 modes, respectively, of coordinated peroxide. A medium intensity band at ca 430 cm^{-1} observed in the IR spectrum of each of the compounds has been assigned to ν (Ti-F).[12] However, a counterpart could not be observed in the corresponding IR spectra probably because of its exceedingly weak nature. The band at ca 250 cm^{-1} most likely owes its origin to a Ti-F deformation mode. The observed positions of ν (O-O) and ν (Ti-O_2) are those that one would expect to observe for a triangularly bonded O_2^{2-}. Considering C_{2v} being the local symmetry of coordinated O_2^{2-} ligand, three vibrations (two A_1 and one B_2) are expected to be IR and Raman active, of which the two A_1 modes (ν_1, ν (O-O) stretching, and ν_2, ν (Ti-O_2) symmetric stretching) are polarised, while the B_2 mode (ν_3, ν (Ti-O_2) asymmetric stretching) is depolarised in the Raman spectra.[12] The ν_1 mode occurs at 800-900 cm^{-1}, and the ν_2 and ν_3 modes fall in the region 500-600 cm^{-1}. On the basis of the sharpness and intensity of the observed IR signals and Raman polarisation measurements on solutions, the frequencies at ca 530 and ca 600 cm^{-1} for the $A_3[Ti(O_2)F_5]$ have been attributed to the ν_2 and ν_3 modes, respectively, of ν (Ti-O_2), while the signals at ca 610 and ca 520 cm^{-1} for $A_2[Ti(O_2)_2F_2]$ have been assigned, respectively, to the ν_2 and ν_3 modes of ν (Ti-O_2). It is probably the changes in stoichiometry of Ti:O_2^{2-}:F^-, and the structures of the complex ions, as one goes from the mono- to the diperoxo

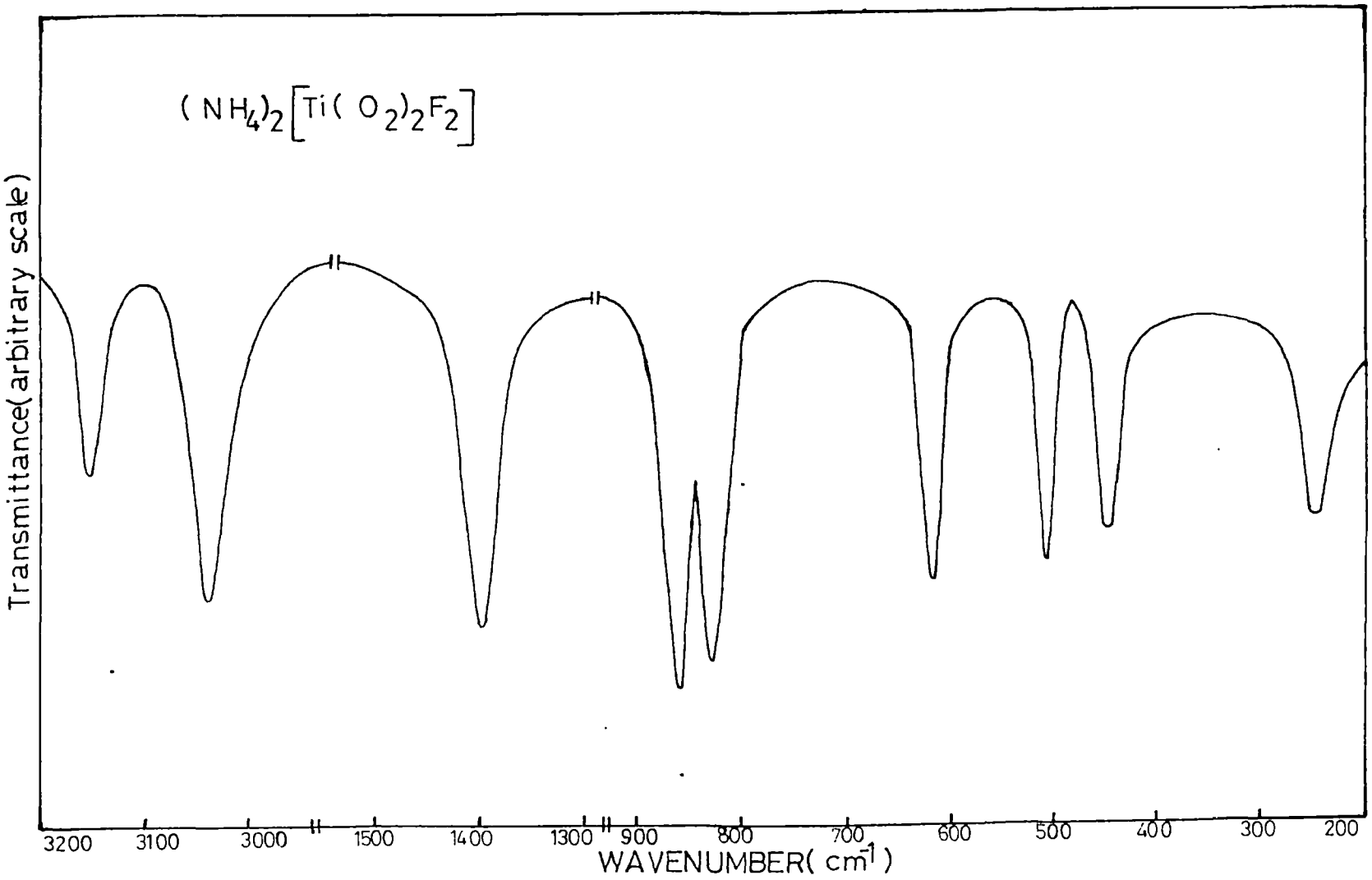
Table 5-5. Molar Conductance Values and Structurally Important Infrared and laser Raman Bands of $A_2[Ti(O_2)_2F_2]$ (A = K or NH_4)

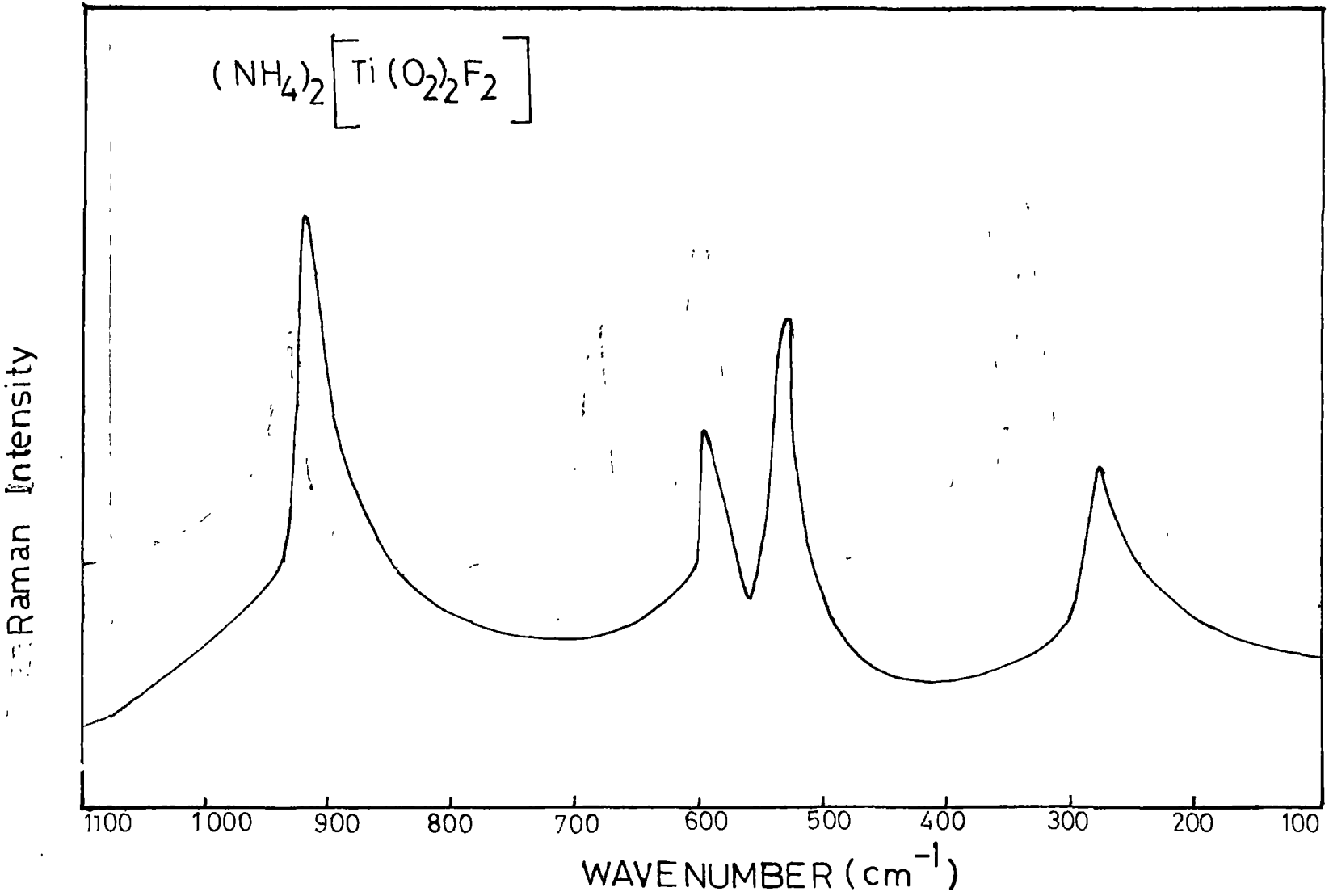
Compound	Molar conductance $\Omega^{-1}cm^2mol^{-1}$	IR cm^{-1}	Raman[a] cm^{-1}	Assignment
$K_2[Ti(O_2)_2F_2]$	235	860vs	860s (p)	ν (O-O) ν_1
		840s	825s (p)	
		620s	600s (p)	ν ($Ti-O_2$) ν_2
		500s	525m (dp)	ν ($Ti-O_2$) ν_3
		430m		ν (Ti-F)
		250m	270m	Ti-F def
$(NH_4)_2[Ti(O_2)_2F_2]$	225	860vs	860s (p)	ν (O-O) ν_1
		830s	830s (p)	
		620s	600s (p)	ν ($Ti-O_2$) ν_2
		510s	520m (dp)	ν ($Ti-O_2$) ν_3
		450m		ν (Ti-F)
		250m	270m	Ti-F def

[a]Abbreviations: p, polarised band; dp, depolarised band

species, that cause the frequency reversal of ν_2 and ν_3. Since the IR spectra of the solids as well as their solutions recorded under identical conditions do not reveal any notable change in the pattern of the spectra or in the positions of the signals, it is believed that the complex species $[Ti(O_2)F_5]^{3-}$ and $[Ti(O_2)_2F_2]^{2-}$ retain their structural identity also in solution. The splitting of


$K_2[Ti(O_2)_2F_2]$
Transmittance(arbitrary scale)
900
800
700
600
500
400
300
200
WAVENUMBER(cm^{-1})


$(NH_4)_2[Ti(O_2)_2F_2]$
Transmittance(arbitrary scale)
3200
3100
3000
1500
1400
1300
900
800
700
600
500
400
300
200
WAVENUMBER(cm^{-1})


$(NH_4)_2[Ti(O_2)_2F_2]$
Raman Intensity
1100
1000
900
800
700
600
500
400
300
200
100
WAVE NUMBER (cm^{-1})

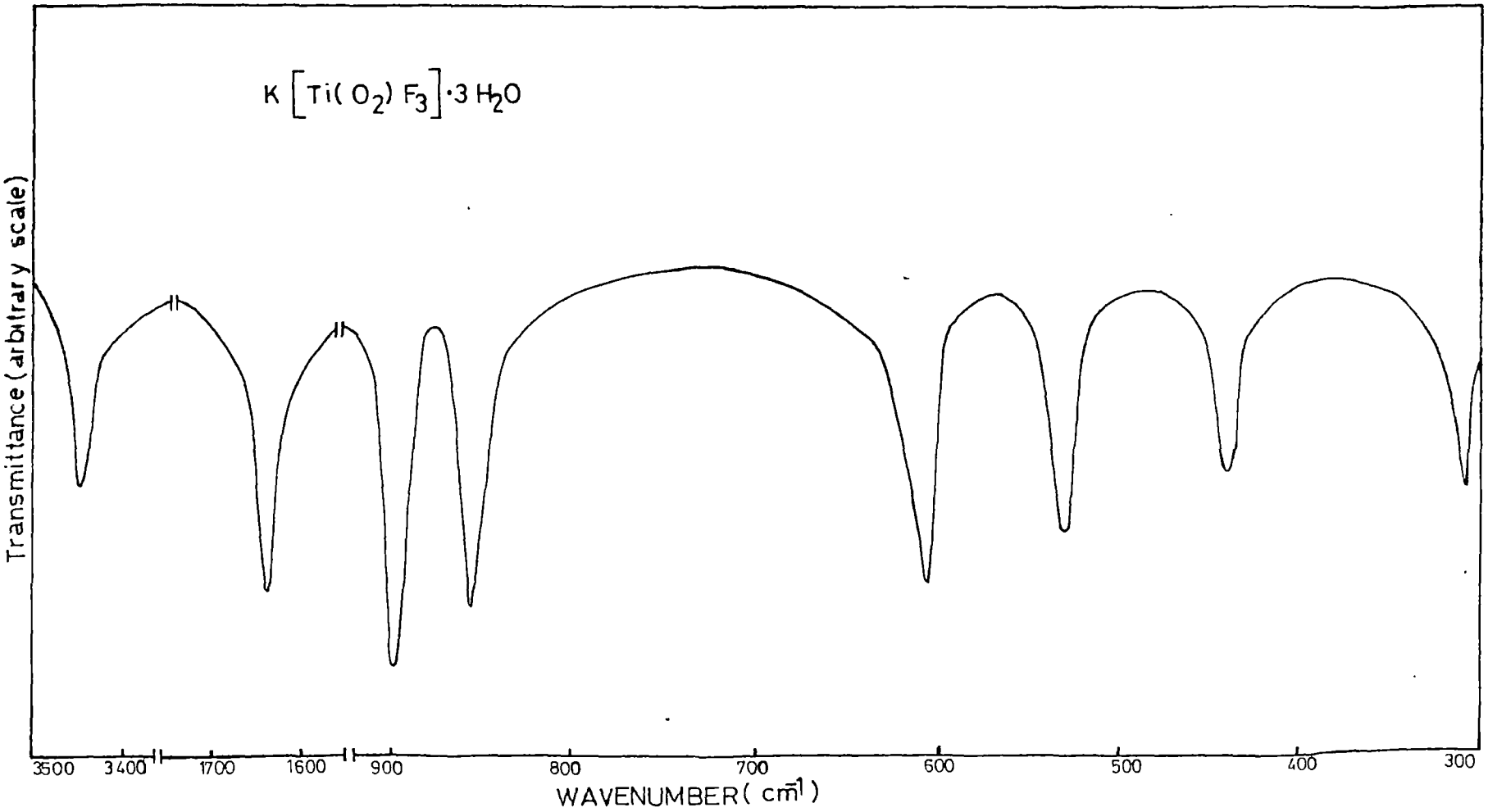
ν (O-O) in the case of the A_2 $[Ti(O_2)_2F_2]$ compounds very likely originates from the coupling of the in-phase —— out-of-phase vibrations of the two coordinated peroxo groups. A clear shift of ν (O-O) from ca 900 to ca 850 cm^{-1} in going from $[Ti(O_2)F_5]^{3-}$ to $[Ti(O_2)_2F_2]^{2-}$ is a clean indication of a decrease in the O-O bond order with an increase in the number of coordinated O_2^{2-} groups. Since peroxide ligands bind to Ti through donation from two antibonding πp orbitals, titanium(IV) will become a worse acceptor with increasing number of O_2^{2-} ligands. This will make titanium(IV) withdraw less electron density from the antibonding πp (O_2^{2-}) orbitals, which will increase their repulsive character and in turn weaken the O-O bond. Hence, O_2^{2-} multisubstitution should result in weakening of the O-O bond, as observed in the present work.

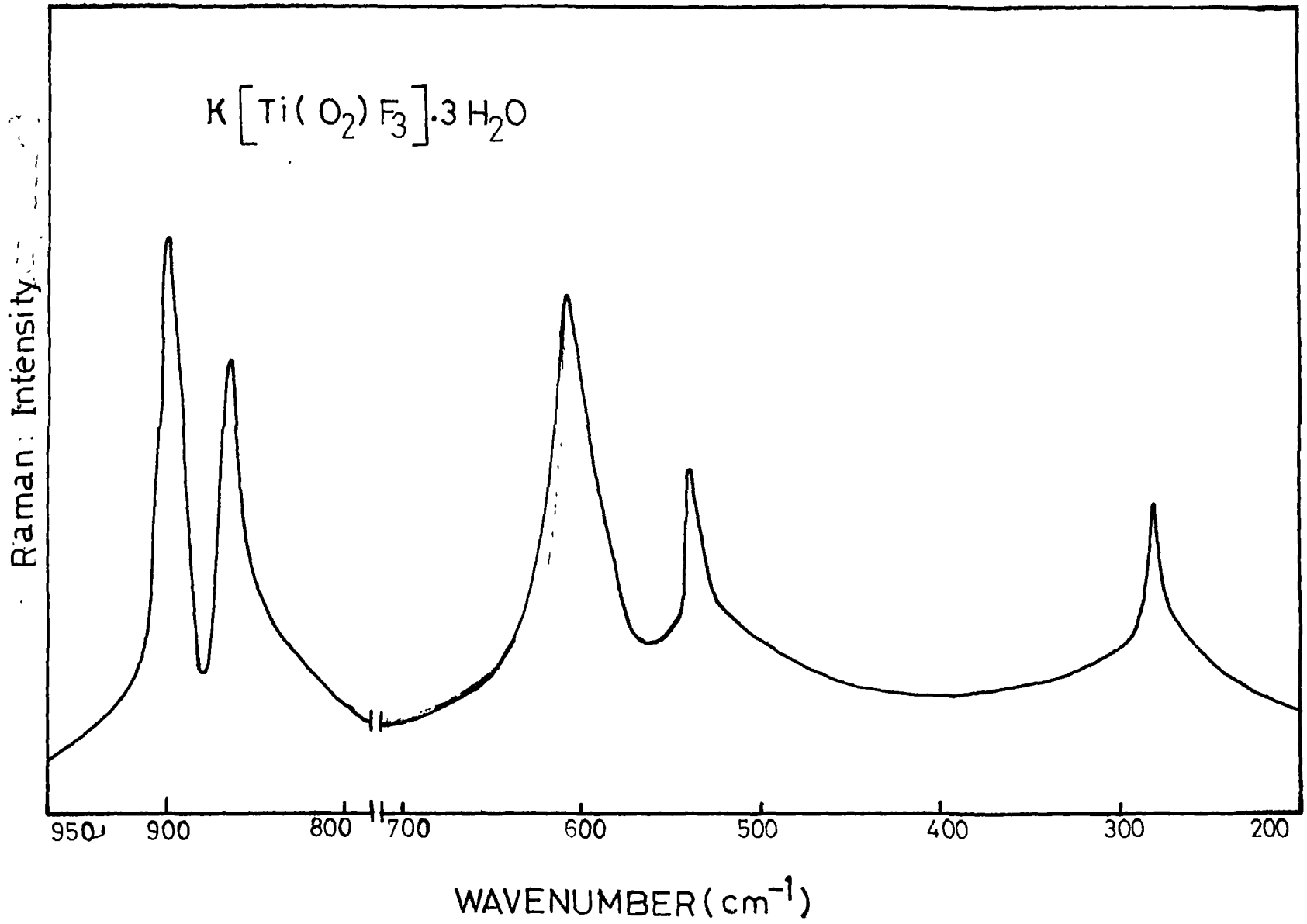
The infrared and laser Raman (lR) spectra of $K[Ti(O_2)F_3].3H_2O$ are also very informative and characteristic. The significant features of the spectra of $K[Ti(O_2)F_3].3H_2O$ involve the bands of coordinated peroxide (O_2^{2-}) ligand, fluoride (F^-) frequencies, O-H stretching and H-O-H bending. The IR as well as the lR spectra of the compound exhibited (Table 5-6) the ν (O-O) and ν (Ti-O_2) stretchings of the coordinated peroxide (O_2^{2-})[12,13] occuring at 900 and 860 cm^{-1} (ω_1), and at 610 cm^{-1} (ω_3) and 530 cm^{-1} (ω_2). The fact that the ν (O-O) (ω_1) and the complementary ν (Ti-O_2) (ω_2 and ν_3) modes in the IR and lR spectra were observed in the positions stipulated for a triangularly bonded peroxide renders it certain that the peroxide (O_2^{2-}) is bonded to the

Table 5-6. Structurally Significant IR and laser Raman (lR) Bands of $K[Ti(O_2)F_3].3H_2O$

Compound	IR, cm^{-1}	Raman cm^{-1}	Assignment
$K[Ti(O_2)F_3].3H_2O$	900vs	900	ν (O-O) ν_1
	860s	860	
	610s	610	ν (Ti-O_2) ν_3
	535s	530	ν (Ti-O_2) ν_2
	440m		ν (Ti-F)
	310m	285	δ (Ti-F)
	1640s		δ (H-O-H)
	3450m		ν (O-H)

titanium(IV) centre in a triangular bidentate (C_{2v}) manner. The other structurally significant bands are those which owe their origin to the presence of coordinated fluoride (F^-) ligand. The positions of the bands and the pattern of the spectra which originate from coordinated fluoride ligand are essentially similar to those observed (vide Supra) for the $A_3[Ti(O_2)F_5]$ and $A_2[Ti(O_2)_2F_2]$ compounds. Any further discussion in this context may thus be redundant. The only point to be emphasised here is the appearance of two additional bands at 3450 and 1640 cm^{-1} in the IR spectrum of trifluoroperoxotitanate(IV) complex which resemble in their shapes and positions those of unco-ordinated water[14] and have been assigned to ν (O-H) and δ(H-O-H) modes.


K [Ti(O2) F3]·3 H2O
Transmittance (arbitrary scale)
3500
3400
1700
1600
900
800
700
600
500
400
300
WAVENUMBER (cm⁻¹)


K [Ti(O2) F3].3 H2O
Raman Intensity
950
900
800
700
600
500
400
300
200
WAVENUMBER (cm-1)

Further, it was emphasised in the literature[15] that the ν (O-H) band at 3455 cm^{-1} is rather typical of lattice water. Therefore, it is inferred that the water molecules are not coordinated to the metal centre.

Following are the main points that emerged out of the present investigations:

Fluoroperoxotitanates(IV) of the types $A_3[Ti(O_2)F_5]$ and $A_2[Ti(O_2)_2F_2]$ (A = Na, K or NH_4), and $K[Ti(O_2)F_3].3H_2O$ can be easily synthesised directly from the reactions of TiO_2, 40% HF, and hydrogen peroxide at pH 6, 9, and 8-9, respectively. While the complex $[Ti(O_2)F_5]^{3-}$ ion very likely has a pentagonal bipyramidal structure so often encountered in transition metal peroxide chemistry, the complex species $[Ti(O_2)_2F_2]^{2-}$ may have a hexa-coordinated structure. The complex $[Ti(O_2)F_3]^-$ may be a penta-coordinated monomer, however, it is more likely that the complex has a distorted octahedral structure through -Ti-F-Ti- interactions. The peroxide ligand is bonded to the metal centre in each case in a triangular bidentate (C_{2v}) manner, and the O-O bond order of co-ordinated O_2^{2-} ligands decreases with the increase in the number of such groups bonded to the metal centre.

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CHAPTER 6

Chapter 6

New Mixed-Ligand Peroxo Compounds of Titanium(IV). Synthesis, Characterisation and Physico- Chemical Studies of $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4), and $[Ti(O_2)_2(L\text{-}L)]$ (L-L = 1,10-phenanthroline or 2,2'-bipyridine) and $[Ti(O_2)_2(thiourea)].H_2O$

Peroxo complexes of titanium(IV) besides having an intrinsic importance can also act as reagents and catalysts in organic synthesis.[1] Some of its compounds have also been proposed as model systems for the biochemistry of titanium.[2] Titanium gives colour reactions with hydrogen peroxide owing to the formation of peroxo-titanate(IV) species in solution[3] but not many of the products have been isolated in the solid state probably because of their stability as solids or might as well be due to the lack of suitable synthetic methods. Interestingly, the introduction of specific heteroligands in the coordination sphere seems to increase the stability[4-9] of such compounds and permits isolation in the solid form providing a scope of studying their properties and making an assessment of their structures. Synthesis of well-defined peroxo-titanium(IV) compounds is thus an important prerequisite. Within the context of the chemistry of peroxo-titanates(IV), heteroligand diperoxotitanates(IV) are scanty.[10,11] The only examples of the afore-said types of compounds are

$A_2[Ti(O_2)_2F_2]$ (A = K or NH_4), as described in Chapter 5, recently synthesised by us, but there is still a lack of information regarding diperoxotitanate(IV) complexes containing bidentate heteroligand. Moreover, very little is known regarding molecular heteroligand peroxo complexes of titanium(IV). An additional interest adheres to latter type of compounds because such compounds may provide a possibility of studies of catalytic oxidation in terms of activation of the O-O bond of the coordinated peroxide.

As a sequel to the work described in Chapter 5 the limit of heteroligand has now been extended from F^- to SO_4^{2-}, 1,10-phenanthroline (o-phen), 2,2'-bipyridine (bipy) and thiourea.

Chapter 6 of the thesis reports first synthesis of complex diperoxotitanates(IV) of the types: $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4), and $[Ti(O_2)_2(L\text{-}L)]$ (L-L = o-phen or bipy), and $[Ti(O_2)_2(thiourea)].H_2O$. The present Chapter also deals with the studies of properties and assessment of structures of the newly synthesised compounds.

Experimental

Reagent grade chemicals were used for the syntheses (B.D.H., E. Merck, S.D's, SISCO, and Loba-Chemie).

Synthesis of Potassium and Ammonium Diperoxomonosulphatotitanate(IV) Tetrahydrates, $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4)

A Typical Procedure

An amount of 1.0g (12.5 mmol) of freshly prepared TiO_2 was dissolved in 30 cm^3 of 7.65M sulphuric acid at room temperatures. To this was added 25 cm^3 (220.5 mmol) of 30% H_2O_2 with stirring and the reaction container was placed in an ice-water bath. To the deep red solution thus obtained was added potassium hydroxide or aqueous ammonia with constant stirring until the pH of the solution was found to lie between 2.5 and 3 with the colour of the solution being changed from red to yellow. While potassium hydroxide was added in the form of a 20% solution, aqueous ammonia was added as a concentrated solution (sp.gr. 0.9). Yellow potassium and ammonium diperoxomonosulphatotitanate(IV) tetrahydrates, $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4), were spontaneously precipitated at pH 2.5-3. The product thus obtained were 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 $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4) are set out in Table 6-1.

Table 6-1. Amounts of Reagents Used for the Synthesis and the Yields of $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4)

Compound	Yield g (%)	Amount of TiO_2 in g (mmol)	Amount of 30% H_2O_2 cm^3 (mmol)	Amount of 7.65 M H_2SO_4 cm^3
$K_2[Ti(O_2)_2SO_4].4H_2O$	3.2 (71)	1.0 (12.5)	25 (220.5)	30
$(NH_4)_2[Ti(O_2)_2SO_4].4H_2O$	3 (76)	1.0 (12.5)	25 (220.5)	30

Synthesis of Diperoxo(1,10-phenanthroline)titanium(IV), $[Ti(O_2)_2(o\text{-phen})]$, Diperoxo(2,2'-bipyridine)titanium(IV), $[Ti(O_2)_2(bipy)]$ and Diperoxo(thiourea)titanium(IV) Monohydrate, $[Ti(O_2)_2(thiourea)].H_2O$

Since the methods of syntheses of $[Ti(O_2)_2(o\text{-phen})]$, $[Ti(O_2)_2(bipy)]$, and $[Ti(O_2)_2(thiourea)].H_2O$ are similar, only a representative method is described.

An aqueous suspension (10 cm^3 of water) of freshly prepared 1.0g (12.5 mmol) of TiO_2 was dissolved by the addition of 1 cm^3 (20 mmol) of 40% HF and warming over a steam-bath. It was then cooled to room temperature followed by the addition of a concentrated ethanolic solution of 1,10-phenanthroline (2.5g, 12.6 mmol), 2,2'-bipyridine (1.95g, 12.5 mmol), and a concentrated aqueous solution of thiourea (0.95g, 12.5 mmol), respectively, maintaining the molar ratio of Ti:ligand as 1:1. An amount of

15 cm^3 (132.3 mmol) of 30% H_2O_2 solution was added to it and the resultant mixture was stirred for ca 10 min. The reaction container was then placed in an ice-water bath and the pH of the solution was adjusted to 7 by adding aqueous ammonia (sp.gr. 0.9). While phenanthroline compound was spontaneously precipitated from the reaction mixture, the corresponding bipyridine and thiourea compounds were obtained by the addition of cold ethanol ca 15 cm^3 with slow stirring until the lemon-yellow product ceased to appear. The compounds were allowed to settle, and then isolated by centrifugation. The products thus obtained were washed three times with ethanol and finally dried in vacuo over concentrated sulphuric acid.

The yields of

$[Ti(O_2)_2(o\text{-phen})]$ was 2.4g (65.7%),

$[Ti(O_2)_2(bipy)]$ was 2.3g (68.6%),

and $[Ti(O_2)_2(thiourea)].H_2O$ was 2g (77.6%).

Elemental Analyses

Quantitative estimations of titanium, peroxide, sulphate, carbon, hydrogen, nitrogen, and potassium were made by the methods described in Chapter 2. The results of elemental analyses for $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4) are reported in Table 6-2, while those for $[Ti(O_2)_2(L\text{-}L)]$ (L-L = o-phen or bipy), and $[Ti(O_2)_2(thiourea)].H_2O$ are given in Table 6-3.

Table 6-2. Analytical Data of $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4)

Compound	Found % (Calcd.%)			
	A or N	Ti	O[a]	SO_4
$K_2[Ti(O_2)_2SO_4].4H_2O$	21.21 (21.83)	12.96 (13.37)	18.1 (17.87)	26.22 (26.82)
$(NH_4)_2[Ti(O_2)_2SO_4].4H_2O$	8.81 (8.86)	14.88 (15.15)	20.4 (20.25)	30.64 (30.39)

[a]Peroxo-oxygen

Table 6-3. Analytical Data of $[Ti(O_2)_2(L\text{-}L)]$ (L-L = o-phen or bipy) and $[Ti(O_2)_2(thiourea)].H_2O$

Compound	Found % (Calcd. %)				
	Ti	O[a]	C	H	N
$[Ti(O_2)_2(o\text{-phen})]$	16.35 (16.43)	22.05 (21.91)	49.2 (49.31)	2.69 (2.73)	9.51 (9.58)
$[Ti(O_2)_2(bipy)]$	17.65 (17.91)	23.95 (23.88)	44.65 (44.77)	2.9 (2.98)	10.38 (10.44)
$[Ti(O_2)_2(thiourea)].H_2O$	23.42 (23.30)	31.01 (31.06)	5.7 (5.82)	2.85 (2.91)	13.45 (13.59)

[a]Peroxo-oxygen

Results and Discussion

The main problem that comes on the way to the study of peroxotitanates(IV) chemistry is probably the lack of a suitable starting reagent for the synthesis of such compounds. Although TiO_2 is a very commonly available source, it suffers from the problem of very poor solubility. For example, whereas V_2O_5 is highly soluble in aqueous hydrogen peroxide, TiO_2 is not. An aged sample of TiO_2 is also not readily soluble in inorganic acids except aqueous HF. The first task was therefore to improve the solubility of TiO_2 so that a simple starting material is easily accessible. It was observed that a freshly prepared TiO_2, obtained by treating a solution of commercially available TiO_2 in 40% HF with aqueous ammonia imparts a better solubility. Accordingly, a solution of freshly prepared TiO_2 in dilute H_2SO_4 was made, and allowed to react with an excess of 30% H_2O_2 solution at an ice-water temperature to obtain a deep-red solution. To facilitate peroxogenation of titanium(IV), the pH of the reaction solution was raised to 2.5-3 whereupon the solution colour changed to yellow accompanied by precipitation of an yellow product. The IR spectrum of the product showed the presence of both coordinated O_2^{2-} and coordinated SO_4^{2-} and the results of chemical analysis revealed a $Ti:O_2^{2-}:SO_4^{2-}$ stoichiometry of 1:2:1. The product was obtained in a high yield.

As a sequel to our efforts on some aspects of titanium chemistry described in Chapter 5 and also in view of the successful isolation of complex diperoxotitanates(IV) involving F^- or SO_4^{2-} as heteroligands, it was of interest to us to synthesise molecular heteroligand diperoxo compounds of titanium(IV) containing N-heterocyclic ligands, namely, 1,10-phenanthroline (o-phen) and 2,2'-bipyridine (bipy), and thiourea. In accord with the synthetic strategy, a clear solution of TiO_2 in water was made by the addition of a few drops of HF and was reacted separately with o-phen, bipy, or thiourea (vide Experimental), the pH of the resultant solutions was raised to 7 by adding aqueous ammonia from which heretofore unreported compounds $[Ti(O_2)_2(o\text{-phen})]$, $[Ti(O_2)_2(bipy)]$, and $[Ti(O_2)_2(thiourea)].H_2O$ were obtained in high yields. While $[Ti(O_2)_2(o\text{-phen})]$ was precipitated spontaneously from the reaction mixture, the other two compounds required the addition of alcohol for bringing about precipitation. It is necessary to mention that addition of a very small amount of HF was required in order to make a clear solution of TiO_2, but the product in each case indicates that under the present experimental conditions F^- does not coordinate to titanium, as evidenced from the results of chemical analyses. The methods described for the syntheses of $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4) as well as $[Ti(O_2)_2(L\text{-}L)]$ (L-L = o-phen or bipy) and $[Ti(O_2)_2(thiourea)].H_2O$ are direct and easy to manipulate.

Characterisation and Structural Assessment

The compounds $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4), and $[Ti(O_2)_2(L\text{-}L)]$ (L-L = o-phen or bipy) and $[Ti(O_2)_2(thiourea)].H_2O$ are yellow in colour and are insoluble. They are diamagnetic and EPR silent in conformity with the occurence of titanium(IV) in each of them. The $A_2[Ti(O_2)_2SO_4].4H_2O$ compounds are rather unstable, whereas $[Ti(O_2)_2(L\text{-}L)]$ and $[Ti(O_2)_2(thiourea)].H_2O$ are stable and can be stored for a prolonged period in sealed containers. Their stabilities can be ascertained by chemical estimation of active oxygen contents and recording their IR spectra. Strong dessication of the compounds $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4), and $[Ti(O_2)_2(thiourea)].H_2O$ over concentrated sulphuric acid did not remove the water of crystallisation. However, the freshly synthesised $A_2[Ti(O_2)_2SO_4].4H_2O$ compounds start losing water on heating at ca 120°C; the dehydration process is accompanied by the simultaneous loss of peroxide, thereby precluding a genuine dehydration. In order to determine the number of peroxo groups (O_2^{2-}), present in the compounds, coordinated to titanium(IV) centre, chemical determination of the peroxide content must be considered important. The peroxide estimation was accomplished by redox titrations separately involving a standard $KMnO_4$ solution and also a standard Ce^{4+} solution. In each case boric acid was used to avoid any loss of active oxygen. The results of replicate determinations of the peroxide as well as those of Ti contents conspicuously suggested the occurence of

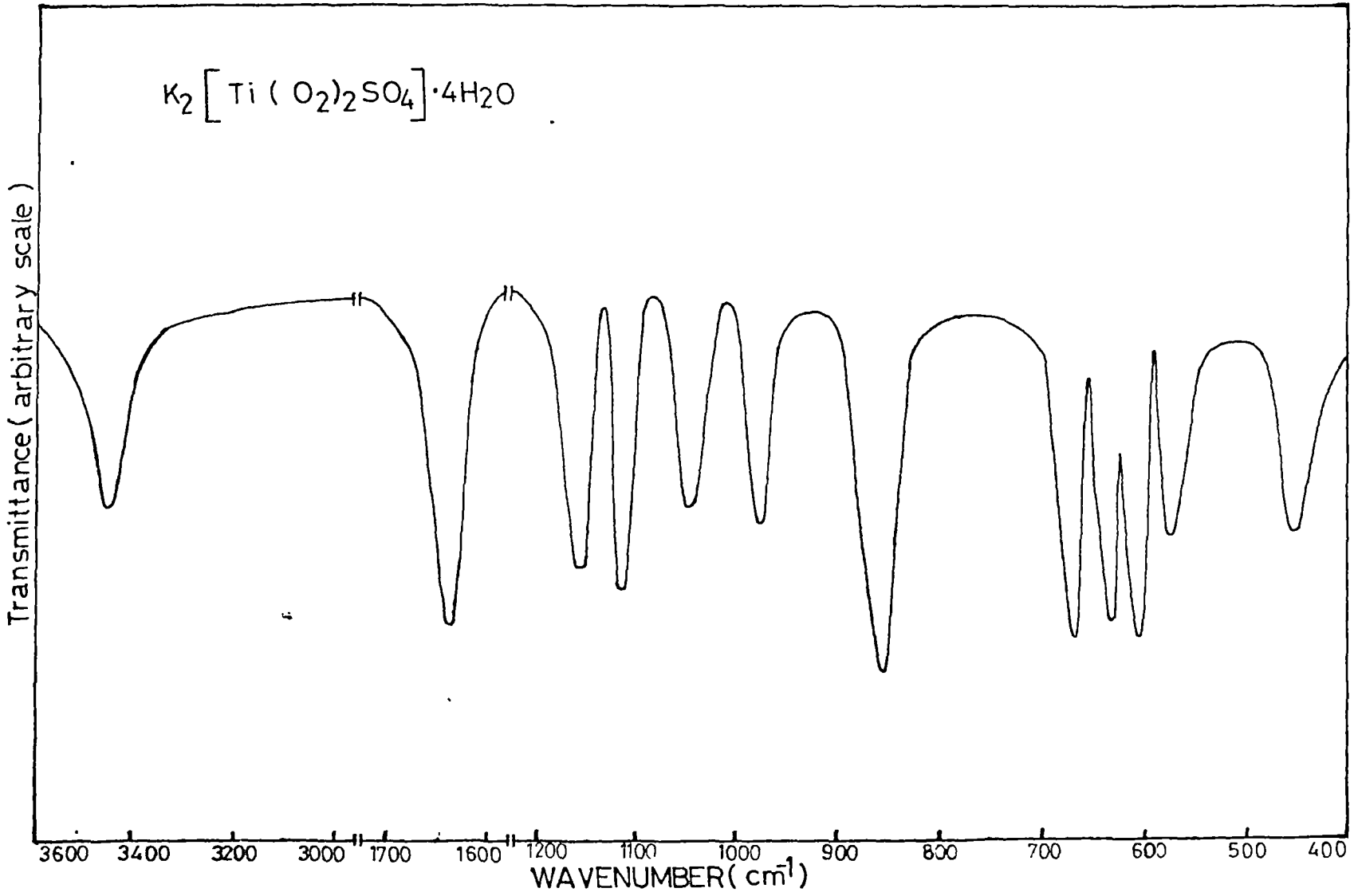
$Ti:O_2^{2-}$ as 1:2 in each of the newly synthesised compounds lending credence to the contention.

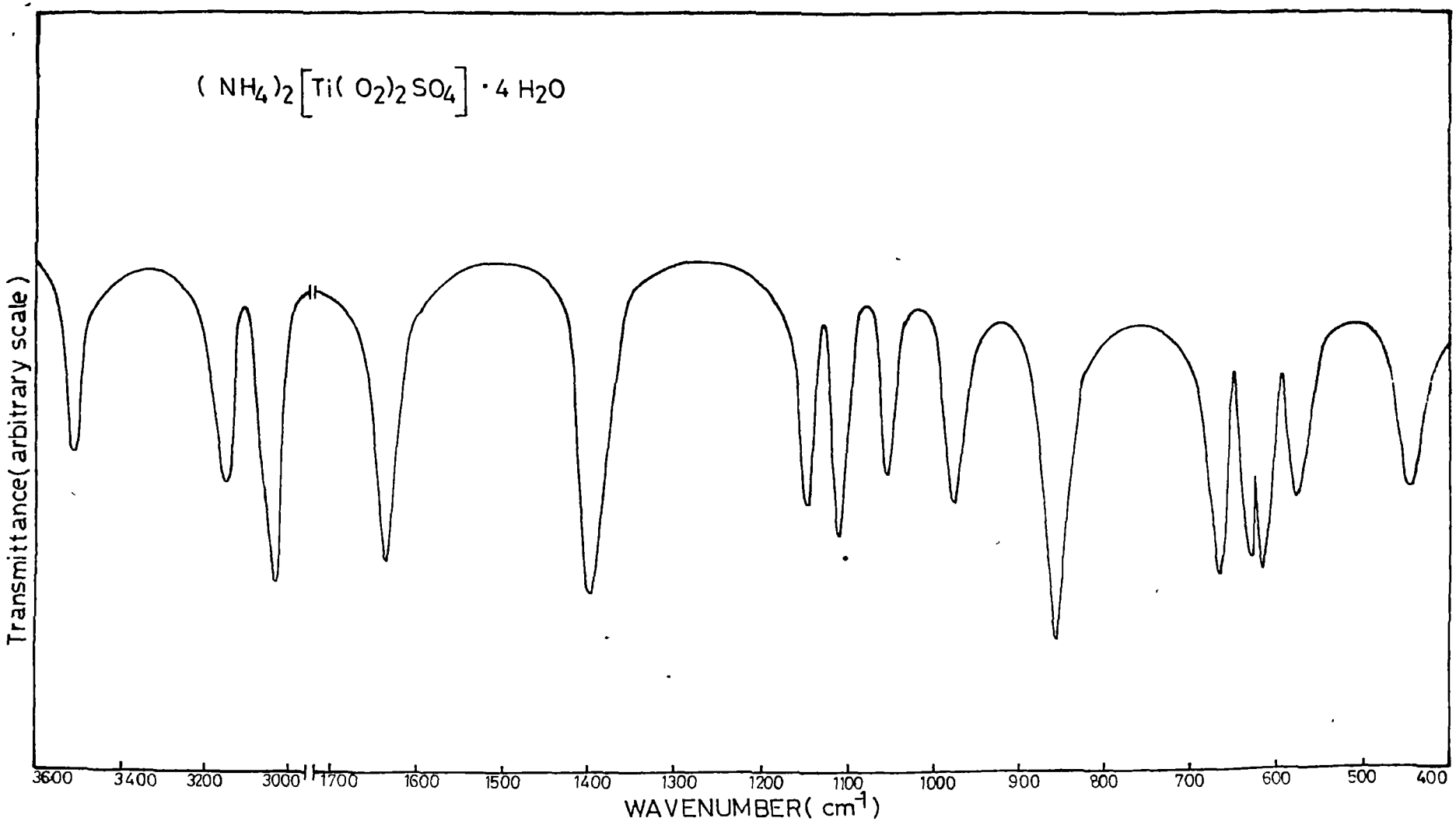
The IR and laser Raman (lR) spectra of the compounds are quite characteristic. Owing to the insolubility of the compounds, the lR spectra were recorded only on solids. The significant features in the spectra of $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4) involve bands of coordinated peroxide and sulphate ligands, O-H stretchings, and H-O-H bendings (Table 6-4). A strong band at ca 860 cm^{-1} in each of the IR and lR spectra has been assigned to a ν (O-O) mode of the coordinated peroxides.[12] The complementary ν (Ti-O_2) mode appeared at ca 620 cm^{-1}. The SO bands arising from the presence of SO_4^{2-} ligand were observed at ca 1150, ca 1120, and ca 1060 cm^{-1} assigned to ν_3, at ca 980 cm^{-1} assigned to ν_1, at ca 675, ca 630 and ca 580 cm^{-1} attributed to ν_4, and at ca 455 cm^{-1} due to ν_2 mode.[13,14] The SO vibrational pattern, especially the splitting of the ν_3 and ν_4 modes into three bands each, in the IR as well as in the lR spectra, clearly suggests a lowering of symmetry of the SO_4^{2-} group from T_d to C_{2v}. Accordingly, it is inferred that both the peroxide as well as the sulphato ligands are bonded to the titanium(IV) centre in a chelated manner. The presence of uncoordinated water is unambiguous in the present cases and the corresponding ν (O-H) and δ(H-O-H) modes of water were observed in positions similar to those observed in various other cases containing lattice water,[15,16] making any further discussion redundant. This as well as the loss of water at ca 120°C suggest that the water molecules in the

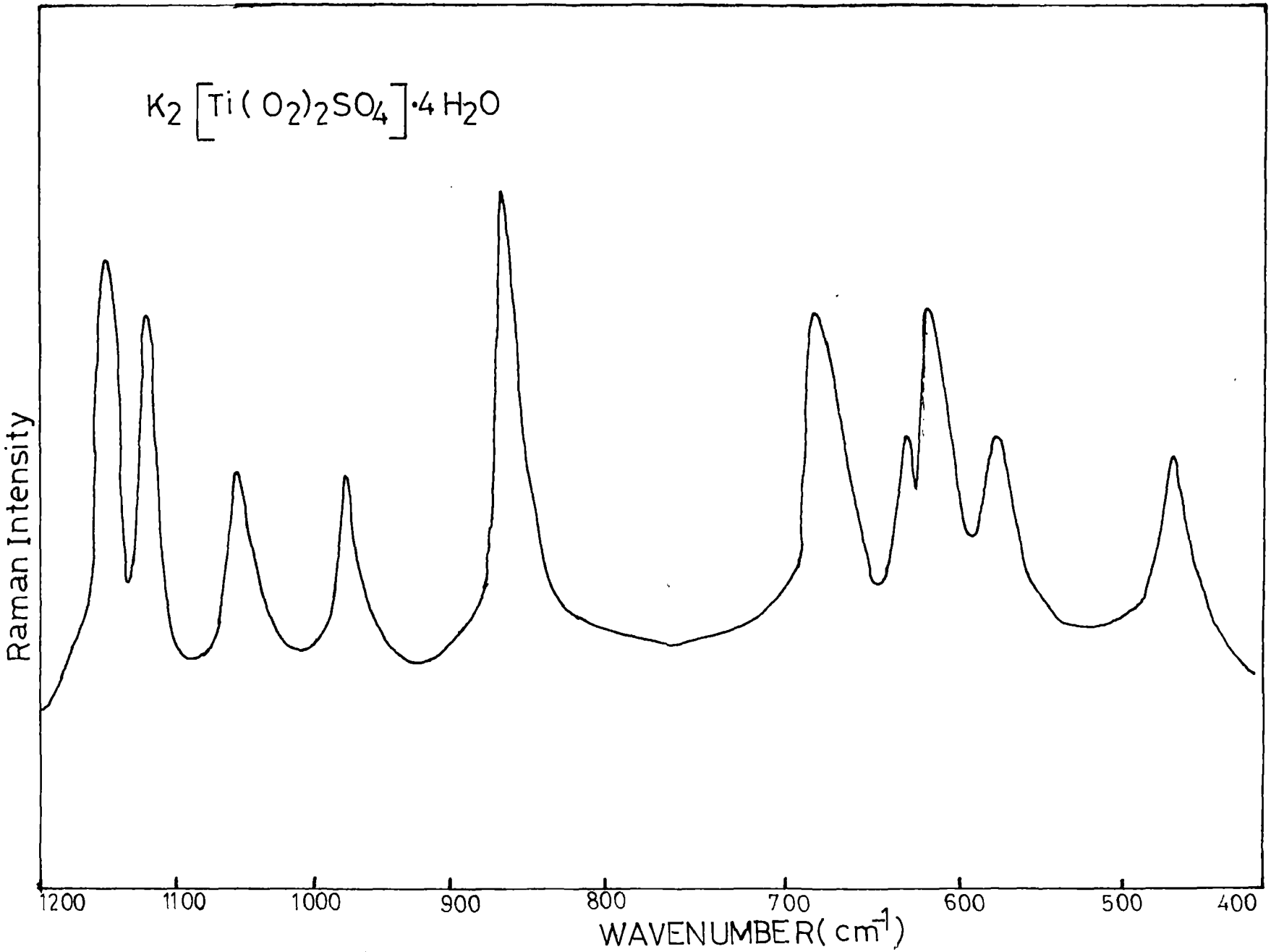
$A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4) are present as lattice water.

Table 6-4. Structurally Significant IR and Raman Bands of $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4)

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$K_2[Ti(O_2)_2SO_4].4H_2O$	855m	860	ν (O-O), ν_1
	610s	620	ν (Ti-O_2)
	980m	980	ν_1
	455m	460	ν_2
	1160s, 1120s, 1050m	1150, 1120, 1060	ν_3 S-O
	675s, 635s, 585m	670, 630, 580	ν_4
	3450m		ν (O-H)
	1640s		δ (H-O-H)
$(NH_4)_2[Ti(O_2)_2SO_4].4H_2O$	860s	850	ν (O-O), ν_1
	620s	620	ν (Ti-O_2)
	980m	980	ν_1
	450m	450	ν_2
	1150m, 1115s, 1060m	1150, 1120, 1050	ν_3 S-O
	670s, 630s, 580m	670, 640 580	ν_4
	3455m		ν (O-H)
	1640s		δ (H-O-H)


$K_2[Ti(O_2)_2SO_4]\cdot 4H_2O$
Transmittance (arbitrary scale)
3600
3400
3200
3000
1700
1600
1200
1100
1000
900
800
700
600
500
400
WAVENUMBER (cm^{-1})


$(NH_4)_2[Ti(O_2)_2SO_4] \cdot 4H_2O$
Transmittance(arbitrary scale)
3600
3400
3200
3000
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
WAVENUMBER(cm^{-1})

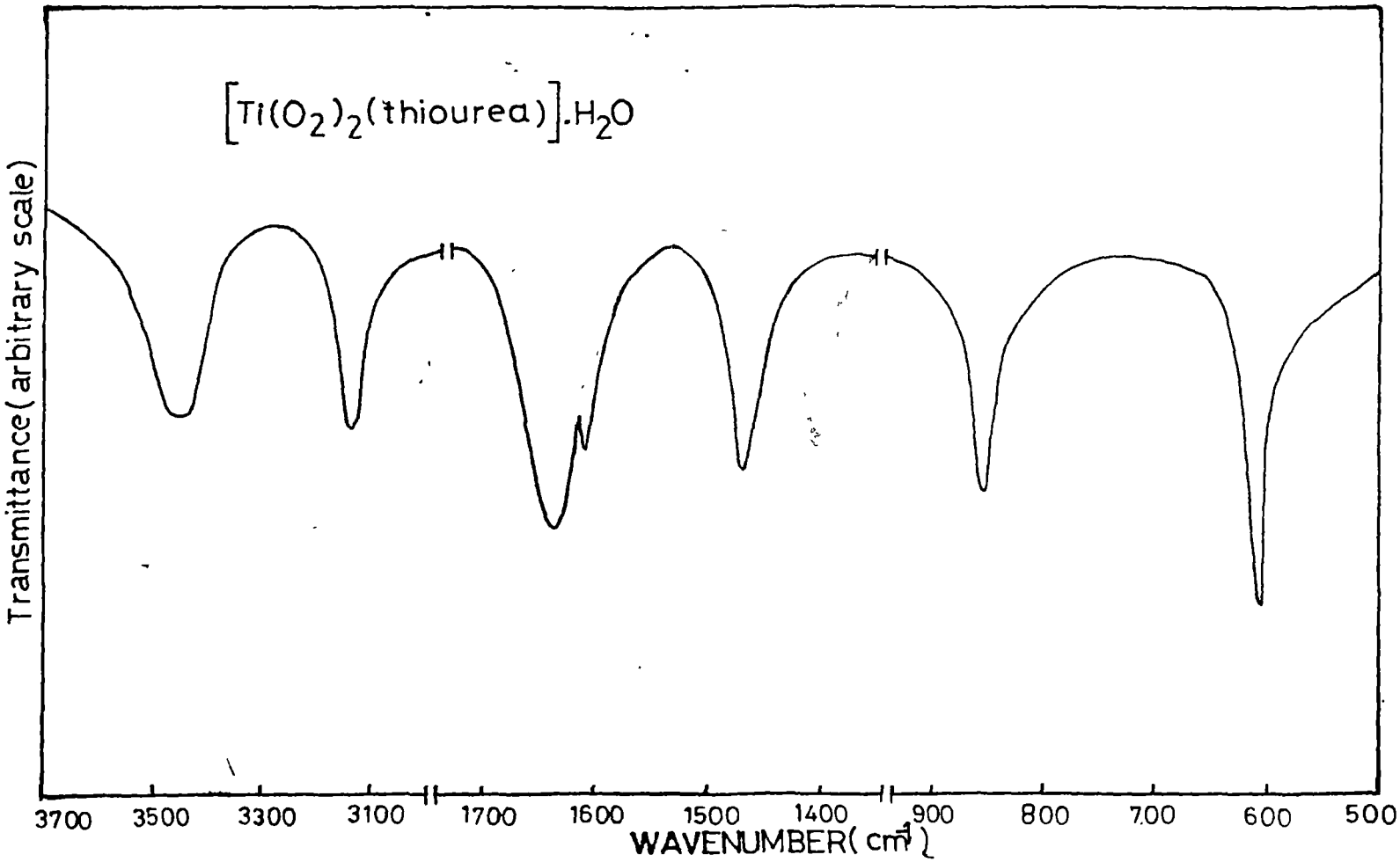

$K_2[Ti(O_2)_2SO_4]\cdot 4H_2O$
Raman Intensity
1200
1100
1000
900
800
700
600
500
400
WAVENUMBER(cm^{-1})

The spectral features of the compounds of the types $[Ti(O_2)_2(L\text{-}L)]$ (L-L = o-phen or bipy), and $[Ti(O_2)_2(thiourea)].H_2O$ are relatively more complicated than those of the other compounds reported in this Chapter. The IR and 1R spectra of all the compounds were recorded at ambient temperatures. The fact that the ν (O-O) and the complementary ν (Ti-O_2) modes in the IR and in the 1R spectra were observed in the positions stipulated for a triangularly bonded peroxide, renders it certain that the peroxide (O_2^{2-}) ligands are bonded to the titanium(IV) centre in a chelated manner in each of the compounds. In addition, the IR spectra of $[Ti(O_2)_2(o\text{-phen})]$, $[Ti(O_2)_2(bipy)]$, and $[Ti(O_2)_2(thiourea)].H_2O$ showed the characteristics of coordinated 1,10-phenanthroline,[17,18] 2,2'-bipyridine,[18,19] and thiourea[20] ligands, respectively. The Ti-N stretching modes originating from the coordinated N-heterocyclic ligands for $[Ti(O_2)_2(o\text{-phen})]$ and $[Ti(O_2)_2(bipy)]$[19] were observed (Table 6-5) at 382, 312 cm^{-1} [18] and at 370, 348 cm^{-1} respectively, providing further support to the occurence of coordinated o-phen and bipy ligands in the corresponding compounds. The IR spectrum of $[Ti(O_2)_2(thiourea)].H_2O$ showed a large negative shift in the N-H region together with a positive shift in the C=S stretching region compared to those of free thiourea suggesting that the thiourea ligand is coordinated to the metal centre through one of its nitrogen atoms[20] in the present compound. Therefore, it is evident that thiourea ligand is coordinated in a monodentate manner. Another important feature of the IR spectrum of $[Ti(O_2)_2(thiourea)].H_2O$ is the appearance of two additional bands

at 3450 and 1645 cm^{-1}, which resemble in their shape and position those observed for H_2O of the $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4), and suggest the occurence of lattice water.[15,16]

Table 6-5. Structurally Significant IR and laser Raman (lR) Bands of $[Ti(O_2)_2(L\text{-}L)]$ (L-L = o-phen or bipy), and $[Ti(O_2)_2(thiourea)].H_2O$

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$[Ti(O_2)_2(o\text{-}phen)]$	850m	860	ν (O-O)
	615s	610	ν ($Ti-O_2$)
	382m, 312m		ν (Ti-N)
$[Ti(O_2)_2(bipy)]$	860m	850	ν (O-O)
	620m	610	ν ($Ti-O_2$)
	370m, 348m		ν (Ti-N)
$[Ti(O_2)_2(thiourea)].H_2O$	855m	865	ν (O-O)
	610s	620	ν ($Ti-O_2$)
	1631m		δ (NH_2)
	1470m		ν (C=S)
	3450m		ν (O-H)
	1645s		δ (H-O-H)
	3147m		ν (NH_2)


[Ti(O2)2(thiourea)].H2O
Transmittance(arbitrary scale)
3700
3500
3300
3100
1700
1600
1500
1400
900
800
700
600
500
WAVENUMBER(cm-1)

In view of the potential use of titanium(IV) peroxo compounds as catalysts, studies involving the complex diperoxotitanates(IV) particularly the newly synthesised molecular heteroligand-peroxo compounds of titanium(IV) have been undertaken; experiments involving such compounds are now underway and the results of which will be described elsewhere.

Thus, it is evident from the results of investigations described in the present Chapter that under the appropriate experimental conditions a host of heteroligand diperoxo compounds of titanium(IV) of the types $A_2[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4), and $[Ti(O_2)_2(L\text{-}L)]$ (L-L = o-phen or bipy), and $[Ti(O_2)_2(thiourea)].H_2O$ can be synthesised. While the complex $[Ti(O_2)_2SO_4]^{2-}$ ion and molecular mixed-ligand peroxo compounds of titanium(IV), viz., $[Ti(O_2)_2(o\text{-}phen)]$ and $[Ti(O_2)_2(bipy)]$ may have hexa-coordinated distorted octahedral structures, the complex $[Ti(O_2)_2(thiourea)].H_2O$ may be a penta-coordinated monomer.

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CHAPTER 7

Chapter 7

Laser Raman Spectroscopic Evidence for the Existence of Oxoperoxotitanate(IV) in Aqueous Solution Containing 'Titanyl' Moiety and Synthesis of an Unusual Example of Peroxotitanate(IV) Complex Potassium Oxoperoxodichlorotitanate(IV) Monohydrate, $K_2[TiO(O_2)Cl_2].H_2O$

Albeit both titanium and vanadium form complexes with hydrogen peroxide, studies on the peroxo chemistry of the former are far less exhaustive than those of the latter. Though solid peroxo complexes of both titanium and vanadium can be synthesised from aqueous solutions, there exists a very significant difference in the types of the compounds obtained thereof. Whereas most of the reported peroxo complexes of vanadium are oxo-peroxo species,[1-4] except for a few highly peroxogenated vanadium(V) complexes which do not contain any oxo group,[5,6] those of titanium present a different picture, and examples of oxoperoxotitanates(IV) are very sparse. The compound $K_2[Ti_2O(O_2)_2(dipic)_2]$ (dipic = dipicoline)[7] is probably the only reported example. In spite of the existence of a few non-peroxo complexes containing TiO^{2+} moiety,[8-11] the chemistry of mixed oxo-peroxo compounds of titanium(IV) remains very poorly investigated. Thus, a systematic study involving such compounds is extremely important. Of concern to us, in view of the

above and also as a sequel to the work on peroxotitanates(IV) described in Chapters 5 and 6, was to generate an oxoperoxotitanate(IV) in solution followed by isolation in the solid state which has now been achieved.

The present Chapter gives an account of the results of such studies including the synthesis, characterisation of the title compound, $K_2[TiO(O_2)Cl_2].H_2O$.

Experimental

The chemicals used were all reagent grade products (B.D.H., E. Merck, S.D's, and Loba-Chemie).

Evidence for the Existence of Oxoperoxotitanate(IV) Complex Containing 'Titanyl' Moiety, and Synthesis of Potassium Oxoperoxodichlorotitanate(IV) Monohydrate, $K_2[TiO(O_2)Cl_2].H_2O$

An amount of 1.0g (12.5 mmol) of freshly prepared TiO_2 was mixed well with 9.4g (126.17 mmol) of potassium chloride in a beaker with the molar ratio of TiO_2:KCl being maintained at 1:10. To this was added 25 cm^3 (220.5 mmol) of 30% H_2O_2 with stirring, and the reaction container was placed in an ice-water bath. The whole was stirred for ca 10 min. An amount of 15 cm^3 of 9M hydrochloric acid was added to the resultant mixture to get a clear deep red solution. Dropwise addition of KOH solution (30% w/v) to the above mixture until the reaction solution attained a pH of 6, changed the colour of the solution to yellow. Laser Raman

spectrum of a sample of the above solution was recorded at ambient temperatures and the spectrum exhibited, in addition to the expected modes of peroxide (O_2^{2-}), a distinct polarised signal at 970 cm^{-1} assignable to ν (Ti=O) showing the existence of oxo-peroxotitanate(IV) containing TiO^{2+} moiety.

The yellow solution obtained as above was then carefully treated with a small amount of pre-cooled ethanol until light yellow precipitate just began to appear. The whole was then kept in an ice-water bath for ca 30 min, and the compound was separated by filtration, washed twice with ethanol, and finally dried in vacuo over concentrated sulphuric acid.

The yield of

$$K_2[TiO(O_2)Cl_2].H_2O \text{ was } 2.5g \ (76\%).$$

Elemental Analyses

Estimations of titanium, peroxide, chloride, and potassium were performed by the methods described in Chapter 2.

Analytical data of $K_2[TiO(O_2)Cl_2].H_2O$

Found: K, 29.5; Ti, 18.3; O_2^{2-} (active oxygen), 12.1; Cl, 26.9%.

Calcd. for $K_2[TiO(O_2)Cl_2].H_2O$; K, 29.65; Ti, 18.25; O_2^{2-} (active oxygen), 12.16; Cl, 26.99%.

Results and Discussion

The chemistry of complex species of titanium(IV) containing the 'titanyl', TiO^{2+}, moiety have been the subject of much discussion.[12-14] The fact that titanium(IV) is capable of existing

as the 'titanyl' species in aqueous acidic solution, like vanadium in the corresponding oxidation state does as VO^{2+}, is now certain.[15,16] Conspicuous absence of reported examples of oxo-peroxotitanate(IV) species in the solid state except for the one[7] mentioned earlier in the introduction section of this Chapter caused us to first explore the possibility of existence of oxo-peroxotitanate(IV) species in solution which would strategically be followed by isolation of the product. It was observed that the reaction of a sample of freshly prepared TiO_2 (obtained by dissolving a commercial variety of TiO_2 in aqueous HF followed by precipitation with aqueous ammonia) with potassium chloride, aqueous hydrochloric acid, and hydrogen peroxide afforded a deep red solution which on being carefully treated with potassium hydroxide solution until the pH was raised to 6 produced an yellow solution characteristic of the formation of a peroxotitanate(IV) in solution. The laser Raman (lR) spectrum of the solution showed — in addition to the expected modes of peroxide (O_2^{2-}) — a distinct polarised signal at 970 cm^{-1} which undoubtedly owes its origin to ν (Ti=O).[15,16] This, therefore, provided a clear information concerning the formation of an oxo-peroxotitanate(IV) species in solution — as anticipated in view of a large excess of O_2^{2-} ion (vide Experimental) - allowing us to state that oxoperoxotitanate(IV) complex containing a true 'titanyl' moiety is capable of being formed under appropriate experimental conditions. The other aim was to isolate such a species in the solid form. In order to achieve this a similar yellow solution was prepared and the cold solution was treated with a small amount of pre-cooled ethanol to just initiate precipitation of a light

yellow compound. On allowing the reaction mixture to stay at an ice-water temperature for ca 30 min afforded a light yellow product in a very good yield. The function of ethanol in the present synthesis was to bring about and facilitate precipitation of the desired product. The product on being isolated, purified, dried, and analysed revealed the stoichiometry of $K:Ti:O_2^{2-}:Cl^-$ as 2:1:1:2. Accordingly, the compound has been tentatively formulated as $K_2[TiO(O_2)Cl_2].H_2O$. Strong desiccation of the compound over concentrated sulphuric acid did not remove the water of crystallisation. Pyrolytic studies reveal that the compound starts losing water at ca 110°C, a temperature at which peroxide is also lost.

The newly synthesised compound, potassium oxoperoxodichlorotitanate(IV) monohydrate, $K_2[TiO(O_2)Cl_2].H_2O$, is a light yellow microcrystalline product. The compound did not permit molar conductance measurement owing to its insolubility in both water and common organic solvents. The result of magnetic susceptibility measurement as well as the fact that the compound is EPR silent lend support to the occurence of titanium(IV) in the aforesaid product. The compound is quite stable for a prolonged period and its stability is ascertained by chemical estimation of peroxide content from time to time. The importance of estimations of active oxygen content in such compounds has been already emphasised in Chapter 5. The results of peroxide estimations, by redox titrations involving separately standard potassium permanganate and cerium(IV) solutions, suggest the presence of one peroxide (O_2^{2-}) per titanium(IV) in the complex.

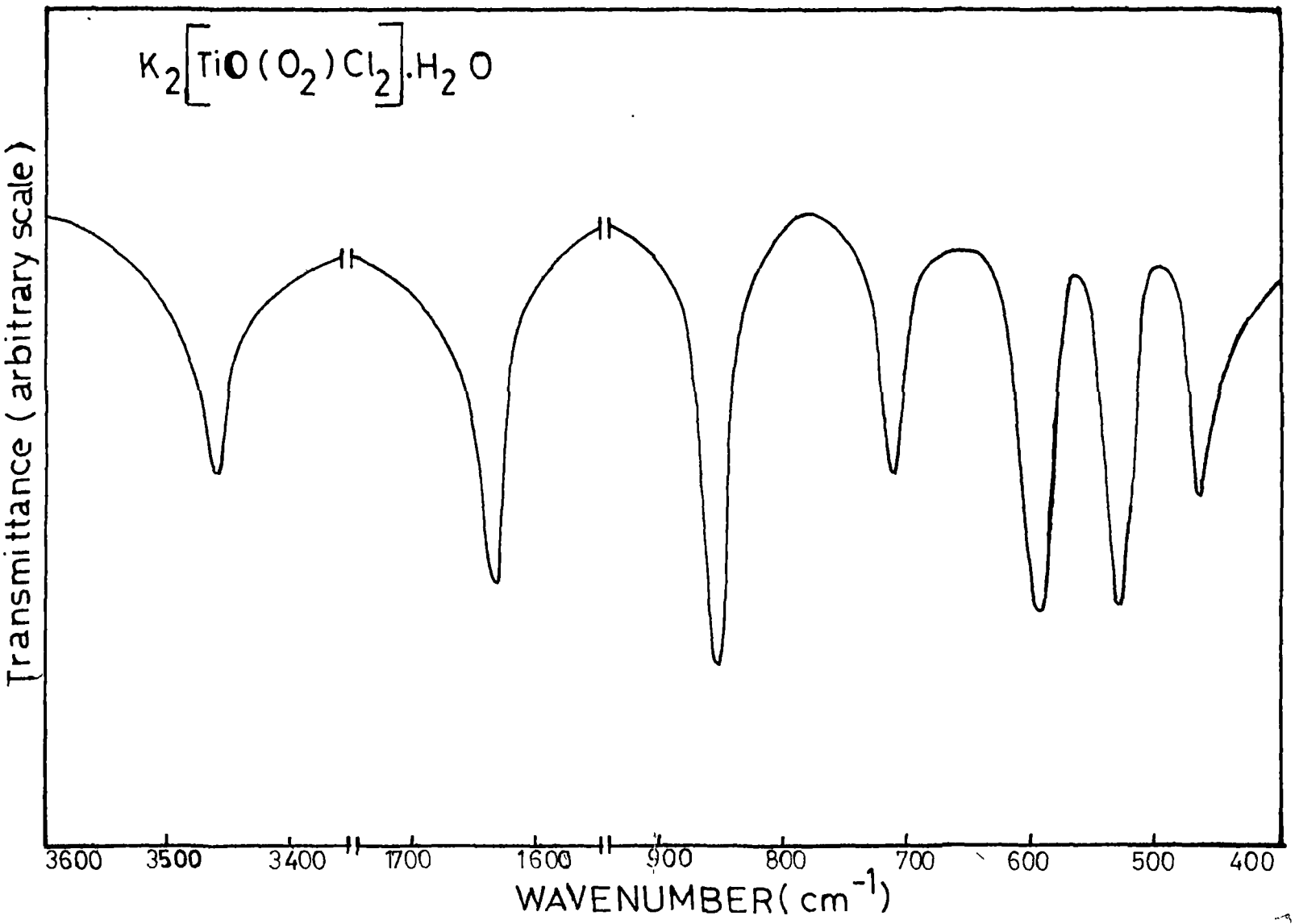
Although the infrared spectrum of the compound is straightforward, the observed bands and their positions are very informative, however. The significant features of the spectrum are the absorptions (Table 7-1) originating from the presence of co-ordinated peroxide (O_2^{2-}) at 860 (vs) cm^{-1} assigned to ν (O-O) (ω_1), at 600 (s) and at 535 (s) cm^{-1} attributed to the complementary ν_3 and ν_2 modes, respectively, of ν (Ti-O_2) vibrations,[4,6,17] and at 470 cm^{-1} due to ν (Ti-Cl).[18] Another important feature of the spectrum is the appearance of a medium intensity band at 720 cm^{-1} and the clear absence of any absorption in the 970 cm^{-1} region. It is, therefore, very reasonable to argue that the terminal oxo group of the 'titanyl' moiety which was present in the complex formed in solution has now lost its identity in the corresponding solid compound leading to the formation of an oxo-bridged (μ-oxo) species through -Ti-O-Ti- interactions as evidenced by the presence of a 720 (m) cm^{-1} band corresponding to ν (-Ti-O-Ti-)[19] vibrations. Two additional bands at 1640 (s) and at 3460 (m) cm^{-1} are typical for those arise from the occurence of uncoordinated water,[20,21] and have been assigned to δ (H-O-H) and ν (O-H) modes, respectively. Taking into account of the results of chemical analyses, magnetic susceptibility and EPR measurements, and IR spectroscopic studies it appeared logical to assign $K_2[TiO(O_2)Cl_2].H_2O$ being the formula of the compound with the complex $[TiO(O_2)Cl_2]^{2-}$ species having a distorted octahedral structure which it has attained through -Ti-O-Ti- interactions with the contiguous titanium centres

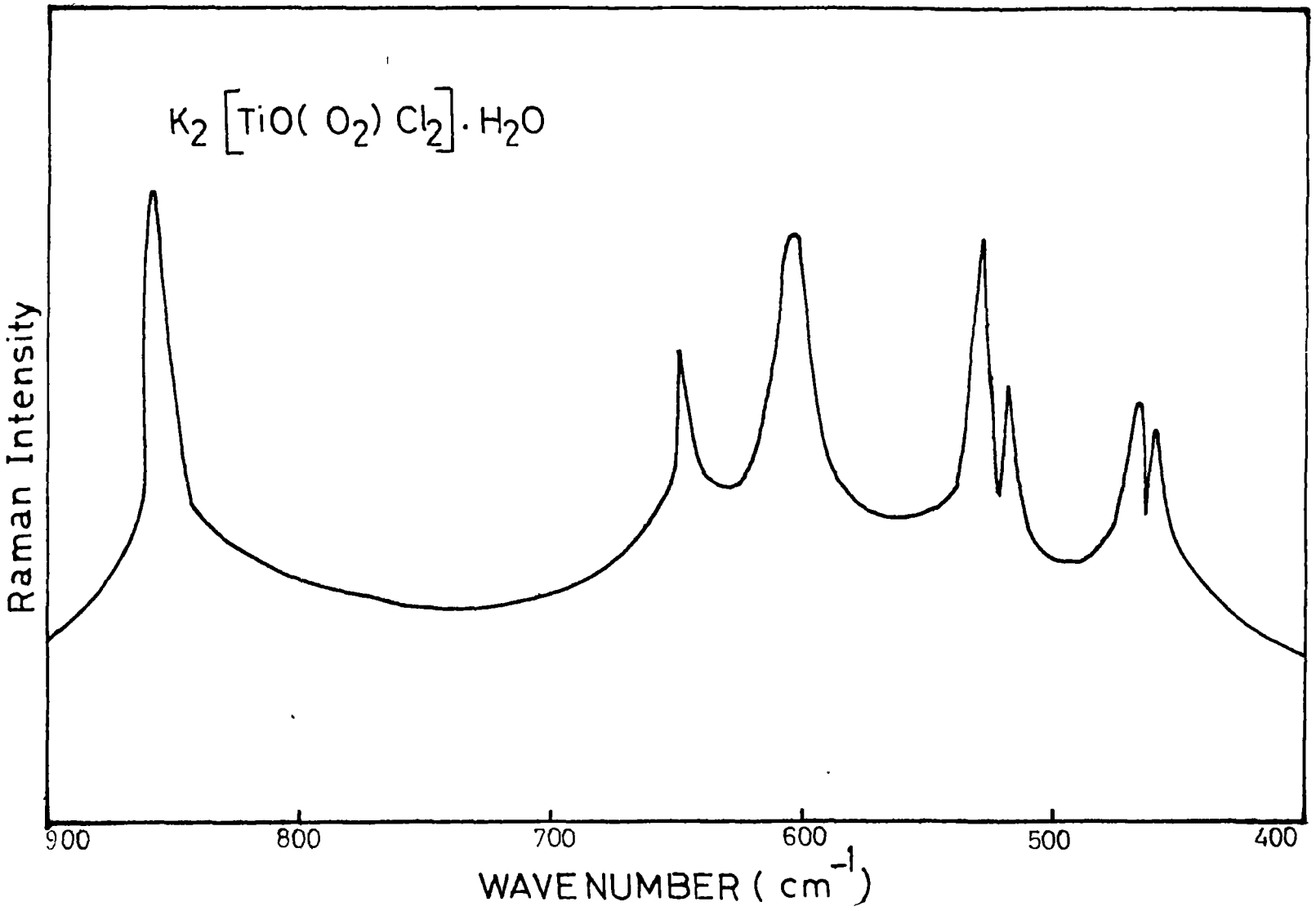
in the crystal lattice. The insoluble nature of the compound adduce support to the polymeric nature of the afore-mentioned complex ion.

Table 7-1. Structurally Important Infrared and laser Raman (lR) Bands of $K_2[TiO(O_2)Cl_2].H_2O$

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$K_2[TiO(O_2)Cl_2].H_2O$	860vs	860	ν (O-O) ν_1
	600s	605	ν (Ti-O_2) ν_3
	535s	530	ν (Ti-O_2) ν_2
	720m		ν (-Ti-O-Ti-)
	470m	480	ν (Ti-Cl)
		650, 520, 460	ν (-Ti-O-Ti-)
	1640s		δ (H-O-H)
	3460m		ν (O-H)

In order to get further support concerning the formula and the proposed structure of the complex, laser Raman (lR) spectrum of the compound was recorded at ambient temperatures. Owing to the insolubility of the compound, the lR spectrum was recorded only on solid. The lR spectrum strongly augment the IR spectral observations. The salient features of lR spectrum are the signals (Table 7-1) at 860, at 650, at 605, at 530, at 520, at 480, and at 460 cm^{-1}. The bands at 860, 605 and 530 cm^{-1} complement the corresponding IR absorptions owing to ν (O-O) ω_1, ν (Ti-O_2) ν_3, and ν (Ti-O_2) ν_2, respectively.[6,17]


$K_2[TiO(O_2)Cl_2].H_2O$
Transmittance (arbitrary scale)
3600
3500
3400
1700
1600
900
800
700
600
500
400
WAVENUMBER (cm^{-1})


$K_2[TiO(O_2)Cl_2] \cdot H_2O$
Raman Intensity
900
800
700
600
500
400
WAVE NUMBER (cm^{-1})

and conform to the occurence of a chelated peroxide (O_2^{2-}) ligand co-ordinated to the metal centre in a triangular bidentate (C_{2v}) manner. The signal at 480 cm^{-1} is related to that observed at 470 cm^{-1} in the IR spectrum of the compound and is assigned to ν (Ti-Cl). It is important to note that, here again, like in the IR spectrum, no signal typical for the Ti=O group could be observed. This renders it certain that the complex ion does not have any Ti=O group. However, signals at 650, 520 and 460 cm^{-1} due to ν $(-Ti-O-Ti-)^{22}$ vibrations supported the proposition that the complex ion in the solid state does not have a monomeric structure with TiO^{2+}('titanyl') unit, instead the complex species polymerises during the process of isolation in the solid state from solution.

In conclusion, it may be noted that like vanadium, the hitherto unreported formation of oxo-peroxotitanate(IV) complex in solution containing a 'titanyl' moiety is evidenced. The complex species formed in solution, under the present experimental conditions, polymerises in the process of its isolation in the solid form via μ-oxo bridges in the crystal lattice. In addition, a distorted octahedral structure of the complex ion $[TiO(O_2)Cl_2]^{2-}$, through -Ti-O-Ti- interactions involving contiguous titanium atoms, is in agreement with all the presently available data. In this way further insight into the chemistry of oxo-peroxotitanate(IV) may be gained.

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CHAPTER 8

Chapter 8

Synthesis and Spectroscopic Studies of Alkali-Metal and Ammonium Oxotetrafluorotitanates(IV), $A_2[TiOF_4]$ (A = K, Cs or NH_4)*

Although both titanium(IV) and vanadium(IV) form oxo-cations TiO^{2+} and VO^{2+}, respectively, in aqueous solution, examples of solid oxo-complexes of the former are fewer as opposed to a host of oxo-vanadates(IV). As a case in point, for example, solid oxo-fluoro complexes of vanadium(IV) include $[VOF_3]^-$ [1], $[VOF_4]^{2-}$ [2], and $[VOF_5]^{3-}$, [3] whereas for titanium $[TiOF_5]^{3-}$ is probably the only well characterised[4] fluoro complex of the metal although $[TiOF_3]^-$ has a reported existence.[5] Of some concern was the complex oxotetra-fluorotitanate(IV), $[TiOF_4]^{2-}$. Despite a number of attempts by other workers,[6,7] synthesis of pure $[TiOF_4]^{2-}$ could not be achieved. The complex in each case was contaminated with other products of titanium. In a recent study[8] involving a high temperature thermal decomposition of a peroxo complex $K_2[Ti(O_2)F_4]$, $K_2[TiOF_4]$ was obtained as one of the main products. Here again, contamination of this product by inseparable species stood in the way of obtaining a pure compound. In view of this and also owing to a considerable interest in the structural assessment of oxotitanates(IV),[9-11] we felt it imperative to improvise routes to

*The work described in this Chapter has been accepted for publication: Ind. J. Chem., 1987, in press

the synthesis of the title compounds in a pure form and make an assessment of their structure.

The present Chapter, indeed the concluding Chapter of the thesis, reports on a general synthesis of pure $A_2[TiOF_4]$ (A = K, Cs or NH_4), their characterisation, and structural assessment based on the results of IR and laser Raman (lR) spectroscopic studies.

Experimental

Reagent grade chemicals were used for the syntheses (B.D.H., S.D's, E. Merck, Loba-Chemie, and IDPL).

Synthesis of Potassium Oxotetrafluorotitanate(IV), $K_2[TiOF_4]$

Freshly prepared 1.0g (12.5 mmol) of TiO_2 was dissolved in 36 cm^3 of 4 M sulphuric acid at room temperature to obtain a clear solution. To this was added a solution of 5.1g (87.93 mmol) of potassium fluoride dissolved in 20 cm^3 of water under constant magnetic stirring with the molar ratio of Ti:KF as 1:7 whereupon a white product appeared immediately. The reaction container was then cooled in an ice-water bath for 15 min and the compound was separated by filtration. It was then dissolved in 50 cm^3 of warm water which on cooling to room temperature gave potassium oxotetrafluorotitanate(IV), $K_2[TiOF_4]$. This was then separated by filtration, washed twice with ethanol, and finally dried <u>in vacuo</u> over concentrated sulphuric acid.

Synthesis of Ammonium Oxotetrafluorotitanate(IV), $(NH_4)_2[TiOF_4]$

An amount of 1.0g (12.5 mmol) of freshly prepared TiO_2 was dissolved in 36 cm^3 of 4 M sulphuric acid at room temperature to get a clear solution. To this was added a solution of 3.25g (87.83 mmol) of ammonium fluoride dissolved in 10 cm^3 of water with the molar ratio of $Ti:NH_4F$ being maintained at 1:7 followed by the addition of ethanol with constant stirring until the white product started appearing. The addition of ethanol was discontinued at this stage and the reaction container was cooled in an ice-water bath for 45 min until the precipitation was complete. The compound was then separated by filtration, washed twice with ethanol, and finally dried in vacuo over concentrated sulphuric acid.

Synthesis of Cesium Oxotetrafluorotitanate(IV), $Cs_2[TiOF_4]$

$Cs_2[TiOF_4]$ was precipitated spontaneously when solid $(NH_4)_2[TiOF_4]$ (2.84 mmol) was added to a clear solution of CsBr (8.52 mmol) dissolved in 10 cm^3 of water. The white product was separated by filtration, washed twice with ethanol, and finally dried in vacuo over concentrated H_2SO_4. The yield of $Cs_2[TiOF_4]$ was 0.9g (78%).

The details of amounts of reagents used and the yields of potassium and ammonium oxotetrafluorotitanates(IV) are set out in Table 8-1.

Table 8-1. Amounts of Reagents Used and the Yields of Potassium and Ammonium Oxotetrafluorotitanates(IV)

Compound	Yield g (%)	Amount of TiO_2 in g (mmol)	Amount of AF in g (mmol)	Amount of 4M H_2SO_4 (cm^3)
$K_2[TiOF_4]$	1.9 (69.7)	1.0 (12.5)	5.1 (87.93)	36
$(NH_4)_2[TiOF_4]$	1.8 (82)	1.0 (12.5)	3.25 (87.83)	36

Elemental Analyses

Quantitative estimations of titanium, fluoride, potassium, and nitrogen were made by the methods described in Chapter 2.

The analytical data are given in Table 8-2, while structurally significant infrared and laser Raman (lR) bands alongwith their assignments are reported in Table 8-3.

Results and Discussion

Taking into account of two important points, (i) that a number of direct methods[6,7] failed to provide pure oxotetrafluorotitanate(IV), $[TiOF_4]^{2-}$, free from other products containing titanium and (ii) 'titanyl', TiO^{2+}, moiety certainly exists in solutions,[9-11] it was thought that an indirect route through the

Table 8-2. Analytical Data of $A_2[TiOF_4]$ (A = K, Cs or NH_4)

Compound	Found % (Calcd. %)		
	A or N	Ti	F
$K_2[TiOF_4]$	35.24 (35.77)	21.89 (22.01)	34.5 (34.86)
$Cs_2[TiOF_4]$	-	11.45 (11.82)	18.24 (18.71)
$(NH_4)_2[TiOF_4]$	15.45 (15.90)	26.80 (27.27)	42.98 (43.18)

prior formation of an oxotitanate(IV) in solution might be appropriate for the synthesis of pure $A_2[TiOF_4]$ (A = K or NH_4). The strategy of the reaction was to produce titanyl sulphate, $TiO(SO_4)$,[12] *in situ* which without isolation would be made to react with an excess of fluoride ion to get an access to $[TiOF_4]^{2-}$. Thus freshly prepared TiO_2 (obtained by dissolving commercial titanium dioxide in 40% HF and then treating with aqueous ammonia) was first dissolved in an excess of dilute sulphuric acid to generate titanyl sulphate, $TiO(SO_4)$,[12] in solution. The clear solution was then treated with alkali-fluoride, AF (A = K or NH_4), to produce $A_2[TiOF_4]$. The role of alkali-fluoride was not only to fluorinate the 'titanyl', TiO^{2+}, species but also to act as the source of counter cations, A^+. Addition of ethanol was required to just initiate precipitation of $(NH_4)_2[TiOF_4]$ owing

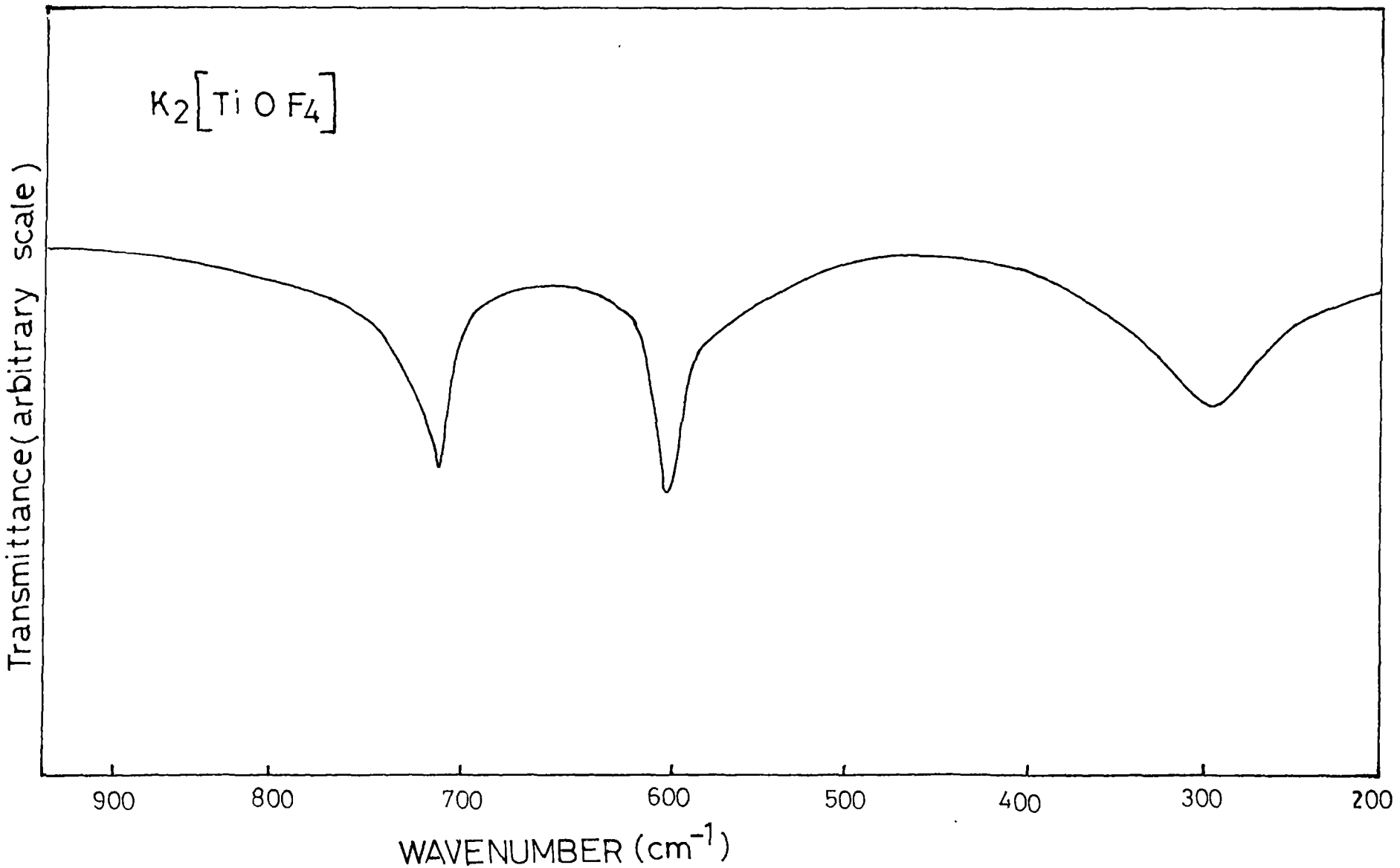
to its high solubility, and recrystallisation of $K_2[TiOF_4]$ from water was necessary to remove any coprecipitated K_2SO_4. The procedure is fairly simple and does not involve any pre-synthesised fluorotitanate or peroxotitanate. Because of the higher yields of products obtained by this method, which is also easy to manipulate, this synthetic route offers an additional advantage. The cesium salt $Cs_2[TiOF_4]$ was prepared by metathesis between $(NH_4)_2[TiOF_4]$ and CsBr (vide Experimental). The success of the present method of synthesis of oxotetrafluorotitanates(IV) depends on the formation of titanyl sulphate species. Thus it is evident from the above discussion that fluoride is a better ligand for TiO^{2+} than sulphate. Indeed our endeavours for synthesising mixed ligand fluoro(sulphato)titanates(IV) have not been successful so far. The results showed that the compounds were binary fluorotitanates(IV) rather than the desired fluoro-(sulphato)titanates(IV). A direct interaction of TiO_2 with aqueous hydrofluoric acid was not conducive because of a pronounced tendency of the metal to form TiF_6^{2-}.

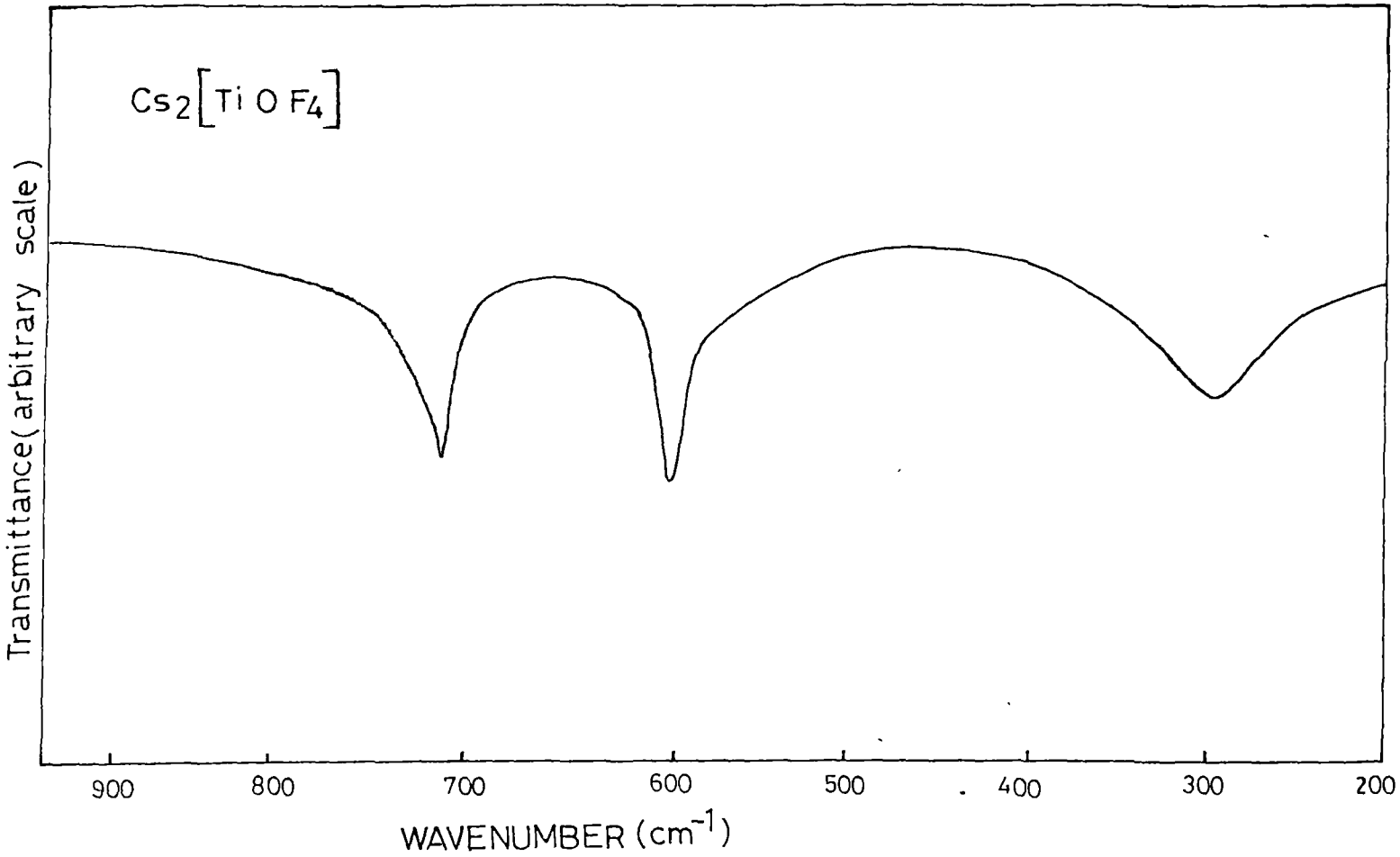
Alkali-metal and ammonium oxotetrafluorotitanates(IV) $A_2[TiOF_4]$ (A = K, Cs or NH_4), are white products and are stable when out of contact with water. The results of elemental analyses suggest that the compounds are pure and are consistent with their formulas. The compounds are all diamagnetic, as evidenced from the results of magnetic susceptibility measurements, in conformity with the contention that titanium occurs in its +4 oxidation state (d^o) in each of them. They are also EPR silent.

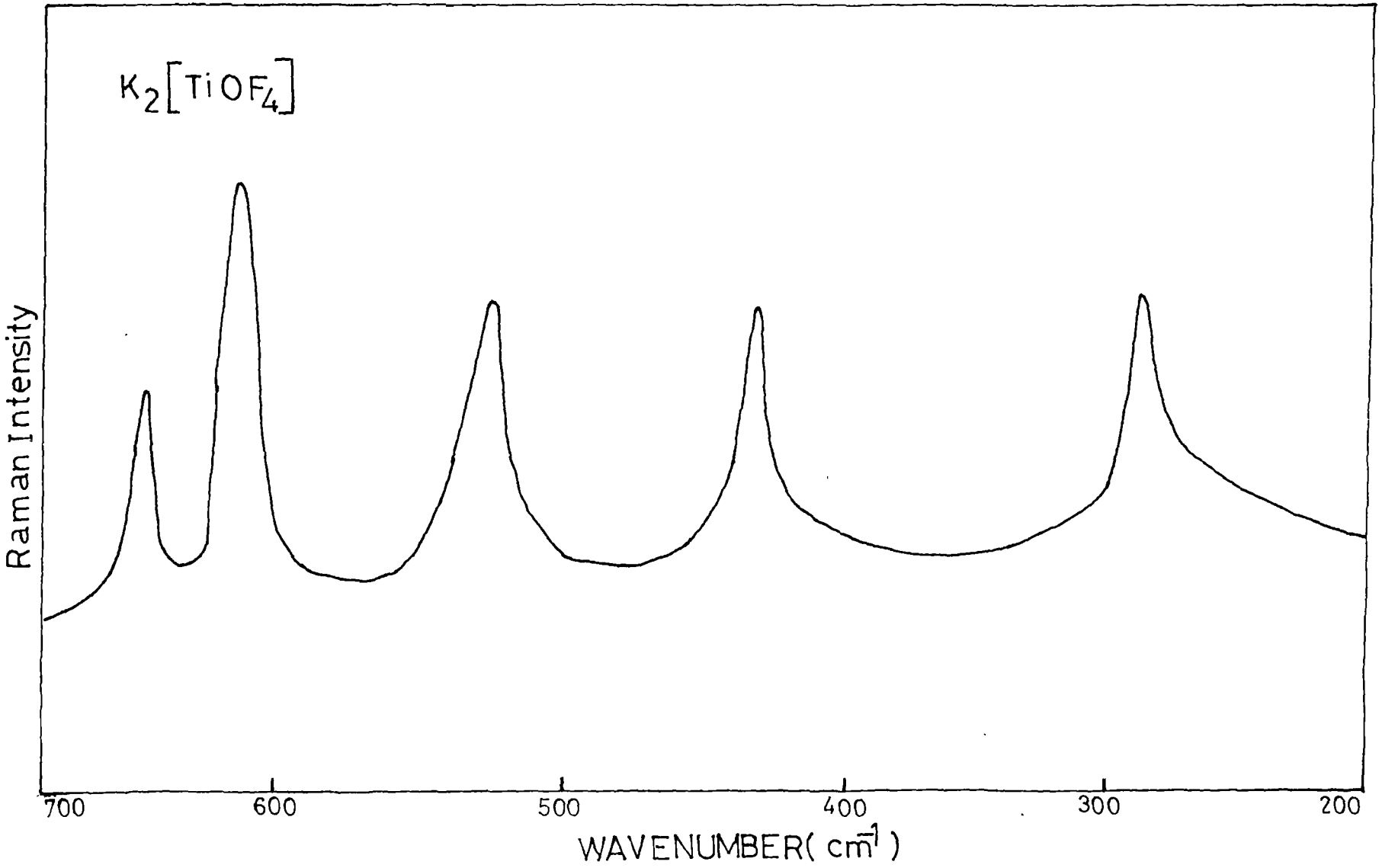
The IR and laser Raman (lR) spectra of all the compounds are identical except for the NH_4^+ modes of the ammonium salt. A typical feature of IR spectra of the compounds is the occurence of an absorption at ca 605 cm^{-1} assignable to ν (Ti-F) arising out of coordinated fluoride and compares very well with those cited in the literature.[13,14] The appearance of a medium intensity

Table 8-3. Structurally Important Infrared and laser Raman Bands of $A_2[TiOF_4]$ (A = K, Cs or NH_4)

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$K_2[TiOF_4]$	720m	650 530 435	ν (-Ti-O-Ti-)
	608m	610	ν (Ti-F)
	300m	285	Ti-F def
$Cs_2[TiOF_4]$	725m	655 535 440	ν (-Ti-O-Ti-)
	605m	612	ν (Ti-F)
	300m	290	Ti-F def
$(NH_4)_2[TiOF_4]$	726m	655 530 435	ν (-Ti-O-Ti-)
	604m	612	ν (Ti-F)
	305m	288	Ti-F def.
	3155m		ν_3 N-H
	3045s		ν_1 N-H
	1400s		ν_4 N-H


$K_2[TiOF_4]$
Transmittance(arbitrary scale)
900
800
700
600
500
400
300
200
WAVENUMBER (cm^{-1})


$Cs_2[TiOF_4]$
Transmittance(arbitrary scale)
900
800
700
600
500
400
300
200
WAVENUMBER (cm^{-1})


$K_2[TiOF_4]$
Raman Intensity
700
600
500
400
300
200
WAVENUMBER(cm^{-1})

band at ca 720 cm^{-1} in the IR spectra of all the three complexes is important and owes its origin to the vibrations of -Ti-O-Ti- moieties.[15] The absence of any band in the region 900-1050 cm^{-1} typical of ν (Ti=O) causes us to infer that the oxo group does not occur as a terminal one but is present as a bridging group giving rise to an infinite chain of -Ti-O-Ti-. The band at ca 300 cm^{-1} in each of the three complexes most likely owes its origin to a Ti-F deformation mode. The bands at 1400, 3045, and 3155 cm^{-1} in the IR spectrum of ammonium salt of the complex $[TiOF_4]^{2-}$ ion have been attributed to ν_4, ν_1, and ν_3 modes of NH_4^+.[16] It is pertinent to mention here that while alkali oxotetrafluorovanadate(V) compounds of the type $A[VOF_4]$ (A = K, Rb, Cs or NH_4) form a monomeric species containing a vanadyl (V=O) moiety,[17] those of the corresponding compounds of titanium(IV) form a polymeric species through -Ti-O-Ti interactions.

The laser Raman (lR) spectra of alkali oxotetrafluoro-titanates(IV) bear a very strong resemblance with each other suggesting that the compounds are structurally similar. The spectra were recorded only on solids, as the compounds decompose at room temperatures in water. The characteristic features of the lR spectra of all the three complexes are the peak at ca 610 cm^{-1} assignable to ν (Ti-F). The assignment is in order.[14] The spectra also display medium intensity bands at ca 650 cm^{-1}, ca 530 cm^{-1}, and at ca 435 cm^{-1} originating from the presence of -Ti-O-Ti- interactions which, in accord with the literature,[18] have been attributed to ν (-Ti-O-Ti-) modes.

It may be concluded from the results of studies described in the present Chapter that while potassium and ammonium oxotetrafluorotitanates(IV), $A_2[TiOF_4]$ (A = K or NH_4), can be synthesised in the pure form directly from the reaction of TiO_2 with 4M H_2SO_4 and AF, the corresponding Cs^+ salt can be prepared by metathesis between CsBr and $(NH_4)_2[TiOF_4]$. Further, the results of IR and laser Raman (lR) spectral data suggest that the metal centre is hexa-coordinated through a -Ti-O-Ti- interaction, and the complex $[TiOF_4]^{2-}$ ion has a polymeric distorted octahedral structure.

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APPENDIX

Appendix

LIST OF PUBLICATIONS

1. A New Route to Potassium and Ammonium Pentaborate Dihydrates, $A[B_5O_6(OH)_4].2H_2O$ (A = K or NH_4), and Synthesis and Structural Assessment of New Fluoro(hydroxy)oxoborate Dihydrates, $A_2[B_2O_2F_2(OH)_2].2H_2O$ (A = K or NH_4)
   M.K. Chaudhuri and B. Das
   J. Chem. Soc., Dalton Trans., 1987, 0000.

2. Alkali-Metal and Ammonium Peroxyfluoroborates. First Synthesis of Peroxyfluoroborate Complexes
   M.K. Chaudhuri and B. Das
   Inorg. Chem., 1985, 24, 2580.

3. Potassium Trifluoroperoxotitanate(IV) Trihydrate, $K[Ti(O_2)F_3].3H_2O$
   M.K. Chaudhuri and B. Das
   Polyhedron, 1985, 4, 1449.

4. Direct Synthesis of Alkali-Metal and Ammonium Pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$, and First Synthesis and Structural Assessment of Alkali-Metal and Ammonium Difluorodiperoxytitanates(IV), $A_2[Ti(O_2)_2F_2]$
   M.K. Chaudhuri and B. Das
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Note

A New Route to Potassium and Ammonium Pentaborate Dihydrates, $A[B_5O_6(OH)_4]\cdot 2H_2O$ (A = K or NH_4), and Synthesis and Structural Assessment of New Fluoro(hydroxy)oxoborate Dihydrates, $A_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ (A = K or NH_4)

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Potassium and ammonium pentaborate dihydrate, $A[B_5O_6(OH)_4]\cdot 2H_2O$ (A = K or NH_4), and *fluoro(hydroxy)oxoborate dihydrates*, $A_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ (A = K or NH_4) have been synthesised, respectively, from the reaction of a suspension of boric acid in water with potassium hydroxide or aqueous ammonia at pH 9 followed by the addition of acetylacetone, and from the reaction of a solution of boric acid and the corresponding AF (A = K or NH_4) in 48% HF at steam-bath temperature Their characterisation and structural assessment are based on the results of elemental analyses and conductance measurements, i r and laser-Raman spectroscopic studies

It is well known that BF_4^- ion undergoes partial hydrolysis in water forming hydroxo(fluoro)borate anions[1] $[BF_n(OH)_{4-n}]^-$, and the complexes derived from them are the subject of active research in boron chemistry[2-6] Mixed fluoroborates and polyborates have also received much attention primarily because of their structural importance[7-11] The synthesis of such compounds is a prerequisite Among the non organo boron compounds pentaborate forms the interesting species $K[B_5O_6(OH)_4]\cdot 2H_2O$ *in which the structural unit has one* tetrahedrally co-ordinated B atom[10] and this has attracted continued interest over the years[7-10] The reported methods of synthesis of this compound involve either boiling of a solution of KOH dissolved in a saturated aqueous solution of boric acid[12] or a potassium fluoride aided reaction of H_3BO_3 partly dissolved in water[10] The role of KF was explained[10] in terms of a catalytic effect on the polymerisation of H_3BO_3 This paper reports a new general route to potassium and ammonium pentaborate dihydrates $A[B_5O_6(OH)_4]\cdot 2H_2O$ (A = K or NH_4) using mild conditions without involving F

There is physico-chemical evidence for the existence of hydroxy(fluoro)borates fluoro(hydroxy)oxoborates,[13] and oxo(hydroxy)borates[8,9] in aqueous solutions, however the isolation of $[B_2O_2F_2(OH)_2]^{2-}$ seems unprecedented In continuation of our earlier work on boron compounds[14] and also in view of a considerable interest in the chemistry of fluoroborates we have developed a suitable method of synthesis of $A_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ (A = K or NH_4) and characterised them by chemical analyses i r and laser-Raman spectroscopic studies

Experimental

The chemicals used were all reagent grade Infrared spectra were recorded on a Perkin Elmer model 983 spectrophotometer separately in KBr and in Nujol media The laser-Raman spectra were recorded at ambient temperatures on a SPEX Ramalog *model 1403 spectrometer using the line at 4880 Å from a* Spectra Physics model 165 argon laser as the excitation source The sample was held either in a quartz capillary or in the form of a pressed pellet Molar conductance measurements were made by use of a Philips PR 9500 conductivity bridge The pH of the reaction solutions was measured with a Systronics type 335 digital pH meter and also with pH indicator (BDH) paper

Synthesis of Potassium and Ammonium Pentaborate Dihydrates, $A[B_5O_6(OH)_4]\cdot 2H_2O$ (A = K *or* NH_4)—Typically to a suspension of boric acid (1 0 g, 16 17 mmol) in water (5 cm^3) was added potassium hydroxide or aqueous ammonia under constant magnetic stirring first to dissolve the boric acid and then to raise the pH of the medium to 9 Potassium hydroxide was added as a 20% solution and aqueous ammonia as its 25 solution (sp gr 0 88) Acetylacetone (6 cm^3) 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 solution at ambient temperatures the corresponding ammonium salt was obtained by concentration 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 $K[B_5O_6(OH)_4]\cdot 2H_2O$ and $NH_4[B_5O_6(OH)_4]\cdot 2H_2O$ were 1 6 g (34%) and 1 4 g (32 %) respectively {Found H, 2 55 B 18 6 K, 13 1 Calc for $K[B_5O_6(OH)_4]\cdot 2H_2O$ H 2 70 B 18 7, K 13 2%, Molar conductance in water 120 Ω^{-1} cm^2 mol^{-1} Found H 4 25 B 19 9 N 5 05 Calc for $NH_4[B_5O_6(OH)_4]\cdot 2H_2O$ H 4 40 B 20 1 N 5 10%, Molar conductance in water 130 Ω^{-1} cm^2 mol^{-1}}

Synthesis of Potassium and Ammonium Difluoro(dihydroxo) dioxodiborate Dihydrates, $A_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ (A = K *or* NH_4)—Boric acid (2 0 g 32 34 mmol) was mixed well with the corresponding AF (A = K or NH_4) in a polyethylene beaker maintaining a B AF ratio of 1 2 5 To this was added 48% HF (8 cm^3, 192 mmol) *to obtain a clear solution This was* then heated for *ca* 30 min over a steam bath in a ventilated hood The volume of the reaction solution was reduced in this process and the required salt was precipitated in high yield It was filtered off washed three times with ethanol, and finally dried *in vacuo* over concentrated sulphuric acid The yields of $K_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ and $[NH_4]_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ were 4 5 g (58%) and 4 2 g (66%) respectively {Found H 2 35 B, 9 10, F, 15 8 K 32 6 Calc for $K_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ H 2 50 B 9 15, F, 15 85, K, 32 5 Found H, 7 10, B, 11 05, F, 19 0 N, 14 1 Calc for $[NH_4]_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ H 7 05 B 11 1, F 19 2 N 14 15%,}

Elemental Analysis—The boron content of each of the compounds was estimated volumetrically as boric acid by titration with a standard solution of sodium hydroxide in the presence of

mannitol [15] Fluoride was estimated as lead chloride fluoride PbClF [16] Potassium and nitrogen were determined by methods described earlier [17] Hydrogen was estimated by a micro analytical technique (RSIC CDRI Lucknow)

Results and Discussion

An interesting aspect of the chemistry of boron is its ability to form polymeric species [18] e g $K[B_5O_6(OH)_4]\,2H_2O$ Although this particular species has been studied by several workers our concern was to develop a general alternative 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 drastic* conditions and also avoiding F ions unlike the earlier methods [10] because fluoride is also a good ligand for boron Strategically it was thought that the desired synthesis could be achieved simply by proper adjustment of pH using potassium hydroxide or aqueous ammonia which also act as the source of counter cation The strategy seems to have worked Thus the present method involves the reaction between a suspension of H_3BO_3 in water and the corresponding alkali at room temperature followed by the addition of acetylacetone It is imperative that slow addition of the alkali is continued until the medium attains pH 9 Addition of the stipulated amount of acetylacetone decreases the pH to 8 owing to its weak acidity Acetylacetone apparently plays two roles *viz* (*i*) it helps to control the pH of the medium and (*ii*) it facilitates precipitation of the compound The new method is easy to manipulate and in this way $A[B_5O_6(OH)_4]\cdot 2H_2O$ ($A = K$ or NH_4) can be synthesised without making use of F ions

The compounds are white microcrystalline products soluble in water Their molar conductances 120 and 130 $\Omega^{-1}\,cm^2\,mol^{-1}$ show that they are 1 1 electrolytes Molar conductances of solutions of the compounds recorded at intervals of 7 15 and 30 d indicated no apparent change in Λ values attesting to their stabilities The i r spectra were recorded in the solid state while laser Raman spectra were recorded both on the solids as well as on their solutions The spectral features are identical to those reported in the literature [7,8] for salts of the ion $[B_5O_6(OH)_4]^-$ Thus we infer that the compounds $K[B_5O_6(OH)_4]\,2H_2O$ and $NH_4[B_5O_6(OH)_4]\,2H_2O$ are the same as those reported in the literature [7,10]

In view of the physico chemical evidence concerning the existence of fluoro(hydroxy)borates in solutions [13] it was expected that similar species could be isolated in the solid state by proper adjustment of experimental conditions It has been found that the reaction of a mixture of H_3BO_3 and AF ($A = K$ or NH_4) in the ratio of 1 2 5 with 48% HF at steam bath temperature leads to the synthesis of $A_2[B_5O_7F_2(OH)_3]\cdot 2H_2O$ ($A = K$ or NH_4) The pH of the solution immediately after formation of the compound was found to be 2 The reaction was facile and the yields of the products were high The steam bath temperature probably facilitates the reaction and the solution volume is reduced considerably allowing the compound to be precipitated

The compounds are white microcrystalline products insoluble in organic solvents They decompose in water and do not melt up to 250 °C The elemental analyses of the K^+ and NH_4^+ salts suggest stoichiometries of K B F H and N B F H as 1 1 1 3 and 1 1 1 7 respectively Accordingly the compounds have been tentatively formulated as $A_2[B_2O_3F_3(OH)]\,2H_2O$ ($A = K$ or NH_4) Strong desiccation over concentrated H_2SO_4 did not remove the water of crystallisation Owing to the pronounced tendency of boron to form a tetrahedral structure a dimeric formula is preferred over a monomeric one and this is supported 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 direct study by i r and laser Raman spectroscopy The i r spectra showed bands at *ca.* 596w *ca.* 746m and *ca.* 1 300w cm^{-1}, and a broad absorption at *ca.* 1 060s cm^{-1} the broadening is probably due to overlap of the B–O [19] and B–F [20] modes The band at *ca.* 596 cm^{-1} has been assigned to ν(B–OH) [21] those at *ca.* 746 and *ca.* 1 300 cm^{-1} to ν_{asym}(B–O–B) and ν_{asym}(B–O–B) respectively [22] In addition the spectra show two bands at *ca.* 1 640m and *ca.* 3 450m cm^{-1} typical of δ(H–O–H) and ν(O–H) of unco ordinated water [23,24] The absorptions at 3 157m 3 040s and 1 400s cm^{-1} in the spectrum of the NH_4^+ salt have been attributed to ν_3 ν_1 and ν_4 modes of NH_4^+ [25] The laser *Raman spectra of both compounds in the solid state exhibited* signals at *ca.* 775 *ca.* 820 and *ca.* 595 cm^{-1} The peaks at *ca.* 775 and *ca.* 595 cm^{-1} have been assigned to ν(B–F) [26] and ν(B–OH) [21], respectively and compare very well with those observed for many fluoro(hydroxy)borate species The signal at *ca.* 820 cm^{-1} has been assigned to ν(B–O) [21] (of the B–O–B framework) However a corresponding band in the i r spectra could not be precisely identified probably owing to its overlap with the B–OH vibration Thus it may be inferred from these results that the complex species contains two tetrahedral boron atoms with a  linkage in addition to one F and OH terminally bonded to each of the two B atoms accordingly the complex ion has been formulated as $[B_5O_7F_3(OH)_3]^{2-}$

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Alkali-Metal and Ammonium Peroxyfluoroborates. First Synthesis of Peroxyfluoroborate Complexes

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It has been known for quite some time that orthoboric acid reacts in solution[1] with hydrogen peroxide giving peroxyboric acid, which most probably contains the $[B_2(O_2)_2(OH)_4]^{2-}$ anion. Alkali-metal salts of this anion are also known and constitute an important oxidizing component in many washing powders. The commercially most important compound in this context is $Na_2B_2(O_2)_2(OH)_4 \cdot 6H_2O$. No heteroligand peroxyborate is known to our knowledge. As a part of our program of synthesis, structural assessment, and studies of reactivities of peroxy compounds of metals,[2] we have extended our investigation to boron and expected that the results obtained would provide internally consistent data regarding the effect of heteroligands on the stability of peroxyborate systems. In this report we present an account of the synthesis and assessment of structures of the first examples of heteroligand peroxyborates of the types $A_2B(O_2)F_3 \cdot 4H_2O$ (A = Na or K) and $(NH_4)_2B_2(O_2)_3F_2$.

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Table I. Analytical Data, Molar Conductance Values, and Structurally Significant IR Bands of $A_2B(O_2)F_3 \cdot 4H_2O$ (A = Na or K) and $(NH_4)_2B_2(O_2)_3F_2$

compd	molar conductance, Ω^{-1} cm^2 mol^{-1}	% found (% calcd) A or N	B	O_A[a]	F	IR, cm^{-1}	assignt
$(NH_4)_2B_2(O_2)_3F_2$	234	14.47 (14.62)	11.64 (11.28)	51.21 (50.07)	19.75 (19.82)	1050 (s, br)	ν_{B-F}
						850 (m)	ν_{O-O}
						3155 (m)	ν_3
						3045 (s)	ν_1
						1400 (s)	ν_4
$Na_2B(O_2)F_3 \cdot 4H_2O$	270	45.35 (45.98)	5.21 (4.96)	14.8 (14.69)	27.11 (26.16)	1060 (s)	ν_{B-F}
						860 (m)	ν_{O-O}
						3450 (m)	ν_{O-H}
						1640 (m)	δ_{H-O-H}
$K_2B(O_2)F_3 \cdot 4H_2O$	255	31.54 (31.27)	4.52 (4.32)	13.2 (12.8)	23.12 (22.79)	1050 (s)	ν_{B-F}
						860 (m)	ν_{O-O}
						3450 (m)	ν_{O-H}
						1640 (m)	δ_{H-O-H}

[a] Peroxy oxygen

Experimental Section

The chemicals used were all reagent grade products. Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer separately in KBr and in Nujol media. Molar conductance measurements were made by using a Philips PR 9500 conductivity bridge at 23 °C, with the concentration of each of the solutions being maintained at 10^{-3} M. The pH of the reaction solutions was measured with a Systronics Type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of $Na_2B(O_2)F_3 \cdot 4H_2O$, $K_2B(O_2)F_3 \cdot 4H_2O$, and $(NH_4)_2B_2(O_2)_3F_2$. General Procedure. To a suspension of 2.0 g (32.34 mmol) of boric acid in *ca. 15 cm^3 of water* was added alkali-metal hydroxide or ammonium hydroxide (AOH; A = Na, K, or NH_4) solution, under constant magnetic stirring, first to completely dissolve the boric acid and then to raise the pH of the medium to 9. While the sodium hydroxide or potassium hydroxide was added as 20% solution, the ammonium hydroxide was added as its 25% solution. 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 resulting solution was adjusted to 9 by the addition of alkali-metal or ammonium hydroxide solution, 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 the 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 AOH solution. Addition of a nearly equal volume of ethanol to the above solution produced white crystalline alkali-metal or ammonium peroxyfluoroborate 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 sulfuric acid.

The yields of $Na_2B(O_2)F_3 \cdot 4H_2O$, $K_2B(O_2)F_3 \cdot 4H_2O$, and $(NH_4)_2B_2(O_2)_3F_2$ were 6.5 g (92%), 6 g (74%), and 4.5 g (72%), respectively.

Elemental Analyses. Boron was estimated gravimetrically, after the peroxy oxygen was expelled, as nitron tetrafluoroborate.[3] The peroxide content in each of the compounds was determined by redox titration with a standard potassium permanganate solution.[4] Sodium and potassium were estimated by the methods described in our earlier papers.[2] Nitrogen and fluoride analyses were obtained from Amdel, Australian Microanalytical Service, Port Melbourne, Victoria 3207, Australia. Fluoride in the $Na_2B(O_2)F_3 \cdot 4H_2O$ compound was also estimated gravimetrically as lead chloride fluoride PbClF.[5] All analytical data, molar conductance values, and structurally significant IR band positions and their assignments are summarized in Table I.

Results and Discussion

Synthesis. The reaction of orthoboric acid with hydrogen peroxide produces the peroxyborate species $[B_2(O_2)_2(OH)_4]^{2-}$ in solution,[1] and the alkali-metal salts of the 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.[6] Thus it was expected that under the appropriate conditions both peroxide (O_2^{2-}) and fluoride (F^-) ligands may be made to coordinate to boron in the presence of each other to produce heteroligand peroxyborate complexes.

The role of pH in the synthesis of such compounds have been emphasized[2] recently. Accordingly the reactions of boric acid with alkali-metal or ammonium hydroxide, 40% HF, and 30% H_2O_2 solutions were conducted at pH 9, which gave rise to the formation of the complex ions $[B(O_2)F_3]^{2-}$, in the case where the alkali-metal hydroxide was either NaOH or KOH, and $[B_2(O_2)_3F_2]^{2-}$, in the case of NH_4OH. The complex ions were isolated as $Na_2B(O_2)F_3 \cdot 4H_2O$, $K_2B(O_2)F_3 \cdot 4H_2O$, and $(NH_4)_2B_2(O_2)_3F_2$ in very high yields by the addition of ethanol, which facilitated precipitation. The peroxyfluoroborate formation reactions are best monitored through peroxy 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 emphasized that a pH 9 reaction medium is very conducive to the formation and isolation of the compounds. Our attempts to explore the possibility of synthesis of peroxyfluoroborates at a lower pH (3 or 4) were in vain. The compounds thus obtained were found to contain very low levels of peroxide.

Characterization and Assessment of Structure. The peroxyfluoroborates 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. The results obtained thereof and those of the analyses of other constituents of the compounds (Table I) suggest the stoichiometry of $B:O_2^{2-}:F^-$ 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 $Na_2B(O_2)F_3 \cdot 4H_2O$, $K_2B(O_2)F_3 \cdot 4H_2O$, and $(NH_4)_2B_2(O_2)_3F_2$. The peroxyfluoroborates do not melt up to 300 °C; however, the $(NH_4)_2B_2(O_2)_3F_2$ compound volatilizes at about 165 °C. Pyrolytic studies reveal that while all the compounds start losing peroxy 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 newly synthesized compounds have been found to lie between 230 and 270 Ω^{-1} cm^2 mol^{-1} 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 most significant feature of IR spectra of the peroxyfluoroborates are the absorptions at ca. 1050 and ca. 860 cm^{-1}, which have been assigned to the ν_{B-F}[7] and ν_{O-O}[2,8] modes respectively originating from the presence of coordinated fluoride and peroxide ligands. The position of ν_{O-O} suggests a strong possibility

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of the O_2^{2-} ligand being bonded to the boron center in a triangular bidentate (C_{2v}) manner,[2,8] and the complex anion $[B(O_2)F_3]^{2-}$ may be a pentacoordinated monomer; however, the possibility that the complex ion is tetrahedral with a terminal O–O group cannot be ruled out. The IR spectrum of the complex anion $[B_2(O_2)_3F_2]^{2-}$ shows a pattern generally similar to that of the $[B(O_2)F_3]^{2-}$ species, except for much greater broadening of the band at 1050 cm^{-1}. It is believed that the stereochemistry of boron in the $[B_2(O_2)_3F_2]^{2-}$ ion is tetrahedral, which is attained through coordination of one O_2^{2-} ligand in a triangular bidentate fashion, one terminal F^- ligand, and one end of a bridging O–O ligand. An alternate structure of the dimer, similar to that found for $NaBO_3 \cdot 4H_2O$, with two O–O bridges connecting the two boron atoms (i.e., a six-membered B_2O_4 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 $[B_2(O_2)_2(OH)_4]^{2-}$, the latter structure appears more likely. The two extra bands at 3450 (m) and 1640 (m) cm^{-1} in the case of the Na^+ and K^+ salts were assigned to the ν_{O-H} and δ_{H-O-H} modes of uncoordinated water.[9] 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 bans at 1400 (s), 3045 (s), and 3155 (m) cm^{-1} in the spectrum of $(NH_4)_2B_2(O_2)_3F_2$ have been attributed to the ν_4, ν_1, and ν_3 modes of NH_4^+.

Thus, it is evident from the present work that, under the appropriate conditions, peroxyfluoroborates can be prepared and such complexes are appreciably stable.

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Registry No. $(NH_4)_2B_2(O_2)_3F_2$, 96455-71-9; $Na_2B(O_2)F_3$, 96455-72-0; $K_2B(O_2)F_3$, 96455-73-1.

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POTASSIUM TRIFLUOROPEROXOTITANATE(IV) TRIHYDRATE, $K[Ti(O_2)F_3]\cdot 3H_2O$

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Abstract—Potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3]\cdot 3H_2O$, with the peroxide (O_2^{2-}) being bonded to the Ti(IV) centre in a triangular bidentate manner (C_{2v}) as evidenced from the IR and laser Raman spectroscopic studies, has been synthesised from the reaction of a solution of TiO_2 in 40% HF with an excess of 30% H_2O_2 and KOH, followed by the addition of aqueous HF to adjust the pH of the reaction solution between 8 and 9.

It has been known that Ti(IV) produces a characteristic colour reaction, with H_2O_2, which is used for the detection of either reagent.[1] Some solid peroxotitanate complexes have been reported, however, there is little agreement over their composition let alone their structure.[1,2] Pentafluoroperoxotitanate(IV) complex, $[Ti(O_2)F_5]^{3-}$, is rather well studied, and constitutes the only example of fluoroperoxotitanate(IV) known to date. Reported herein are the synthesis and assessment of molecular structure by IR and laser Raman spectroscopic studies of a new fluoroperoxotitanate(IV), potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3]\cdot 3H_2O$.

EXPERIMENTAL

The chemicals used were all reagent grade products. IR spectra were recorded on a Perkin–Elmer Model 983 spectrophotometer. The laser Raman (LR) spectra were recorded on a SPEX Ramalog Model 1403 spectrometer. The 4880 Å laser line from the 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 counting processsing system. The spectra were recorded at ambient temperatures by making a freshly prepared solution of the sample, or a pressed pellet of the compound. Molar conductance was measured using a Philips PR9500 conductivity bridge. The pH of the reaction solution was measured with a Systronic Type 335 digital pH meter, and also with pH indicator (BDH) paper. Magnetic susceptibility was measured by the Gouy method, using $Hg[Co(NCS)_4]$ as the calibrant.

Synthesis of potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3]\cdot 3H_2O$. An amount of 1.0 g (12.5 mmol) of TiO_2 was dissolved in 10 cm^3 (200 mmol) of 40% HF by heating for *ca* 10 min over a steam-bath. The clear solution was cooled to 20°C, and 20 cm^3 (176.4 mmol) of 30% H_2O_2 was added under stirring, followed by the addition of 17.5 g (311.9 mmol) of powdered potassium hydroxide. The colourless solution thus obtained was maintained at *ca* 20°C for 15 min. Dropwise addition of 40% HF to the solution, until the pH of the medium was reduced to 8–9, changed colour of the reaction solution to yellow and afforded yellow microcrystalline potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3]\cdot 3H_2O$. Addition of hydrofluoric acid was stopped at this stage and the product was isolated by centrifugation, washed 3–4 times with ethanol, and finally dried *in vacuo* over concentrated sulphuric acid. Yield of $K[Ti(O_2)F_3]\cdot 3H_2O$ was 2 g (69%).

Elemental analysis. Peroxide, fluoride and potassium were estimated by the methods described in earlier papers.[3] Titanium content in the compound was determined gravimetrically by estimating as TiO_2, after precipitation with cupferron.[4] Found: K, 17.3; Ti, 20.45; O_2^{2-} (active oxygen), 14.2; F, 24.3%. Calc. for $K[Ti(O_2)F_3]\cdot 3H_2O$: K, 17.0; Ti, 20.82; O_2^{2-} (active oxygen), 13.91; F, 24.78%.

RESULTS AND DISCUSSION

The pentafluoroperoxotitanate(IV), $[Ti(O_2)F_5]^{3-}$, was synthesised from the reaction of TiF_6^{2-} with

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H_2O_2. It was expected, however, that a viable synthesis of fluoroperoxotitanates(IV) may be possible from TiO_2 under suitable conditions. In view of this and also considering the importance of pH in the syntheses of peroxometalates,[3,5] the reaction of a solution of TiO_2 in 40% HF with hydrogen peroxide and KOH was conducted followed by adjusting the pH of the reaction medium between 8 and 9 by the addition of 40% HF. This has led to the successful synthesis of potassium trifluoroperoxotitanate(IV) trihydrate,

$$K[Ti(O_2)F_3]\cdot 3H_2O,$$

in a high yield. It is believed that TiO_2 dissolves in 40% HF producing fluorotitanate(IV) in solution which subsequently undergoes peroxygenation in the presence of H_2O_2 and KOH ultimately leading to the synthesis of the complex $[Ti(O_2)F_3]^-$ ion at a pH 8–9. Further lowering of pH to 6 by the addition of 40% HF produced the already known complex $K_3[Ti(O_2)F_5]$.[6,7]

Potassium trifluoroperoxotitanate(IV) trihydrate, $K[Ti(O_2)F_3]\cdot 3H_2O$, is stable in the absence of moisture, and in water it decomposes slowly as evident from the comparatively higher molar conductance at room temperature. The results of a magnetic susceptibility measurement show that the compound is diamagnetic suggesting the occurrence of titanium(IV). Estimation of peroxide, accomplished by red-ox titrations separately involving standard potassium permanganate and Ce^{4+} solutions, conspicuously suggested the presence of one O_2^{2-} per titanium atom in the compound.

The IR spectrum of the compound showed bands at 900vs and 860s cm^{-1}, at 610s cm^{-1}, at 535s cm^{-1}, at 440 m and 310 cm^{-1}, while the laser Raman spectra, recorded in the solid state as well in a solution, were similar exhibiting peaks at 900 and 860 cm^{-1}, at 610 cm^{-1}, at 530 cm^{-1} and at 285 cm^{-1}. The peaks, at 900 and 860 cm^{-1} assigned to ν_{-O-O-} (ν_1), at *ca* 530 cm^{-1} to ν_{Ti-O_2} (ν_2), at 610 cm^{-1} to ν_{Ti-O_2} (ν_3), and at *ca* 300 cm^{-1} to δ_{Ti-F}, are in order and well precedented in the literature.[3,5–7] The additional bands in the IR spectrum are assigned to ν_{Ti-F} (440 cm^{-1}), ν_{O-H} (3450 cm^{-1}), and δ_{H-O-H} (1640 cm^{-1}) modes respectively of un-coordinated water.[8–10] The fact that the ν_{-O-O-} (ν_1) and the complementary ν_{Ti-O_2} (ν_2 and ν_3) modes in the IR and LR spectra were observed in the positions stipulated for a triangularly bonded peroxide, renders it certain that the peroxide (O_2^{2-}) is bonded to the Ti(IV) centre in a triangular bidentate (C_{2v}) manner.

Thus, it may be inferred that potassium trifluoroperoxotitanate(IV) trihydrate,

$$K[Ti(O_2)F_3]\cdot 3H_2O,$$

with the peroxide ligand being bonded to the metal in a triangular bidentate fashion, can be synthesised directly from TiO_2. The complex $[Ti(O_2)F_3]^-$ may be a penta-coordinated monomer; however, it is more likely that it has an octahedral or a distorted octahedral structure through –Ti–F–Ti– interactions.

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Direct Synthesis of Alkali-Metal and Ammonium Pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$, and First Synthesis and Structural Assessment of Alkali-Metal and Ammonium Difluorodiperoxytitanates(IV), $A_2[Ti(O_2)_2F_2]$

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Yellow alkali-metal and ammonium pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4), have been synthesized directly from the reaction of TiO_2 in 40% HF with 30% H_2O_2 at pH 6 maintained by the addition of the corresponding alkali metal or ammonium hydroxide. Novel alkali-metal and ammonium difluorodiperoxotitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4), have been synthesized from the reaction of a solution of TiO_2 in 40% HF with 30% H_2O_2 at pH 9 maintained by the addition of the corresponding AOH, followed by precipitation with ethanol. The compounds are all diamagnetic and permit molar conductance measurements. The IR and laser Raman spectra suggest that the peroxide groups are bonded to the Ti^{4+} center in a triangular bidentate (C_{2v}) manner and that ν_{O-O} decreases with the increase in the number of coordinated peroxide groups.

There has been a considerable recent interest in metal complexes that contain peroxide.[1,2] Some of this interest originates from the probable biochemical significance of peroxymetal complexes[1,3] and the potential use of hetero ligand peroxymetal compounds containing macrocyclic ligands as models for biological systems.[3] Our interest in this area stems from developing suitable methods of syntheses and making assessment of structures of hetero ligand peroxymetal compounds. We have embarked on a research program designed to find suitable methods for syntheses. Within the context of the present work there are certain aspects of the chemistry of peroxytitanates(IV), as reported in the literature,[4,5] that remain unclear. Notably important among them are the lack of a direct method for synthesizing alkali-metal and ammonium pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$, and the absence of any reported existence of difluorodiperoxytitanate(IV) complexes, $A_2[Ti(O_2)_2F_2]$. Reported in this paper are a direct general method for the synthesis of $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4), and the synthesis, characterization, and assessment of structure of novel hetero ligand peroxytitanate(IV) compounds of the type $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4), and also a set of internally consistent data concerning the effect on ν_{O-O} modes with the increase in number of such groups coordinated to the Ti^{4+} center in going from $[Ti(O_2)F_5]^{3-}$ to $[Ti(O_2)_2F_2]^{2-}$. The syntheses have been achieved by conducting the reactions under two different, in each case specific, pH conditions.

Experimental Section

The chemicals used were all reagent grade products. IR spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer. Laser Raman (LR) spectra were recorded on a Spex Ramalog Model 1402 spectrometer. The 4880-Å laser line from the 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 a photon-counting processing system. The sample was held either in a quartz capillary or in the form of a pressed pellet, unless otherwise stated, and the spectra were recorded at ambient temperatures. Molar conductance measurements were made in aqueous solution with a Philips PR 9500 conductivity bridge. The pH of the reaction solutions was measued with a Systronics Type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of Alkali-Metal and Ammonium Pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4). In a typical reaction, to a stirred cold solution of 2.0 g (25 mmol) of TiO_2 in 20 cm^3 (400 mmol) of 40% hydrofluoric acid, obtained by heating the mixture for ca. 20 min,

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Table I. Analytical Data, Molar Conductance Values, and Structurally Significant IR and Raman Bands of $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4) and $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4)

compd	molar conductance, Ω^{-1} cm^2 mol^{-1}	% found (% calcd) A or N	Ti	O[a]	F	IR, cm^{-1}	Raman,[b] cm^{-1}	assignt
$(NH_4)_3[Ti(O_2)F_5]$	365	18.51 (18.35)	21.2 (20.9)	14.2 (13.97)	41.8 (41.48)	905 vs	900 s (p)	ν_{O-O} (ν_1)
						600 s	590 m (dp)	ν_{Ti-O_2} (ν_3)
						530 s	530 s (p)	ν_{Ti-O_2} (ν_2)
						430 m		ν_{Ti-F}
						225 m	270 m	Ti-F def
$Na_3[Ti(O_2)F_5]$	350	28.1 (28.28)	19.3 (19.64)	13.6 (13.12)	38.4 (38.96)	900 vs	900 s (p)	ν_{O-O} (ν_1)
						600 s	600 m (dp)	ν_{Ti-O_2} (ν_3)
						549 s	525 s (p)	ν_{Ti-O_2} (ν_2)
						450 m		ν_{Ti-F}
						240 m	250 m	Ti-F def
$K_3[Ti(O_2)F_5]$	370	39.8 (40.14)	16.7 (16.39)	11.2 (10.95)	32.9 (32.51)	900 vs	900 s (p)	ν_{O-O} (ν_1)
						600 s	600 m (dp)	ν_{Ti-O_2} (ν_3)
						530 s	520 s (p)	ν_{Ti-O_2} (ν_2)
						430 m		ν_{Ti-F}
						230 m	270 m	Ti-F def
$(NH_4)_2[Ti(O_2)_2F_2]$	225	15.21 (15.06)	25.3 (25.75)	34.8 (34.4)	20.8 (20.43)	860 vs, 830 s	860 s (p), 830 s (p)	ν_{O-O} (ν_1)
						620 s	600 s (p)	ν_{Ti-O_2} (ν_2)
						510 s	520 m (dp)	ν_{Ti-O_2} (ν_3)
						450 m		ν_{Ti-F}
						250 m	270 m	Ti-F def
$K_2[Ti(O_2)_2F_2]$	235	34.7 (34.28)	21.3 (21)	28.4 (28.06)	16.3 (16.66)	860 vs, 840 s	860 s (p), 825 s (p)	ν_{O-O} (ν_1)
						620 s	600 s (p)	ν_{Ti-O_2} (ν_2)
						500 s	525 m (dp)	ν_{Ti-O_2} (ν_3)
						430 m		ν_{Ti-F}
						250 m	270 m	Ti-F def

[a] Peroxy oxygen. [b] Abbreviations: p, polarized band; dp, depolarized band.

was added 20 cm^3 (176.4 mmol) of 30% H_2O_2 at ca. 20 °C. After the solution was stirred for ca 10 min at 20 °C, the corresponding alkali-metal or ammonium hydroxide, AOH, was added in small portions with slow stirring until the pH of the solution was raised to 6, whereupon yellow microcrystalline alkali-metal or ammonium pentafluoroperoxytitanate(IV), $A_3[Ti(O_2)F_5]$, was precipitated in a very high yield. While sodium or potassium hydroxide was added in the form of powder, ammonium hydroxide was added as its concentrated solution (specific gravity 0.9). The cooling bath was removed, and the compound was separated by centrifugation, washed three times with ethanol, and finally dried in vacuo over concentrated sulfuric acid. The yields of $(NH_4)_3[Ti(O_2)F_5]$, $Na_3[Ti(O_2)F_5]$, and $K_3[Ti(O_2)F_5]$ were 5.5 g (96%), 5.5 g (90%), and 6.5 g (89%), respectively.

Synthesis of Alkali-Metal and Ammonium Difluorodiperoxytitanates(IV), $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4). In a typical procedure, representative of the general method, 1.0 g (12.5 mmol) of TiO_2 was dissolved in 10 cm^3 (200 mmol) of 40% HF by warming over a steam bath for ca. 20 min. The clear solution was cooled to ca. 20 °C followed by the addition of 20 cm^3 (176.4 mmol) of 30% H_2O_2 with stirring. To the solution was added the corresponding alkali-metal or ammonium hydroxide with occassional stirring, in a manner analogous to that mentioned under the synthesis of $A_3[Ti(O_2)F_5]$, until the pH of the reaction solution was raised to 9. The color of the solution first turned red and then yellow, giving a yellow precipitate at pH ca. 6, which slowly went into solution, with simultaneous decrease in the intensity of color, with the progress of addition of alkaline medium. The ultimate color of the solution at pH 9 was very faint yellow. Addition of ethanol to this solution afforded a very faint yellowish white microcrystalline alkali-metal or ammonium difluorodiperoxytitanate(IV) compound, $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4), in a nearly quantitative yield. The isolation, purification, and drying of the compounds were accomplished in similar manners as described earlier in this section. Yields of $(NH_4)_2[Ti(O_2)_2F_2]$ and $K_2[Ti(O_2)_2F_2]$ were 2.2 g (94%) and 2.6 g (91%), respectively.

Elemental Analyses. Peroxide, fluoride, nitrogen, sodium, and potassium were estimated by the methods described earlier.[6] Titanium content in each of the compounds was estimated gravimetrically as TiO_2, after precipitation with cupferron.[7]

The analytical data, molar conductance values, and structurally significant IR and Raman band positions along with their assignments are summarized in Table I.

Results and Discussion

The complexity involved in the chemistry of the Ti–H_2O_2 system is evident from the different color reactions observed with small variation of pH.[4] This is probably the reason why not much is known about peroxytitanates.[4,5] Pentafluoroperoxytitanate(IV), $[Ti(O_2)F_5]^{3-}$, is the most often quoted example of a typical peroxytitanate compound, albeit a few more have also been reported.[8,9] However, no direct method of and the optimum pH required for the synthesis of the complex are known to date. The procedure recommended and generally used for the purpose requires the $[TiF_6]^{2-}$ complex as the essential precursor,[4,5] which results in an extra preparation step. From our experience in the field of peroxymetalate chemistry,[6] and also considering some of the known aspects of titanium chemistry, it was expected that the pentafluoroperoxytitanate(IV) complexes could be synthesized directly from TiO_2 under appropriate conditions. The strategy for the present reaction was that TiO_2 would dissolve in aqueous HF, forming fluorotitanate(IV), in situ, which without isolation would then be made to react with H_2O_2, under a favorable pH of the reaction medium, to afford the complex $[Ti(O_2)F_5]^{3-}$. The reaction took place accordingly and afforded yellow microcrystalline alkali-metal and ammonium pentafluoroperoxytitanates(IV), $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4), in very high yields. The procedure is straightforward and simple, and the suitable pH for the synthesis was found to be 6. The spontaneous separation of the compound from the reaction solution at pH 6 is an additional advantage of the method.

In order to synthesize hitherto unknown fluoroperoxytitanate(IV) complexes containing two peroxy groups bonded per Ti^{4+} center, the reaction of a solution of TiO_2 in 40% HF was

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conducted at a much higher concentration of the alkaline medium (pH 9) with the anticipation that an increased pH would favor and facilitate introduction of more than one O_2^{2-} group into the coordination sphere of Ti^{4+} at the expense of some F^- ligands already bonded to the metal. Thus the synthesis of difluorodiperoxytitanate(IV) complexes, $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4), was achieved at pH 9. That pH 9 is conducive to the synthesis was ascertained from the facts that $A_3[Ti(O_2)F_5]$, which formed at pH 6, started becoming first pale and ultimately very pale at pH 9 and that the product isolated at pH 9 showed a clear shift of the ν_{O-O} mode in the IR spectrum to a lower frequency (ca. 860 cm^{-1}) compared to that (ca. 900 cm^{-1}) typical of $A_3[Ti(O_2)F_5]$ complexes (Table I). The product isolated at pH values between 6 and 8 showed two ν_{O-O} modes at ca. 900 and ca. 860 cm^{-1}, suggesting thereby that the peroxide uptake process is in progress but is not complete until pH 9. A plausible mechanism, in view of the compounds isolated at pH 6 and 9 as $A_3[Ti(O_2)F_5]$ and $A_2[Ti(O_2)_2F_2]$, respectively, is that a fluorotitanate(IV) complex is first formed, from the reaction of TiO_2 with 40% HF, which subsequently undergoes stepwise peroxygeneration to afford $[Ti(O_2)F_5]^{3-}$ and $[Ti(O_2)_2F_2]^{2-}$. This certainly indicates that O_2^{2-} can displace some of the F^- around a Ti^{4+} center at higher pH values. It is quite reasonable to assume that other hetero ligand peroxy complexes of titanium could be obtained directly from TiO_2; syntheses of such compounds are under study. Also, since the diperoxytitanates(IV) undergo deperoxygenation with lowering of pH (<7) of the medium, mixed species (e.g. fluoro(sulfato)-, fluoro(oxalato)-, and fluoro(acetylacetonato)titanates(IV)) should be readily accessible.

Characterization and Assessment of Structure. Yellow $A_3[Ti(O_2)F_5]$ and light yellow $A_2[Ti(O_2)_2F_2]$ are soluble in water, and at room temperature they do not exhibit any noticeable tendency for hydrolysis. They permit molar conductance measuremetns, and the conductances of $A_3[Ti(O_2)F_5]$ (A = Na, K, NH_4) and $A_2[Ti(O_2)_2F_2]$ (A = K, NH_4) have been found to lie in the range 350–370 and 220–240 Ω^{-1} cm^2 mol^{-1}, respectively, in conformity with their formulas. The diamagnetic nature of the compounds, as evidenced by the results of magnetic susceptibility measurements, supports the view that titanium occurs in its +4 oxidation state in each of the newly synthesized compounds. The peroxide estimation, accomplished by redox titrations separately involving a standard potassium permanganate and a standard Ce^{4+} solution, conspicuously suggests the presence of one or two peroxide groups per formula weight of the $A_3[Ti(O_2)F_5]$ and the $A_2[Ti(O_2)_2F_2]$ cases, respectively.

The O–O and metal–O_2 vibrations of peroxymetal compounds are important spectroscopic probes for molecular structure assessment in such systems and are amenable to direct study by IR and Raman spectroscopy. Typically the IR and laser Raman (LR) spectra of the $A_3[Ti(O_2)F_5]$ compounds exhibit peaks at ca. 900, ca. 600, and ca. 530 cm^{-1}, and the corresponding peaks for the $A_2[Ti(O_2)_2F_2]$ compounds appear at ca. 860 and 830, ca. 610, and ca. 520 cm^{-1}. The peaks at ca. 900 or 860 and 830 cm^{-1} have been assigned to ν_{O-O}, while the ones at ca. 600 or 610 cm^{-1} and at ca. 530 or 520 cm^{-1} correspond to ν_{Ti-O_2} modes of coordinated peroxide. The band at ca. 430 cm^{-1} observed only in the IR spectra of the compounds has been attributed to the ν_{Ti-F} mode. The assignments are in order.[6,10,11] The observed positions of ν_{O-O} and ν_{Ti-O_2} are those that one would expect to observe for a triangularly bonded O_2^{2-}. Considering C_{2v} being the local symmetry of coordinated O_2^{2-} ligand, three vibrations (two A_1 and one B_2) are expected to be IR and Raman active, of which the two A_1 modes (ν_1, ν_{O-O} stretching, and ν_2, ν_{Ti-O_2} symmetric stretching) are polarized, while the B_2 mode (ν_3, ν_{Ti-O_2} asymmetric stretching) is depolarized in the Raman spectra.[11] The ν_1 mode occurs at 800–900 cm^{-1}, and the ν_2 and ν_3 modes fall in the region 500–600 cm^{-1}. On the basis of the sharpness and intensity of the observed LR signals and Raman polarization measurements on solutions, the frequencies at ca. 530 and ca. 600 cm^{-1} for the $A_3[Ti(O_2)F_5]$ have been attributed to the ν_2 and ν_3 modes, respectively, of ν_{Ti-O_2}, while the signals at ca. 610 and ca. 520 cm^{-1} for $A_2[Ti(O_2)_2F_2]$ have been assigned respectively to the ν_2 and ν_3 modes of ν_{Ti-O_2}. It is probably the changes in stoichiometry of Ti:O_2:F, and the structures of the complex ions, as one goes from the mono- to the diperoxy species, that cause the frequency reversal of ν_2 and ν_3. Since the LR spectra of the solids as well as their solutions, recorded under identical conditions, do not reveal any notable change in the pattern of the spectra or in the positions of the signals, it is believed that the complex species $[Ti(O_2)F_5]^{3-}$ and $[Ti(O_2)_2F_2]^{2-}$ retain their structural identity also in solution. The splitting of ν_{O-O} in the case of the $A_2[Ti(O_2)_2F_2]$ compounds very likely originates from the coupling of the in-phase–out-of-phase vibrations of the two coordinated peroxo groups. A medium-intensity band at ca. 430 cm^{-1} in the IR spectra of each of the compounds has been assigned to ν_{Ti-F}. However, a counterpart could not be observed in the corresponding LR spectra. The band at ca. 250 cm^{-1} most likely owes its origin to a Ti–F deformation mode. A clear shift of ν_{O-O} from ca. 900 to ca. 850 cm^{-1} in going from $[Ti(O_2)F_5]^{3-}$ to $[Ti(O_2)_2F_2]^{2-}$ is a clean indication of a decrease in the O–O bond order with an increase in the number of coordinated O_2^{2-} groups. Since peroxide ligands bind to Ti through donation from two antibonding π_p orbitals, Ti^{4+} will become a worse acceptor with increasing number of O_2^{2-} ligands. This will make Ti^{4+} withdraw less electron density from the antibonding π_p (O_2^{2-}) orbitals, which will increase their repulsive character and in turn will weaken the O–O bond. Hence, O_2^{2-} multisubstitution should result in weakening of the O–O bond, as observed in the present work.

It may be inferred that fluoroperoxytitanates(IV) of the types $A_3[Ti(O_2)F_5]$ and $A_2[Ti(O_2)_2F_2]$ can be synthesized directly from the reactions of TiO_2, 40% HF, and hydrogen peroxide at pH 6 and 9, respectively, adjusted by the addition of the corresponding alkali-metal or ammonium hydroxide, AOH. While the complex $[Ti(O_2)F_5]^{3-}$ ion may be a heptacoordinated monomer, the complex species $[Ti(O_2)_2F_2]^{2-}$ may have a hexacoordinated structure. However, the chances of polymeric structures of the complexes through weak –Ti–F–Ti– interactions cannot be totally ruled out. The O_2^{2-} group, in each case, is bonded to the Ti^{4+} center in a triangular bidentate (C_{2v}) manner, with the O–O bond order being decreased by the increase in the number of each groups coordinated to the metal center.

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Registry No. $(NH_4)_3[Ti(O_2)F_5]$, 18639-68-4; $Na_3[Ti(O_2)F_5]$, 99398-68-2; $K_3[Ti(O_2)F_5]$, 12021-39-5; $(NH_4)_2[Ti(O_2)_2F_2]$, 99416-55-4; $K_2[Ti(O_2)_2F_2]$, 99416-56-5.

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