



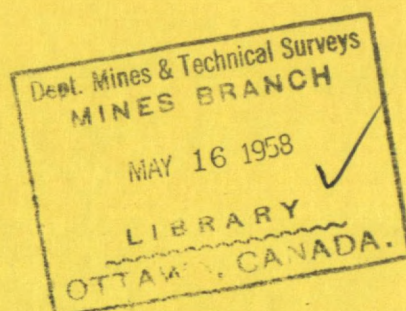
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SOME NEW FLUORIDE COMPLEXES OF  
TRIVALENT TITANIUM

by

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# SOME NEW FLUORIDE COMPLEXES OF TRIVALENT TITANIUM<sup>1</sup>

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## ABSTRACT

Three new complex fluorides of trivalent titanium have been isolated from the products of electrolysis, under an inert atmosphere, of molten baths of KCl, NaCl, or mixtures of KCl and NaCl, containing either  $K_2TiF_6$  or  $Na_2TiF_6$ . Electrolytic baths containing a mixture of KCl and NaCl with either  $K_2TiF_6$  or  $Na_2TiF_6$  yielded a violet-colored, face-centered cubic compound identified as  $K_2NaTiF_6$ , which was virtually insoluble in water and amenable to electrostatic separation from the metallic titanium also produced in the electrolysis. Baths containing molten mixtures of  $K_2TiF_6$  and KCl gave a pale violet compound  $K_3TiF_6$ , which was slightly soluble in water. Baths containing  $Na_2TiF_6$  and NaCl gave a deep violet-colored compound  $Na_3TiF_6$  which was almost insoluble in water. The compounds  $K_3TiF_6$  and  $Na_3TiF_6$  have structures which approximate to cubic. The compounds  $K_2NaTiF_6$  and  $Na_3TiF_6$  are more stable to atmospheric oxidation than is  $K_3TiF_6$ . X-Ray diffraction patterns have been recorded for these compounds and some of their physical and chemical properties determined.

## 1. INTRODUCTION

The mechanism of titanium production by the electrolysis of fused alkali halide baths containing complex titanium salts of the type  $Na_2TiF_6$  or  $K_2TiF_6$  has recently been discussed by Wurm, Gravel, and Potvin (1). In the course of their work, certain products were obtained which yielded X-ray diffraction patterns corresponding to no previously published data. A preliminary notice of the isolation of the compounds giving rise to these patterns appeared in the above-mentioned publication. The present paper represents an amplification of this information and gives details of the X-ray and other data obtained on three new complex titanium fluorides which were isolated from the electrolytic products.

## 2. EXPERIMENTAL PROCEDURES

The alkali titanofluorides, having the formula  $M_2TiF_6$ , based on tetravalent titanium, are readily soluble in molten alkali chlorides in the temperature range 650° C. to 850° C., depending upon the particular compounds involved.

The electrolytic baths contained, at the start of the electrolysis, 20 to 30% of either  $Na_2TiF_6$  or  $K_2TiF_6$  in solution in a molten mixture of NaCl and KCl, having approximately the eutectic composition of 55% KCl, by weight. In certain later electrolyses, solutions of  $Na_2TiF_6$  in NaCl and of  $K_2TiF_6$  in KCl were used to yield products in which only one type of alkali ion was present in each case.

When these molten baths were subjected to electrolysis under an argon atmosphere, using a water-cooled stainless-steel cathode and a graphite crucible containing the melt as anode, the products of the electrolysis, examined after they had cooled and solidified, showed the following phenomena:

(a) Surrounding the cathode was a spherical core or "nut", composed of dendritic metallic titanium crystals embedded in a salt of deep violet color.

(b) Around the outside of this "nut" was the solidified salt bath, having a pale violet color.

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The cathodic "nut" was crushed and separated into its constituents by electrostatic means, yielding the titanium metal and the violet salt substantially free from each other. The crystalline salts were examined by the standard procedures of X-ray diffraction analysis, using  $\text{CoK}_\alpha$  radiation and 57.3 mm. diameter Debye-Scherrer powder cameras. Occasionally, for greater precision in measuring line spacings, a 114.6 mm. diameter camera was used.

The solidified melt surrounding the "nut" was examined similarly, both directly as obtained and also after it was leached with boiling distilled water in the proportion of 2 g. of crushed melt to 25 ml. of water to dissolve the alkali chlorides and concentrate the remaining materials which carry the violet color. Residues of deep violet color, almost insoluble in water, were obtained by this leaching. These residues were analyzed chemically for sodium, potassium, total and trivalent titanium, chloride, and fluoride. Certain reference materials, used for preparing X-ray patterns in attempts to identify the unknown substances, were also analyzed chemically; these included the pure starting titanofluorides,  $\text{Na}_2\text{TiF}_6$  and  $\text{K}_2\text{TiF}_6$ , and sodium titanate. All the chemical analyses referred to in this paper were done in the Chemical Laboratory of the Division of Mineral Dressing and Process Metallurgy, Mines Branch, Ottawa.

A résumé of the analytical procedures used is as follows:

*Potassium and sodium.*—Fluorine removed by evaporation of the sample with dilute sulphuric acid three times; titanium removed by hydrolysis of aqueous solution of product; potassium and sodium determined with a Perkin-Elmer flame photometer.

*Fluorine.*—HF steam-distilled off at 135°–140° C. from an aqueous perchloric acid solution of the sample. Fluorine determined amperometrically at pH = 7.0 using thorium nitrate solution previously standardized against NaF.

*Chlorine.*—Determined by potentiometric titration with 0.05 N  $\text{AgNO}_3$  of a sulphuric/nitric acid solution of the sample. Less than one drop of reagent was required for a 0.2 g. sample, in those cases where chlorine was not expected to be present.

*Titanium (total).*—Residue from fluorine distillation reduced with zinc amalgam and titrated with ferric alum.

*Titanium (trivalent).*—Sample dissolved in aqueous sulphuric acid and titrated with ferric alum, all under an argon atmosphere. Alternatively, sample dissolved in ferric alum solution, and the reduced iron (equivalent to the trivalent titanium) titrated with standard potassium dichromate.

### 3. EXPERIMENTAL RESULTS

A comparison of the X-ray diffraction patterns of a considerable group of electrolytic products, using either  $\text{Na}_2\text{TiF}_6$  or  $\text{K}_2\text{TiF}_6$  as the starting material, in solution in mixed NaCl–KCl, showed that the principal products in all the solidified melt samples were sodium and potassium chlorides, each containing some of the other in solid solution. However, of greater interest was a group of weaker diffractions which was the same regardless of the initial material used. The violet materials, obtained as residues after the alkali chlorides were leached out, gave this same group of diffractions but in much greater strength. The same pattern was obtained from the violet material obtained from the cathodic "nut". In some of the leached products, no other pattern was detectable, and thus, presumably, the material giving rise to this set of diffractions was reasonably pure in these particular products.

The chemical analyses of the insoluble residues resulting from the water leaching of the electrolytic fusion products using  $\text{K}_2\text{TiF}_6$  or  $\text{Na}_2\text{TiF}_6$  with the mixed alkali chlorides are given in Table I. The two analyses obviously correspond to the same substance.

TABLE I

Element	Product using $\text{Na}_2\text{TiF}_6$ as starting material, % by weight	Product using $\text{K}_2\text{TiF}_6$ as starting material, % by weight	Theoretical for $\text{K}_2\text{NaTiF}_6$ , % by weight
Na	$9.5 \pm 0.1$	$9.5 \pm 0.1$	8.74
K	$27.5 \pm 0.1$	$27.4 \pm 0.1$	29.72
Ti (total)	$17.7 \pm 0.25$	(i) $17.7 \pm 0.25$ (ii) $17.6 \pm 0.25$ Mean $17.7 \pm 0.25$	18.21
Ti (trivalent)	$17.7 \pm 0.5$	$17.6 \pm 0.5$	18.21
F	$40.2 \pm 0.25$	$43.1 \pm 0.25$	43.33
Cl	None detectable	None detectable in 50 mg. sample	Nil

It can be seen from these analyses that the molecular formula for either material is very close to  $\text{K}_2\text{NaTiF}_6$ . The theoretical figures for this compound are also given in Table I.

From the chemical data alone, however, the material could equally well be a mixture of  $\text{K}_3\text{TiF}_6$  and  $\text{Na}_3\text{TiF}_6$  in the proportion of approximately 2:1. It therefore remained to determine whether this material (to which has been assigned the formula  $\text{K}_2\text{NaTiF}_6$ ) is, in fact, a discrete compound in its own right, or merely one particular composition in a solid-solution series  $\text{K}_3\text{TiF}_6$ - $\text{Na}_3\text{TiF}_6$ , should such a series exist. The fact that the same composition was obtained using either  $\text{K}_2\text{TiF}_6$  or  $\text{Na}_2\text{TiF}_6$  in molten  $\text{NaCl}$ - $\text{KCl}$  as the starting material strongly supports the view that a single compound was present, rather than merely one particular composition in a solid-solution series. If it were a member of a solid-solution series, one might expect to obtain different compositions in the two cases. The matter was resolved with reasonable certainty by studying the products of electrolyses in which either  $\text{K}^+$  or  $\text{Na}^+$  ions were the sole alkali ions present.

The material obtained from the electrolysis of  $\text{Na}_2\text{TiF}_6$  in  $\text{NaCl}$  was a deep violet in color, virtually insoluble in water, and gave the analysis given in Table II. This analysis corresponds very closely to  $\text{Na}_3\text{TiF}_6$ , and the titanium is all in the trivalent state, in accordance with the color of the material.

TABLE II

Element	% by weight	Theoretical for $\text{Na}_3\text{TiF}_6$
K	None detectable	Nil
Na	$29.9 \pm 0.1$	29.88
Ti (total)	$20.2 \pm 0.25$	20.74
Ti (trivalent)	$20.2 \pm 0.5$	20.74
F	$49.7 \pm 0.25$	49.38
Cl	0.034	Nil

The preparation of the corresponding potassium compound was more troublesome, since the material obtained by leaching out the  $\text{KCl}$  was readily oxidized in air. By evaporation of the water under an argon atmosphere, however, a product was obtained which contained either some unchanged or regenerated  $\text{K}_2\text{TiF}_6$ , a trace of residual  $\text{KCl}$ , and a compound of pale violet color, slightly soluble in water. In the analysis of this material, the chloride present was used as a measure of the  $\text{KCl}$ , the tetravalent titanium (i.e. total titanium minus trivalent titanium) used as a measure of the  $\text{K}_2\text{TiF}_6$  present, and the remainder of the composition calculated accordingly. The results of this analysis are given in Table III.

The molecular formula of the compound calculated on this basis is  $\text{K}_{2.997}\text{TiF}_{5.994}$ .

TABLE III

Element	% by weight
Na	None detected
K	41.6±0.1
F	40.7±0.25
Cl	0.02
Ti (total)	17.1±0.25
Ti (trivalent)	15.4±0.5
Ti (tetravalent)	1.7 (by difference)

i.e.  $K_3TiF_6$ , and the composition of the product then works out at  $K_3TiF_6$ , 90.9%;  $K_2TiF_6$ , 8.4%; KCl, 0.34%.

When this product was examined by microscope, a very small amount of KCl was visible. Approximately 10% of colorless needle-shaped crystals were observed, having one refractive index  $\omega = 1.475$  and the other ( $\epsilon$ ) slightly lower; this is in accord with the known optical properties of  $K_2TiF_6$ . The remaining material, about 90%, had a refractive index of approx. 1.406 and was slightly anisotropic. These proportions are in excellent accord with the above chemical analyses.

The material to which the formula  $K_2NaTiF_6$  has been assigned was strictly isotropic optically and had a refractive index of 1.408. The compounds  $Na_3TiF_6$  and  $K_3TiF_6$  were both slightly birefringent,  $Na_3TiF_6$  having refractive indices of  $\omega = 1.387$  and  $\epsilon = 1.382$ , and  $K_3TiF_6$  having refractive indices of  $\omega = 1.406$  and  $\epsilon =$  slightly lower than 1.406.

The mixed potassium-sodium material gave a face-centered cubic pattern based on a

TABLE IV  
X-RAY POWDER DIFFRACTION PATTERN OF COMPOUND  
 $K_2NaTiF_6$

(hkl)	Mean observed intensity*	Mean observed $d$ -spacing, Å	Calculated† $d$ -spacing, Å
111	35	4.8362	4.8306
002	15	4.1853	4.1835
022	100	2.9519	2.9581
113	7	2.5133	2.5227
222	50	2.4114	2.4153
004	90	2.0871	2.0917
133	3	1.9205	1.9195
024	8	1.8657	1.8709
224	50	1.7042	1.7079
115, 333	15	1.6064	1.6102
044	60	1.4766	1.4791
135	8	1.4088	1.4143
006, 244	5	1.3861	1.3945
026	25	1.3224	1.3229
335	3	1.2825 (?)	1.2759
226	10	1.2597	1.2614
444	25	1.2066	1.2077
117, 155	7	1.1704	1.1716
046	5	1.1571	1.1603
246	40	1.1167	1.1181
137, 355	5	1.0907	1.0893
008	15	1.0449	1.0459
228, 066	25	0.98562	0.98605
048	35	0.93561	0.93545
119, 357	5	0.91824	0.91839

\*Strongest line assessed visually as 100.

†Based on a cubic cell edge of 8.3669 Å.

TABLE V  
X-RAY DIFFRACTION PATTERN OF THE COMPOUND  $\text{Na}_3\text{TiF}_6$

Line No.	Observed intensity*	Observed $d$ -spacing, Å	Line No.	Observed intensity*	Observed $d$ -spacing, Å
1	50	4.646	26	5	1.438
2	20	4.525	27	12	1.415†
3	60	3.976	28	10	1.391
4	8	3.566	29	20	1.357†
5	100	2.837†	30	5	1.313
6	20	2.765	31	5	1.281
7	40	2.496	32	20	1.265
8	40	2.427	33	10	1.249
9	60	2.393	34	10	1.234
10	5	2.330	35	10	1.216
11	30	2.216	36	10	1.193
12	30	2.155	37	5	1.169
13	90	1.999	38	5	1.154
14	10	1.947†	39	5	1.137
15	5	1.854	40	5	1.125
16	27	1.812	41	10	1.112
17	30	1.793	42	10	1.073
18	30	1.769	43	10	1.052
19	10	1.719	44	5	1.038
20	70	1.650	45	5	1.027
21	80	1.618	46	5	0.9906
22	40	1.608	47	5	0.9723
23	8	1.549	48	20	0.9473
24	5	1.500	49	10	0.9385
25	7	1.467	50	20	0.9322

\*Strongest line assessed visually as 100.

†Diffuse.

‡Doublet.

TABLE VI  
X-RAY DIFFRACTION PATTERN OF THE COMPOUND  $\text{K}_3\text{TiF}_6$

Line No.	Observed intensity*	Observed $d$ -spacing, Å	Line No.	Observed intensity*	Observed $d$ -spacing, Å
1	35	4.978	18	7	1.678
2	20	4.355	19	5	1.629
3	40	3.076	20	5	1.544
4	100	3.024	21	30	1.517
5	5	2.761	22	10	1.383
6	5	2.643	23	5	1.340
7	10	2.496	24	5	1.246
8	10	2.403	25	3	1.187
9	5	2.308	26	5	1.169
10	10	2.263	27	3	1.158
11	40	2.186	28	3	1.122
12	17	2.106	29	3	1.031
13	10	1.994	30	3	1.012
14	5	1.902	31	3	0.9982
15	5	1.845	32	3	0.9799
16	40	1.773	33	3	0.9610
17	17	1.741	34	3	0.9504

\*Strongest line assessed visually as 100.

cell edge of 8.3669 Å. The  $d$ -spacings observed, together with the indices of the various reflections and the calculated  $d$ -spacings using the above cell edge, are given in Table IV.

The X-ray spacings for the compound  $\text{Na}_3\text{TiF}_6$  are given in Table V. It can be shown

that the main diffractions conform approximately to a cubic arrangement but that some distortion either of cell edge or of angle has occurred to cause a departure from the true cubic structure. The crystallography was not studied further because no single crystals of this compound of sufficient size were obtained.

Similarly, the compound  $K_3TiF_6$  gave the X-ray diffraction data shown in Table VI. These data also indicate a slight distortion from a cubic structure, though probably not in the same way as for  $Na_3TiF_6$ . Again the crystallography has not been studied further.

#### 4. DISCUSSION

The question to be decided is whether the material to which has been assigned the formula  $K_2NaTiF_6$  should properly be regarded as a compound in its own right, or whether it is merely one particular member in a solid-solution series of which the end members are the compounds  $Na_3TiF_6$  and  $K_3TiF_6$ , if such a solid-solution series in fact exists.

It has been shown that both end members are slightly anisotropic optically, whereas the material containing both potassium and sodium is strictly isotropic. This is strong, though not conclusive, evidence that  $K_2NaTiF_6$  is a definite compound, since certain cases are known in which an optically isotropic member of a solid-solution series exists where neither end member is isotropic. A notable example of this exceptional optical behavior is in the melilite solid-solution series (2); here the end members, akermanite  $2CaO.MgO.2SiO_2$  (3) and gehlenite  $2CaO.Al_2O_3.SiO_2$  (4), are both anisotropic but an intermediate composition of approximately 65% akermanite: 35% gehlenite is isotropic.

If this behavior were applicable in the present instance, then the refractive index of the mixed sodium-potassium material would have to lie between the values given by the two end members,  $Na_3TiF_6$  and  $K_3TiF_6$ . This is not the case, however, as the refractive index of  $K_2NaTiF_6$  is 1.408 whereas the values for  $K_3TiF_6$  are 1.406 and slightly below 1.406, and the values for  $Na_3TiF_6$  are 1.387 and 1.382. In a solid-solution series, it is normal for the refractive index of an intermediate member to approximate to the value obtained by a linear interpolation between the values for the end members. In this case the intermediate material gives a value lying outside the range of values given by the end members; hence this is not analogous to the melilite behavior. This strongly suggests that the material  $K_2NaTiF_6$  is to be considered as a compound and not as a member of a solid-solution series.

This optical evidence is further supported by the X-ray diffraction data, which show that the pattern given by  $K_2NaTiF_6$  can be completely indexed according to a cubic unit cell; by contrast, neither  $K_3TiF_6$  nor  $Na_3TiF_6$  possesses a cubic structure, although both are close to it. Thus, the fact that neither the potassium nor the sodium compound is cubic, whereas the mixed potassium-sodium material is strictly so, is a cogent argument in favor of regarding  $K_2NaTiF_6$  as a true compound. It may be mentioned by way of contrast that in the case of the melilites, referred to above, all members of the series, including the isotropic member, have a tetragonal structure with a  $c/a$  ratio in the range 0.6 to 0.7.

The above arguments support the validity of the contention that  $K_2NaTiF_6$  is a definite compound in its own right. The strongest evidence, however, lies in the fact that the same composition is obtained regardless of whether  $K_2TiF_6$  or  $Na_2TiF_6$  is used as the starting material with the NaCl/KCl eutectic in the electrolytic preparation.

There are, thus, the following arguments in favor of the  $K_2NaTiF_6$  being a definite compound:

- (a) Its isotropic optical behavior, as contrasted with those of  $K_3TiF_6$  and  $Na_3TiF_6$ .
- (b) The value of its refractive index as compared with those of  $K_3TiF_6$  and  $Na_3TiF_6$ .
- (c) Its cubic X-ray pattern.
- (d) The constancy of its chemical composition, irrespective of starting material.

Additional unequivocal evidence could have been provided by conducting liquidus determinations across the system  $K_3TiF_6$ - $K_2NaTiF_6$ - $Na_3TiF_6$ , when, if  $K_2NaTiF_6$  were a true compound, a peak in the liquidus curve would have been obtained at that composition. It would also have been of interest to attempt to prepare the mixed potassium-sodium material from an appropriate mixture of the pure potassium and sodium compounds. However, the small quantities of material available precluded these two lines of investigation from being followed.

It is of interest to note that an exactly analogous series of compounds is known in the complex aluminofluorides, viz.  $K_3AlF_6$ ,  $K_2NaAlF_6$ , and  $Na_3AlF_6$ ; in this series, the mixed potassium-sodium compound is cubic and neither the sodium nor the potassium compound alone is cubic. Thus,  $K_3AlF_6$  (potassium cryolite) is tetragonal with  $c_0 = 8.468 \text{ \AA}$  and  $a_0 = 5.944 \text{ \AA}$  (5);  $K_2NaAlF_6$  (elpasolite) is cubic with  $a_0 = 8.109 \text{ \AA}$  (6); and  $Na_3AlF_6$  (cryolite) is monoclinic (almost orthorhombic, and not far removed from tetragonal) with  $a_0 = 7.80 \text{ \AA}$ ,  $b_0 = 5.61 \text{ \AA}$ ,  $c_0 = 5.46 \text{ \AA}$ , and  $\beta = 90^\circ 11'$  (7).

In addition, many other six-coordinated complexes of transitional elements containing two different alkali elements crystallize in the cubic system. The corresponding compounds containing one alkali element only in many cases either do not exist, or are not very stable, or do not crystallize in the cubic system. This behavior is due to the greater ease of packing three alkali ions of two different sizes (two larger, and one smaller) than of packing three ions of equal size.

The three compounds described in this paper are examples of new complexes in which the titanium is present in the trivalent state. Various compounds have been described in a more or less complete manner from a chemical viewpoint, in which the titanium in the trivalent condition was the starting material, and which were supposed still to contain the titanium in that state. In no case, however, was there any specific analysis for trivalent titanium in the product, but merely for total titanium content. Also, no crystallographic data (either optical or X-ray) have been provided for such compounds. These earlier publications included the following:

(a) Work by Piccini (8) in which compounds designated as  $(NH_4)_3TiF_6$ ,  $K_2TiF_6$ , and  $(NH_4)_2TiF_6$  were produced by the electrolytic reduction of fluotitanates in an aqueous solution of either  $NH_4F$  or  $KF$ . These compounds were in no case obtained in the pure state.

(b) Work by Petersen (9) in which  $(NH_4)_3TiF_6$  was obtained by the cadmium reduction of aqueous  $K_2TiF_6$  in warm hydrochloric acid solution with subsequent addition of  $NH_4F$ .

(c) Work by Stähler and his co-workers (10, 11) in which hydrated complexes of titanium trihalides were produced; these workers also prepared hydrated trivalent sulphates, oxalates, acetates, formates, and thiocyanates. In all cases the titanium was considered as forming part of a coordination complex.

(d) Work by Schumb and Sundström (12) in which ammine complexes of titanium di- and tri-chlorides were prepared.

In a recent patent (13), complexes containing divalent and trivalent titanium are claimed, but they were not isolated nor identified precisely.



Thus, in the present work, three new compounds have been described which are complexes containing trivalent titanium. They have been characterized by chemical analysis, optical data, and X-ray crystallographic study.

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