

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

ABSTRACT

BIMALENDU DAS

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
INDIA

FEBRUARY 1988

"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

(ii)

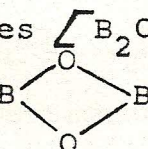
oxotetrafluorotitanates (IV). Another piece of a problem, as emphasised in this Chapter, is the lack of evidence regarding the existence of complex diperoxotitanate (IV) species in the solid state. This Chapter also projects the scope of work on the chosen aspects of boron and titanium chemistry.

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, $A \left[B_5O_6(OH)_4 \right] \cdot 2H_2O$ ($A = K$ or NH_4), and synthesis and structural assessment of new fluoro(hydroxo)oxoborate dihydrates, $A_2 \left[B_2O_2F_2(OH)_2 \right] \cdot 2H_2O$ ($A = K$ or NH_4). The synthesis of $A \left[B_5O_6(OH)_4 \right] \cdot 2H_2O$ ($A = K$ 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 $A \left[B_5O_6(OH)_4 \right] \cdot 2H_2O$, recorded at 23°C, were found to be in order (ca $120 \Omega^{-1} cm^2 mol^{-1}$), and time dependent molar conductivity studies of the compounds suggest that they do not undergo decomposition in water at ambient temperatures.

(iii)

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 IR spectroscopic studies. The compounds decompose in water at ambient temperatures thus precluding their molar conductance measurements. The results of IR and IR spectroscopic studies suggest that the complex species $[B_2O_2F_2(OH)_2]^{2-}$ contains two tetrahedral boron atoms with a B  B linkage.

Chapter 4 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

(iv)

$\left[\text{B}(\text{O}_2)\text{F}_3 \right]^{2-}$ 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 $\left[\text{B}_2(\text{O}_2)_3\text{F}_2 \right]^{2-}$ 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), $\text{A}_3 \left[\text{Ti}(\text{O}_2)\text{F}_5 \right]$ (A = Na, K or NH_4), first synthesis and structural assessment of potassium trifluoroperoxotitanate(IV) trihydrate, $\text{K} \left[\text{Ti}(\text{O}_2)\text{F}_3 \right] \cdot 3\text{H}_2\text{O}$, and potassium and ammonium difluorodiperoxotitanates (IV), $\text{A}_2 \left[\text{Ti}(\text{O}_2)_2\text{F}_2 \right]$ (A = K or NH_4). In view of the difficulties encountered in the synthesis of $\text{A}_3 \left[\text{Ti}(\text{O}_2)\text{F}_5 \right]$ (A = Na, K or NH_4) using the literature reported method, a direct procedure has been developed for the synthesis of $\text{A}_3 \left[\text{Ti}(\text{O}_2)\text{F}_5 \right]$. 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, $\text{K} \left[\text{Ti}(\text{O}_2)_3\text{F}_3 \right] \cdot 3\text{H}_2\text{O}$, 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 is bonded to the titanium(IV) centre in a triangular bidentate (C_{2v}) manner. The compound is stable in the absence of moisture. $\text{K} \left[\text{Ti}(\text{O}_2)_3\text{F}_3 \right] \cdot 3\text{H}_2\text{O}$, which decomposes in water at ambient temperatures precluding molar conductance measurement, is diamagnetic.

The synthesis of light-yellow potassium and ammonium difluorodiperoxotitanates (IV), $\text{A}_2 \left[\text{Ti}(\text{O}_2)_2\text{F}_2 \right]$ ($\text{A} = \text{K}$ 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, $\text{A}_2 \left[\text{Ti}(\text{O}_2)_2\text{F}_2 \right]$ ($\text{A} = \text{K}$ 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 $\text{A}_2 \left[\text{Ti}(\text{O}_2)_2\text{F}_2 \right]$

