

Synthesis & Characterisation of Potassium, Cesium & Ammonium Oxotetrafluorotitanates(IV)

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A high yield synthetic route to potassium and ammonium oxotetrafluorotitanates(IV) has been developed based on the reaction of freshly precipitated TiO_2 with 4 *M* sulphuric acid to produce TiO_2^{2+} cation which reacts with corresponding alkali fluorides (AF) in the molar ratio 1:7 (Ti:AF) to afford the desired compounds. The corresponding Cs^+ salt is prepared from the ammonium salt by metathesis. The compounds, all of which are white products, have been characterised on the basis of elemental analyses, room temperature magnetic susceptibility measurements, and IR and laser Raman (IR) spectral data. The IR and laser Raman (IR) spectra provide evidence for a distorted octahedral structure of $[\text{TiOF}_4]^{2-}$ ion with -Ti-O-Ti- interactions.

Solid oxo-complexes of Ti(IV) are rather fewer as compared to those of V(IV)¹⁻³. In the case of Ti(IV), $[\text{TiOF}_5]^{3-}$ is the only well characterised⁴ fluoro complex, although existence of $[\text{TiOF}_3]^-$ is also reported⁵. Of some interest is the complex oxotetrafluorotitanate(IV), $[\text{TiOF}_4]^{2-}$. Despite a number of attempts^{6,7}, synthesis of pure $[\text{TiOF}_4]^{2-}$ could not be achieved. In a recent study⁸ involving high temperature thermal decomposition of a peroxo complex $\text{K}_2[\text{Ti}(\text{O}_2)_4]$, $\text{K}_2[\text{TiOF}_4]$ has been obtained as one of the main products. As a sequel to our efforts on some aspects of titanium chemistry^{1,9,10} and also in view of considerable interest on structural assessment of oxotitanates(IV)^{11,12}, we felt it imperative to synthesise the title compounds in pure forms and characterise them by elemental analyses, and IR and laser Raman (IR) spectral data.

Materials and Methods

Reagent grade chemicals were used throughout. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer and laser Raman (IR) spectra on a SPEX Ramalog model 1403 spectrophotometer. 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 count processing system. The spectra were recorded at ambient temperature by holding the samples either in a quartz capillary or in the form of a pressed pellet. Magnetic susceptibility measurements were made at room temperature by Gouy's method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant.

Ammonium oxotetrafluorotitanate(IV), $(\text{NH}_4)_2[\text{TiOF}_4]$

Freshly prepared TiO_2 (lg, 12.5 mmol) was dissolved in 4 *M* sulphuric acid (36 ml) at room temperature to get a clear solution and to this was added a solution of ammonium fluoride (3.25g, 87.83 mmol) in water (10 ml) followed by addition of ethanol with constant stirring until the white product started appearing. The addition of ethanol was discontinued at this stage, the reaction mixture was cooled in an ice-water bath for 45 min until the precipitation was complete, filtered, and the precipitate washed twice with ethanol and finally dried *in vacuo* over conc sulphuric acid, yield 1.8g (82%).

Potassium oxotetrafluorotitanate(IV), $\text{K}_2[\text{TiOF}_4]$

It was prepared as above, except ethanol was not added for precipitation since a white product appeared immediately. The reaction mixture was cooled in an ice-water bath for 15 min and the compound separated by filtration. It was dissolved in warm water (50 ml) which on cooling to room temperature afforded the desired compound which was filtered off, washed twice with ethanol and finally dried *in vacuo* over conc sulphuric acid, yield 1.9g (69.7%).

Cesium oxotetrafluorotitanate(IV), $\text{Cs}_2[\text{TiOF}_4]$

$\text{Cs}_2[\text{TiOF}_4]$ precipitated out spontaneously when solid $(\text{NH}_4)_2[\text{TiOF}_4]$ (2.84 mmol) was added to a clear solution of CsBr (8.52 mmol) dissolved in water (10 ml). The white product obtained was

Table 1 — Analytical Data of Potassium, Cesium and Ammonium Oxotetrafluorotitanates(IV)

Complex	Found (calc), %		
	K or N ^a	Ti ^b	F ^c
K ₂ [TiOF ₄]	35.24 (35.77)	21.89 (22.01)	34.50 (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)

(a) Determined as described earlier (see ref. 14)

(b) Determined after precipitation with cupferron (ref. 13a)

(c) Determined as lead chloride fluoride (ref. 13b)

washed with ethanol and finally dried *in vacuo* over conc sulphuric acid, yield 0.9g (78%).

Results and Discussion

The analytical data of the compounds are given in Table 1. Taking into account two important points, (i) that a number of direct methods^{6,7} failed to provide pure [TiOF₄]²⁻ and (ii) titanyl cation (TiO²⁺) certainly exists^{11,15,16} in solution, it was thought that an indirect route via the prior formation of an oxotitanates(IV) in solution might be appropriate for the synthesis of pure oxotetrafluorotitanates(IV) reported in this study. Thus freshly prepared TiO₂ (obtained by dissolving commercial titanium dioxide in 40% hydrofluoric acid and then treating with aqueous ammonia) was first dissolved in an excess of dil sulphuric acid to produce titanyl sulphates¹⁷, TiO(SO₄), in solution. The clear solution was then treated with alkali fluoride (AF) to produce the desired compound. The role of alkali fluoride was not only to fluorinate the titanyl (TiO²⁺) but also to act as a source of counter alkali metal cation. For the preparation of the ammonium compound addition of ethanol was required to just initiate precipitation owing to high solubility of the ammonium salt. Recrystallisation of K₂[TiOF₄] from water was necessary to remove any coprecipitated K₂SO₄. The method is fairly simple and does not involve hydrofluoric acid. The cesium salt Cs₂[TiOF₄] was prepared by metathesis between (NH₄)₂[TiOF₄] and CsBr. It is evident from the above discussion that fluoride is a better ligand for TiO²⁺ than sulphate. Indeed our endeavours to synthesise mixed ligand fluoro(sulphato)titanates(IV) have not been successful so far.

Potassium, cesium and ammonium oxotetrafluorotitanates(IV) are white solids and are stable when out of contact with water. All the com-

pounds are diamagnetic, in conformity with the view that titanium occurs in its +4 oxidation state (*d*⁰) in these compounds. They are also EPR silent. The IR and laser Raman (IR) spectra of all the compounds are identical except for $\nu(\text{NH}_4^+)$ mode of the ammonium salt. The occurrence of $\nu(\text{Ti-F})$ mode due to coordinated fluoride around 605 cm⁻¹ compares favourably with the literature reports¹⁸⁻²⁰. The appearance of a medium intensity band at ~720 cm⁻¹ may be assigned to $\nu(\text{Ti-O-Ti})$. The absence of $\nu(\text{Ti=O})$ mode at ~980 cm⁻¹ indicates that the oxo group does not occur as a terminal one but is present as a bridging group. The band at ~300 cm⁻¹ in the compounds may be assigned to a Ti-F deformation mode. The bands at 1400 (s), 3045(s) and 3155(m) cm⁻¹ in the IR spectrum of ammonium salt have been attributed to ν_4 , ν_1 and ν_3 modes of NH₄⁺ (ref. 22), respectively.

The laser Raman (IR) spectra of all the three complexes are similar and exhibit a strong signal at ~610 cm⁻¹ assignable to $\nu(\text{Ti-F})$ ²⁰. The spectra also display medium intensity bands at ~650, ~530 and ~435 cm⁻¹ originating from -Ti-O-Ti- interactions which, in accord with the literature¹², have been attributed to $\nu(-\text{Ti-O-Ti-})$.

Thus, the results of IR and laser Raman (IR) spectral data suggest that the metal centre is hexacoordinated through a -Ti-O-Ti- interaction, and the complexes have polymeric distorted octahedral structures.

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