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)

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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(hydroxo)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-organoboron 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 hydroxo(fluoro)borates, fluoro(hydroxo)oxoborates,[13] and oxo(hydroxo)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 4 880 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, 13.25%. Molar conductance in water (10^{-3} mol dm^{-3}): 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, 20.15; N, 5.10%. Molar conductance in water (10^{-3} mol dm^{-3}): 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 (Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow).

Results and Discussion

An interesting aspect of the chemistry of boron is its ability to form polymeric species,[18] *e.g.* $K[B_5O_6(OH)_4]\cdot 2H_2O$. 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, $A[B_5O_6(OH)_4]\cdot 2H_2O$ (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 Ω^{-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 $K[B_5O_6(OH)_4]\cdot 2H_2O$ and $NH_4[B_5O_6(OH)_4]\cdot 2H_2O$ are the same as those reported in the literature.[7–10]

In view of the physicochemical evidence concerning the existence of fluoro(hydroxo)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 $A_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ (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 stoicheiometries 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 $A_2[B_2O_2F_2(OH)_2]\cdot 2H_2O$ (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_{sym}(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(hydroxo)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 $\mathrm{B}\!\begin{smallmatrix}\diagup\mathrm{O}\diagdown\\ \diagdown\mathrm{O}\diagup\end{smallmatrix}\!\mathrm{B}$ 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 $[B_2O_2F_2(OH)_2]^{2-}$.

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