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AN ELEGANT DIRECT ROUTE FOR THE PREPARATION OF PYRIDINIUM, AMMONIUM AND ALKALI METAL HEXAFLUOROTITANATES (IV)

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SUMMARY

Pyridinium hexafluorotitanate (IV) has been prepared by a one step procedure. Addition of titanium tetrachloride to pyridinium poly(hydrogen fluoride) yields nearly quantitative amounts of pyridinium hexafluorotitanate(IV). Making use of pyridinium hexafluorotitanate as precursor, ammonium and alkali metal (Na, K, Rb and Cs) hexafluorotitanates have been prepared in good yields. These salts have been characterised by IR, N.M.R. (^{1}H, ^{13}C and ^{19}F), X-ray powder diffraction data and chemical analysis.

INTRODUCTION

Industrially useful [1-10] hexafluorotitanate salts have been prepared either by using TiF_4 [11-13] or TiO_2 as the starting material. These procedures need high temperatures and further processing. A one step procedure has been developed and standardised. The yields are good and the purity of the salts is high. Details are given below.

EXPERIMENTAL

Preparation of pyridinium hexafluorotitanate(IV)

Pyridinium poly(hydrogen fluoride) is prepared [14] and stored in a polythene vessel. 50 ml of pyridinium

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poly(hydrogen fluoride), PPHF, is taken in a polythene flask fitted with a guard tube and a dropper containing 17.3g (0.091M) of titanium tetrachloride (BDH). The contents are stirred and cooled with an ice bath. To this cooled solution is added $TiCl_4$ drop by drop, over a period of one hour. The reaction is found to be very vigorous and exothermic. The gas, HCl released during the reaction escapes through the guard tube. After addition, the contents are stirred for a further period of one hour. The resulting straw coloured liquid is transferred to a 1 litre polypropelene beaker and dry acetone (600 ml) is added with stirring, till the precipitation of pyridinium hexafluorotitanate is complete. The precipitate, a colourless solid is filtered under suction and repeatedly washed with acetone, dried in vacuum and weighed. The weight was found to be 28g. Based on the amount of $TiCl_4$ taken this amounted to an yield of 95%.

The compound, $(C_5H_5NH)_2TiF_6$, has a high solubility in water (377.6 g in 100 ml at 24°C). It is insoluble in alcohol, acetone, acetonitrile, pyridine and chloroform. It can be recrystallized from water, filtered, washed well with acetone and ether, and then dried in vacuum. The colourless needle shaped crystals have a melting point 185°C (dec). As prepared from aqueous solutions it is reported to decompose around 90°C [13], this discrepancy is hard to explain. The compound has been characterised by spectral analysis IR and NMR (^1H, ^{13}C and ^{19}F) [15-17]. Chemical analysis [found : Pyridine 48.53%, Ti 14.90%, F - 34.95%; Calcd. Pyridine - 49.08%, Ti - 14.88%, F - 34.41%] indicates a high purity for the prepared compound (~99%).

Preparation of ammonium and alkali metal (Na, K, Rb and Cs) hexafluorotitanates

To each solution of 5.0g (0.0155M) of pyridinium hexafluorotitanate (IV) in 10 ml of water was added a solution with minimum quantity of water containing 1.80 g

(0.0336M) of NH_4Cl/1.9g (0.0325M) of NaCl/2.5g (0.0336 M) of KCl/5.6g (0.034M) RbBr and 6.9g (0.0324M) of cesium bromide respectively. The mixture was well stirred. The mixture containing the ammonium salt was clear, whereas, precipitation occurred on mixing the other solutions. To the clear solution, as well as to the other solutions 50 ml of 95% alcohol is added and stirred to favour complete precipitation. The precipitate was filtered, washed with alcohol and dried under vacuum. The yield of all the salts, based on the amount of pyridinium hexafluorotitanate taken varied between 92% - 97%).

These hexafluorotitanate salts (IV) were analysed for titanium and fluorine. They were further characterised by IR spectral and X-ray powder diffraction data [18-22]. The data indicated the salts were very pure.

The pyridinium salt is obtained in quantitative yields. The other salts are obtained by easy metathetical reaction with the pure pyridinium salt. This method therefore provides a direct one step route for these salts.

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