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

ABSTRACT

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"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 <u>eight</u> 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.

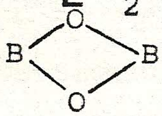
<u>Chapter 1</u> presents a brief introduction pertaining to the research embodied in the thesis. It highlights (i) the importance of and the interest in the studies of peroxo-element chemistry in general, and heteroligand peroxoborate and heteroligand peroxotitanate(IV) compounds in particular, and (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 $A_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ (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.

<u>Chapter 4</u> of the thesis provides an account of the first reported synthesis of peroxofluoroborate complexes, $A_2[B(O_2)F_3]\cdot 4H_2O$ (A = Na or K), and $(NH_4)_2[B_2(O_2)_3F_2]$, their characterisation, and assessment of structures. The complexes $A_2[B(O_2)F_3]\cdot 4H_2O$ (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, $K[Ti(O_2)F_3]\cdot 3H_2O$, 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, $K[Ti(O_2)F_3]\cdot 3H_2O$, in a high yield. The compound has been characterised by elemental analyses, magnetic susceptibility measurement and IR and 1R spectroscopic studies. IR and 1R 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. $K[Ti(O_2)F_3]\cdot 3H_2O$, 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 1R 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 ν (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 $[Ti(O_2)_2(L-L)]$ (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 $[Ti(O_2)_2(L-L)]$ (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 <u>Chapter 7</u>.

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 ν (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^0) 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).