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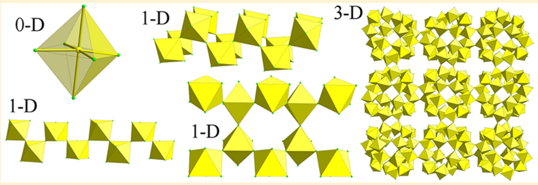
Increasing Structural Dimensionality of Alkali Metal Fluoridotitanates(IV)

Igor M. Shlyapnikov,* Evgeny A. Goreshnik, and Zoran Mazej*

Department of Inorganic Chemistry and Technology, Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia

Supporting Information



ABSTRACT: Reactions between AF (A = Li, Na, K, Rb, Cs) and TiF_4 (with starting $n(AF):n(TiF_4)$ molar ratios in the range from 3:1 to 1:3) in anhydrous hydrogen fluoride yield $[TiF_6]^{2-}$, $[TiF_5]^{-}$, $[Ti_4F_{19}]^{3-}$, $[Ti_2F_9]^{-}$, and $[Ti_6F_{27}]^{3-}$ salts. With the exception of the A_2TiF_6 compounds, which consist of A^+ cations and octahedral $[TiF_6]^{2-}$ anions, all of these materials arise from the condensation of TiF_6 units. The anionic part in the crystal structures of $A[TiF_5]$ (A = K, Cs) and $A[TiF_5]\cdot HF$ (A = Na, K, Rb) is composed of infinite $([TiF_5]^{-})_\infty$ chains built of TiF_6 octahedra sharing joint vertices. Each structure shows a slightly different geometry of the $([TiF_5]^{-})_\infty$ chains. The crystal structure of $Na[Ti_2F_9]\cdot HF$ is constructed from polymeric $([Ti_2F_9]^{-})_\infty$ anions that appear as two parallel infinite zigzag chains comprising TiF_6 units, where each TiF_6 unit of one chain is connected to a TiF_6 unit of the other chain through a shared fluorine vertex. Slow decomposition of single crystals of $K_4[Ti_8F_{36}]\cdot 8HF$ and $Rb_4[Ti_8F_{36}]\cdot 6HF$ (Shlyapnikov, I. M.; et al. *Chem. Commun.* **2013**, *49*, 2703) leads to the formation of $[Ti_2F_9]^{-}$ (Rb) and $[Ti_6F_{27}]^{3-}$ (K, Rb) salts. The former displays the same $([Ti_2F_9]^{-})_\infty$ double chain as in $Na[Ti_2F_9]\cdot HF$, while the anionic part in the latter, $([Ti_6F_{27}]^{3-})_\infty$, represents the first example of a three-dimensional network built of TiF_6 octahedra. The $([Ti_6F_{27}]^{3-})_\infty$ anion was also found in $[H_3O]_3[Ti_6F_{27}]$. The crystal structure determination of $Cs_3[Ti_4F_{19}]$ revealed a new type of polymeric fluoridotitanate(IV) anion, $([Ti_4F_{19}]^{3-})_\infty$. Similar to the $([Ti_2F_9]^{-})_\infty$ anion, it is also built of zigzag double chains comprising TiF_6 units. However, in the former there are fewer connections between TiF_6 units of two neighboring chains than in the latter.

■ INTRODUCTION

In solid titanium tetrafluoride and various ternary titanium(IV) fluorides, the Ti^{4+} cations are always found in octahedral coordination of six fluorine atoms, like cations of the majority of transition metals in a fluoride environment (with exception of heavier transition elements and cations with d^8 and d^9 electron configurations).[1] In crystal structures, such negatively charged MF_6 units are found to be isolated or linked by sharing of one, two, or three fluorine atoms (shared vertices, edges, or faces of octahedra), forming in this way larger discrete oligomeric anions (0-D geometry) or extended infinite polyanions with one- (1-D; chains, columns), two- (2-D; layers), or three-dimensional (3-D network) geometry.

Although the number of theoretically possible combinations of TiF_6 units leading to oligomeric and polymeric fluoridotitanium(IV) anions is infinite, the number of structurally characterized fluoridotitanate(IV) anions to date is limited to 15 species, determined in the crystal structures of about 100 compounds (Table S1).[2,3] Almost three-quarters of the characterized compounds are hexafluoridotitanate(IV) ($[TiF_6]^{2-}$) salts. Other oligomeric fluoridotitanate(IV) anions with 0-D geometry are presented by $[Ti_2F_{10}]^{2-}$,[4,5] $[Ti_2F_{11}]^{3-}$,[6−8] $[Ti_4F_{18}]^{2-}$,[9−11] $[Ti_4F_{19}]^{3-}$,[12] $[Ti_4F_{20}]^{4-}$,[8] $[Ti_5F_{23}]^{3-}$,[8] $[Ti_8F_{36}]^{4-}$,[13] and $[Ti_{10}F_{45}]^{5-}$.[14] Known polymeric fluoridotitanate(IV) anions include five 1-D examples {$([TiF_5]^{-})_\infty$,[14−16] $([Ti_2F_9]^{-})_\infty$,[8,9] $([Ti_3F_{13}]^{-})_\infty$,[14] $([Ti_7F_{30}]^{2-})_\infty$,[17] and $([Ti_9F_{38}]^{2-})_\infty$[18]} and two 2-D examples {two modifications of $([Ti_8F_{33}]^{-})_\infty$ anion[18,19]}.

Reports on fluoridotitanate(IV) salts of alkali metals are limited to well-known A_2TiF_6 (A = Li, Na, K, Rb, Cs) and mixed-cation $Li(NH_4)TiF_6$,[20] $LiCsTiF_6$,[21] $Na_3Li(TiF_6)_2$,[22] NH_4NaTiF_6,[23] $NaRbTiF_6$,[24] and $NaCsTiF_6$[24] compounds with isolated monomeric $[TiF_6]^{2-}$ anions,[25] the mixed-anion compound Na_3HTiF_8 with $[TiF_6]^{2-}$ and $[HF_2]^{-}$ anions,[26] $Cs[Ti_8F_{33}]$ with polymeric $([Ti_8F_{33}]^{-})_\infty$ anions appearing as layers,[19] and recently synthesized $Cs[Ti_2F_9]$,[9] $K_4[Ti_8F_{36}]\cdot 8HF$,[13] and $Rb_4[Ti_8F_{36}]\cdot 6HF$[13] with the infinite polymeric double-chain-like $([Ti_2F_9]^{-})_\infty$ anion and the octameric discrete fluoridotitanate(IV) anion $[Ti_8F_{36}]^{4-}$. The existence of "$Cs_2Ti_2F_{10}$" has been claimed on the basis of its IR and Raman spectra.[27] Concerning their use, studies showed that K_2TiF_6 displays good photocatalytic performance,[28] and a remarkable improvement in the hydrogen storage properties of $NaAlH_4$ upon introduction of K_2TiF_6 as a catalyst precursor has also been also observed.[29]

The possibility of incorporation of HF into a crystal structure by its coordination to metal centers and/or to fluorinated anions is known,[30] and it was recently observed in the alkali metal fluoridotitanate(IV) compounds $K_2(HF)TiF_6$,[31] $K_4[Ti_8F_{36}]\cdot 8HF$,[13] and $Rb_4[Ti_8F_{36}]\cdot 6HF$.[13] In almost all cases,

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HF molecules are coordinated to discrete fluorido anions. The only case of a similar hydrogen-bonding interaction between HF and a polymeric chainlike anion could be found in the compound $(pipzH_2)_4[Mn_2F_9]_2[MnF_4(H_2O)_2][MnF_4(HF)_2]$.[32] In contrast to the examples of hydrogen-bonding interactions between HF and discrete anions, where the position of the HF molecules in the crystal structure is mostly ruled by steric factors during packing of molecules upon crystallization, in this case two HF molecules act as ligands to the MnF_4 unit to fill vacant sites of Mn octahedral coordination, and then the formed $[MnF_4(HF)_2]$ unit is coordinated to the Mn_2F_9 chain via hydrogen bonds.

In the present work, attempts to synthesize and structurally characterize new alkali metal fluoridotitanate(IV) compounds were made by a systematic study of reactions between alkali metal fluorides (AF, A = Li, Na, K, Rb, Cs) and titanium tetrafluoride (TiF_4) in different molar ratios in the medium of anhydrous hydrogen fluoride (aHF). Two different isolation techniques of grown crystals were applied in order to obtain also phases with coordinated HF molecules.

RESULTS AND DISCUSSION

Reactions between AF (A = Li, Na, K, Rb, Cs) and TiF_4 were carried out in aHF at ambient temperature (Table S2). A few experiments were also done in the aprotic solvents SO_2 and CH_2Cl_2. The main varied parameter was the starting molar ratio between reactants, which ranged from $n(AF):n(TiF_4)$ = 3:1 to $n(AF):n(TiF_4)$ = 1:3. Attempts both to synthesize compounds in larger amounts (so-called bulk) and to grow single crystals from nAF/TiF_4 solutions (or from preliminarily synthesized bulk) were made. Grown crystals were isolated in two different ways: by complete drying under dynamic vacuum or by isolation from the mother liquor.

Reaction Products Obtained Using an $n(AF):n(TiF_4)$ = 3:1 Starting Ratio. Since $Na_3(HF_2)(TiF_6)$ (Na_3HTiF_8)[26] is known, the attempt was made to prepare the analogous potassium compound. Instead of the desired $K_3(HF_2)(TiF_6)$, only a few single crystals of $K_2(HF)TiF_6$[31] were grown from an $n(KF):n(TiF_4)$ = 3:1 aHF solution. Vibrational bands that could be assigned to KHF_2 were also detected in the crystallization product by Raman spectroscopy.

Reaction Products Obtained Using an $n(AF):n(TiF_4)$ = 2:1 Starting Ratio. As expected, chemical reactions between alkali metal fluorides AF and TiF_4 with a starting molar ratio $n(AF):n(TiF_4)$ = 2:1 in superacidic aHF yielded well-known A_2TiF_6 compounds (eq 1):

$$2AF + TiF_4 \rightarrow A_2TiF_6 \qquad (A = Li, Na, K, Rb, Cs) \tag{1}$$

Further crystallization of the synthesized hexafluoridotitanate(IV) salts led to single crystals of the corresponding A_2TiF_6 phases and in the potassium case to the previously known solvated $K_2TiF_6{\cdot}HF$ phase.[31] Attempts to isolate the $A_2TiF_6{\cdot}n$HF (A = Li, Na, Rb, Cs) compounds with coordinated HF molecules failed. Only A_2TiF_6 phases were obtained, as shown by Raman spectroscopy and X-ray diffraction analysis of grown crystals.

Reaction Products Obtained Using an $n(AF):n(TiF_4)$ = 1.5:1 Starting Ratio. The attempt to prepare single crystals of the unknown compounds $A_3[Ti_2F_{11}]$ (A = Na, K) from AF/TiF_4/aHF solution [$n(AF):n(TiF_4)$ = 1.5:1] failed. After crystallization, only single crystals of $K_2TiF_6{\cdot}HF$[31] and $K[TiF_5]{\cdot}HF$ (using KF) and Na_2TiF_6 and $Na[TiF_5]{\cdot}HF$ (using NaF) were observed. Attempts to synthesize $A_3[Ti_2F_{11}]$ (A = Rb, Cs) were also unsuccessful. Mixtures of $A[TiF_5]$ and A_2TiF_6 were obtained, as shown by Raman spectroscopy (Figure S1).

Reaction Products Obtained Using an $n(AF):n(TiF_4)$ = 1:1 Starting Ratio. In this work, salts of Na, K, Rb and Cs with polymeric $([TiF_5]^-)_\infty$ anions were synthesized for the first time by carrying out chemical reactions between the corresponding alkali metal fluorides and TiF_4 with the starting molar ratio $n(AF):n(TiF_4)$ = 1:1 in aHF (eq 2):

$$AF + TiF_4 \rightarrow A[TiF_5] \qquad (A = Na, K, Rb, Cs) \tag{2}$$

As shown by the preparation of $K[TiF_5]$, this type of compound can be also prepared using SO_2 or CH_2Cl_2 as the solvent (Figure S2). Attempts to synthesize $Li[TiF_5]$ in a similar manner were unsuccessful. A mixture of Li_2TiF_6 and unreacted TiF_4 was always formed, as shown by Raman spectroscopy.

The formation of $A[TiF_5]$ phases was proved by Raman spectroscopy and chemical analyses (for $Na[TiF_5]$, $\omega(Ti)$ = 28.2% and $\omega(F)$ = 56.5%, corresponding to $n(Ti):n(F)$ = 1:5.1; for $KTiF_5$, $\omega(Ti)$ = 27.0% and $\omega(F)$ = 51.3%, corresponding to $n(Ti):n(F)$ = 1:4.8; for $Rb[TiF_5]$, $\omega(Ti)$ = 21.3% and $\omega(F)$ = 41.2%, corresponding to $n(Ti):n(F)$ = 1:4.9).

Crystals of solvated phases $A[TiF_5]{\cdot}HF$ (Na, K, Rb) were formed during crystallization from aHF solutions. They were found to be stable only in the mother liquor. Further drying under dynamic vacuum led to their decomposition with the formation of $A[TiF_5]$ phases. Single crystals of $Cs[TiF_5]{\cdot}n$HF have never been observed. The Raman spectra recorded on grown crystals still covered with the mother liquor corresponded only to $CsTiF_5$.

Reaction Products Obtained Using an $n(AF):n(TiF_4)$ = 1:1.33 (3:4) Starting Ratio. An attempt to prepare pure $Cs_3[Ti_4F_{19}]$ by the reaction between CsF and TiF_4 in aHF with the starting molar ratio $n(CsF):n(TiF_4)$ = 3:4 resulted in a mixture of $Cs[TiF_5]$, $Cs_3[Ti_4F_{19}]$, and $Cs[Ti_2F_9]$, as shown by Raman spectroscopy (Figure S3).

Reaction Products Obtained Using an $n(AF):n(TiF_4)$ = 1:1.5 Starting Ratio. An attempt to prepare single crystals of the unknown compounds $A_2[Ti_3F_{14}]$ (A = K, Cs) using the starting molar ratio $n(AF):n(TiF_4)$ = 1:1.5 also failed. For A = Cs, only a few single crystals of $Cs[TiF_5]$ were found between powdered material of unknown composition, while for A = K, cube-shaped crystals of the $[Ti_6F_{27}]^{3-}$ salt were grown.

Reaction Products Obtained Using an $n(AF):n(TiF_4)$ = 1:2 Starting Ratio. Carrying out chemical reactions and crystallizations between AF (A = Li–Cs) and TiF_4 with a starting molar ratio $n(AF):n(TiF_4)$ = 1:2 in aHF unexpectedly revealed several complicated solid-state structures of grown crystals.

The chemical reaction between AF (A = Na, Cs) and TiF_4 with the starting molar ratio $n(AF):n(TiF_4)$ = 1:2 afforded white powdered $Na[Ti_2F_9]$ (chemical analysis: $\omega(Ti)$ = 31.83% and $\omega(F)$ = 57.33%, corresponding to $n(Ti):n(F)$ = 2:9.1) and previously known $Cs[Ti_2F_9]$[9] (eq 3):

$$AF + 2TiF_4 \rightarrow A[Ti_2F_9] \qquad (A = Na, Cs) \tag{3}$$

As in the case of $Li[TiF_5]$, there was no indication of $Li[Ti_2F_9]$ formation. Only single crystals of Li_2TiF_6 were observed upon crystallization of LiF/2TiF_4 from aHF solution.

The attempt to crystallize $Na[Ti_2F_9]$ in aHF resulted in single crystals of the solvated compound $Na[Ti_2F_9]{\cdot}HF$, while the crystallization of $Cs[Ti_2F_9]$ from aHF yielded only single

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Table 1. Crystal Data and Refinement Results for $A_2[TiF_6]$, $A[TiF_5]$, $A[TiF_5]\cdot HF$, $A_3[Ti_4F_{19}]$, $A[Ti_2F_9]$, $A[Ti_2F_9]\cdot HF$, and $A_3[Ti_6F_{27}]$ Compounds

	Li_2TiF_6	Rb_2TiF_6	$K[TiF_5]$	$Cs[TiF_5]$	$Na[TiF_5]\cdot HF$
formula weight (g/mol)	175.74	332.84	181.97	275.78	185.87
crystal system	tetragonal	trigonal	monoclinic	orthorhombic	monoclinic
space group	$P4_2/mnm$	$P\bar{3}m1$	$C2/c$	$Pnam$	$C/2c$
a (Å)	4.6332(5)	5.9051(5)	20.277(3)	5.3986(2)	15.1768(9)
b (Å)	4.6332(5)	5.9051(5)	6.1768(8)	14.0057(5)	6.4171(3)
c (Å)	8.930(1)	4.7780(5)	14.380(2)	6.4536(3)	10.8580(7)
α (deg)	90	90	90	90	90
β (deg)	90	90	110.960(9)	90	108.266(2)
γ (deg)	90	120	90	90	90
V (Å^3)	191.70(4)	144.29(2)	1681.9(4)	487.97(3)	1004.2(1)
Z	2	1	16	4	8
T (K)	200	200	133	150	200
R_1[a]	0.026	0.034	0.055	0.023	0.042
wR_2[b]	0.071	0.101	0.147	0.056	0.120

	$K[TiF_5]\cdot HF$	$Rb[TiF_5]\cdot HF$	$Rb[Ti_2F_9]$	$Na[Ti_2F_9]\cdot HF$	$Cs_3[Ti_4F_{19}]$
formula weight (g/mol)	201.98	248.35	352.21	309.80	951.21
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$C2/c$	$C2/c$	$P2_1/c$	$Pnma$	$Cmcm$
a (Å)	13.671(2)	13.823(6)	15.0380(7)	5.3084(3)	5.3999(4)
b (Å)	8.1382(6)	8.295(3)	5.3244(3)	10.0736(6)	15.2661(12)
c (Å)	10.061(1)	10.264(5)	18.531(1)	13.8566(8)	21.4921(15)
α (deg)	90	90	90	90	90
β (deg)	114.217(4)	114.35(2)	93.788(5)	90	90
γ (deg)	90	90	90	90	90
V (Å^3)	1020.9(2)	1072.1(8)	1480.5(1)	740.98(7)	1771.7(2)
Z	8	8	8	4	4
T (K)	200	150	157	200	150
R_1[a]	0.055	0.049	0.028	0.042	0.028
wR_2[b]	0.156	0.151	0.067	0.097	0.063

	$K[Ti_6F_{27}]$	$Rb[Ti_6F_{27}]$	$[H_3O]_3[Ti_6F_{27}]$
crystal system	cubic	cubic	cubic
space group	–	–	$Pn\bar{3}n$
a (Å)	17.1353(4)	17.2937(4)	17.2014(9)
V (Å^3)	5030.98	5172.1(3)	5089.7(8)
Z	–	–	8
T (K)	200	150	150
R_1[a]	–	–	0.056
wR_2[b]	–	–	0.122

[a] R_1 is defined as $\sum||F_o| - |F_c||/\sum|F_o|$ for $I > 2\sigma(I)$. [b] wR_2 is defined as $\{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

crystals of the latter[9] with no indications of $Cs[Ti_2F_9]\cdot n$HF phases.

During the investigation of the AF/2TiF$_4$/aHF (A = K, Rb) system, it was found that slow crystallization of the AF/2TiF$_4$ mixture (A = K, Rb) dissolved in aHF resulted in single-crystal growth of $K_4[Ti_8F_{36}]\cdot 8HF$ and $Rb_4[Ti_8F_{36}]\cdot 6HF$.[13] Their crystal structure determination revealed that both structures contain discrete octameric $[Ti_8F_{36}]^{4-}$ anions constructed from eight TiF$_6$ octahedral units connected into a cube.[13] Those crystals are stable only in the mother liquor. With time both compounds release HF and decompose. For both K and Rb, the final products were cube-shaped crystals ($a \approx 17$ Å; Table 1) containing $([Ti_6F_{27}]^{3-})_\infty$ anions (Figure S4), and for rubidium a second—major—phase, $Rb[Ti_2F_9]$, was also found (Figure S5).

According to Raman spectra, the chemical reaction between AF (A = K, Rb) and 2TiF$_4$ in aHF resulted in a mixture of various phases containing anions such as $[TiF_5]^-$, $[Ti_2F_9]^-$, $[Ti_6F_{27}]^{3-}$, $[Ti_8F_{36}]^{4-}$, etc. In the last three phases, the n(AF):n(TiF$_4$) ratio corresponds to 1:2.

During the crystallization process, aHF is slowly removed (over a few days or sometimes even months) from a saturated solution. The grown single crystals are isolated either by quick removal of the volatiles or by addition of perfluorinated oil onto them when the mother liquor is still present. The second method prevents or slows the release of bound HF. In the attempts to synthesize bulk quantities, all of the volatiles are quickly removed (in a few minutes to a few hours) on a vacuum system after the reactions seem to be completed.

Reaction Products Obtained Using an n(AF):n(TiF$_4$) = 1:3 Starting Ratio. Further attempts to prepare $A[Ti_3F_{13}]$ compounds with larger amounts of TiF$_4$ than in $A[Ti_2F_9]$ failed. The products of reactions with the starting molar ratio n(AF):n(TiF$_4$) = 1:3 in different solvents (HF, SO$_2$, CH$_2$Cl$_2$) were mixtures of various phases (TiF$_4$, $A[TiF_5]$, $A_3[Ti_4F_{19}]$, $A[Ti_2F_9]$, $[Ti_6F_{27}]^{3-}$ salts, etc.) as shown by Raman spectra of the recovered bulk products and X-ray diffraction analysis of

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the grown crystals. Although $Cs[Ti_8F_{33}]$[19] has been reported ($n(AF):n(TiF_4)$ = 1:8), $A[Ti_2F_9]$, $K_4[Ti_8F_{36}]\cdot 8HF$, and $Rb_4[Ti_8F_{36}]\cdot 6HF$[13] with $n(AF):n(TiF_4)$ = 1:2 represent the limit with the largest amount of TiF_4 when AF/TiF_4 reactions proceed in liquid aHF, SO_2, or CH_2Cl_2. Single crystals of $Cs[Ti_8F_{33}]$ were grown unintentionally as a byproduct during the high-temperature (300 °C) synthesis of TiF_4.[19] The presence of Cs was explained by impurities in the autoclave used.

Crystal Structures of $A_2[TiF_6]$, $A[TiF_5]$, $A[TiF_5]\cdot HF$, $A_3[Ti_4F_{19}]$, $A[Ti_2F_9]$, $A[Ti_2F_9]\cdot HF$, and $A_3[Ti_6F_{27}]$ Compounds. The corresponding crystal data and refinement results are summarized in Table 1.

Crystal Structures Containing Monomeric $[TiF_6]^{2-}$ Anions. In the solid state, all alkali metal hexafluoridotitanate(IV) phases consist of alkali metal cations and octahedral $[TiF_6]^{2-}$ anions.[25] In this section, the crystal structures of A_2TiF_6 (A = Li, Rb) determined on single crystals during this study are reported.

Li_2TiF_6. Lithium hexafluoridotitanate(IV) is known to crystallize in the tetragonal crystal system belonging to the trirutile structural type.[33,34] The single-crystal structure determined at 200 K is in agreement with the structure determined from powder data.[33,34] Li_2TiF_6 crystallizes in space group $P4_2/mnm$ with two formula units per unit cell (Figure 1).

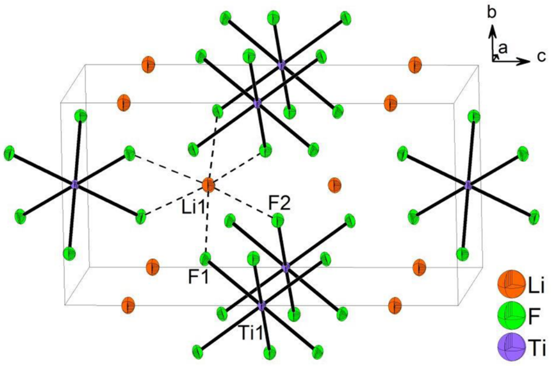

Figure 1. Crystal structure of Li_2TiF_6. Thermal ellipsoids are drawn at the 50% probability level.

The asymmetric unit of the crystal structure is composed of four atoms: one titanium atom, two fluorine atoms, and one lithium atom. The $[TiF_6]^{2-}$ anion is a symmetry-generated octahedral species with four Ti−F1 and two Ti−F2 bond lengths equal to 1.864(1) and 1.872(2) Å, respectively. Each F atom is bound to one Ti atom and coordinated to two Li atoms. Lithium atoms are octahedrally coordinated by six fluorine atoms with Li···F distances ranging from 2.008(5) to 2.090(6) Å, resulting in a bond valence sum (∑BV) of 0.970 for Li atoms (Table S3). Two fluorine atoms coordinated to lithium belong to the same $[TiF_6]^{2-}$ anion and the other four fluorine atoms to four other anions, so each lithium atom is coordinated to five $[TiF_6]^{2-}$ anions (Figure 1).

Rb_2TiF_6. Rubidium hexafluoridotitanate(IV) crystallizes in three structural types (trigonal K_2GeF_6 type, hexagonal K_2MnF_6 type, and cubic K_2PtCl_6 type),[25] but no data concerning its single-crystal structure could be found in the literature. Single-crystal structure determination of Rb_2TiF_6 showed that at 200 K it crystallizes in space group $P\bar{3}m1$ with one formula unit per unit cell and is isostructural with trigonal modifications of K_2TiF_6 and Cs_2TiF_6 (Figure 2). The $[TiF_6]^{2-}$ anion is an octahedral species with all of the Ti−F bond lengths equal to 1.864(4) Å. Each Rb atom is coordinated by 12 fluorine atoms with Rb···F distances ranging from 2.946(4) to 3.112(4) Å, resulting in ∑BV = 0.982 for the Rb atoms (Table S3). Three of the fluorine atoms coordinated to rubidium belong to three different $[TiF_6]^{2-}$ anions, while the other nine are equally divided among three other $[TiF_6]^{2-}$ anions.

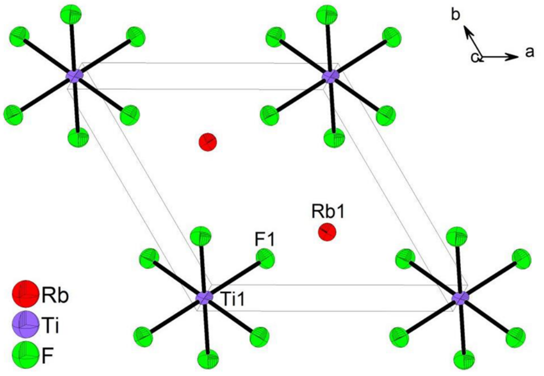

Figure 2. Crystal structure of Rb_2TiF_6. Thermal ellipsoids are drawn at the 50% probability level.

Crystal Structures Containing $([TiF_5]^-)_\infty$ Chainlike Anions. Until now, there have not been any reports about compounds with an $A^+:Ti^{4+}$ molar ratio equal to 1:1 (A = alkali metal). Nevertheless, two compounds with cations of similar size, namely, $[H_3O][TiF_5]$[15] and $[NH_4][TiF_5]$,[16] have been described. Both crystal structures, determined at room temperature, contain infinite polymeric $([TiF_5]^-)_\infty$ anions, appearing as zigzag single chains of TiF_6 octahedra, linked by cis vertices. In spite of the same motif of TiF_5 chain construction, their conformations are different (Figure S6). That in $[H_3O][TiF_5]$ has considerably higher symmetry. There is the only one crystallographically independent titanium atom in its structure, and all of the Ti atoms are situated in the same plane, whereas the TiF_5 chains in $[NH_4][TiF_5]$ are constructed from four independent Ti atoms, so the octahedra in the chains are tilted and the chains are much more irregular. An anion of similar geometry but with a higher rate of irregularity (Figure S6) has been recently determined in the crystal structure of $[XeF_5][TiF_5]$.[14]

$Na[TiF_5]\cdot HF$. Sodium pentafluoridotitanate crystallizes from aHF solution as $Na[TiF_5]\cdot HF$. The compound is constructed from anionic $([TiF_5]^-)_\infty$ infinite single chains, Na^+ cations, and coordinated HF molecules. The zigzag $[TiF_5]$ chains consist of TiF_6 octahedra that share cis vertices. There is one crystallographically independent titanium atom coordinated by six crystallographically unique fluorine atoms, forming slightly distorted TiF_6 octahedra. The $Ti-F_t$ bonds between titanium atoms (Ti) and terminal fluorine atoms (F_t) have lengths ranging from 1.769(2) to 1.888(2) Å and are shorter than the bonds between Ti and bridging fluorine atoms (F_b), which have lengths of 1.965(1) Å for Ti−F3 and 2.009(1) Å for Ti−F7.

Each TiF_6 unit is connected to two adjacent units via F3 and F7 fluorine atoms, which are at cis positions of a single octahedron and are situated on special positions. The observed Ti1−F3−Ti1 and Ti1−F7−Ti1 angles are 180.0° and

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154.5(2)°, respectively. Thus, formed $([TiF_5]^-)_\infty$ zigzag chains are almost planar and oriented along the *c* axis (Figure 3).

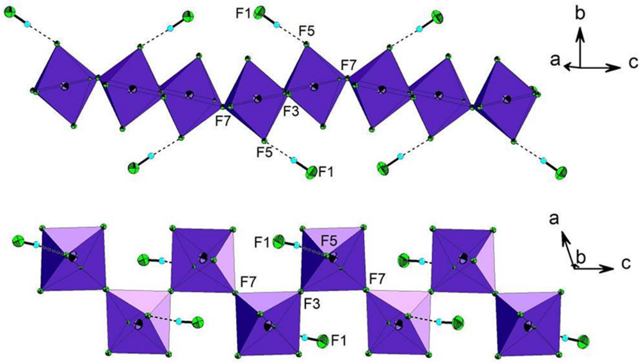

Figure 3. Geometry of $([TiF_5]^-)_\infty$ anions in $Na[TiF_5]\cdot HF$ and hydrogen bonding between HF molecules and the polymeric anions.

Hydrogen bonding between HF molecules and $([TiF_5]^-)_\infty$ anions represents the first example of HF interactions with the infinite polymeric anionic species. HF molecules interact with TiF_5 chains by hydrogen bonds in such a way that each TiF_6 octahedron has one interaction with one HF molecule, wherein (Ti−)F5···(H−)F1 distances are 2.478(3) Å, which allows the hydrogen bonds to be considered as strong.[35] Moreover, all of the HF molecules are orientated so that they are situated above vacant cites of the zigzag chain (Figure 3).

The zigzag TiF_5 chains are closely packed in the crystal structure, forming a distorted hexagonal array (Figure S7). Between the chains there are two crystallographically independent Na^+ cations, occupying sites with different surroundings (Figure 4). $Na1^+$ cations occupy vacancies with heptacoordination situated between two parallel planar chains, translated straight along the *b* axis, while the other vacancies, situated between neighboring chains along the *a* axis, have hexacoordination and are occupied by $Na2^+$ cations. Each type of Na^+ cation is coordinated by two HF molecules, with Na1··· F1(H) distances of 2.396(2) Å and Na2···F1(H) distances of 2.392(2) Å, so each HF molecule forms two contacts with two Na^+ cations, linking the cations into virtual chains, and hydrogen-bonds to the polymeric $([TiF_5]^-)_\infty$ anion. Other Na···F distances are in the range 2.207(2)−2.523(3) Å, leading to ∑BV = 0.9598 for Na1 and 1.0300 for Na2.

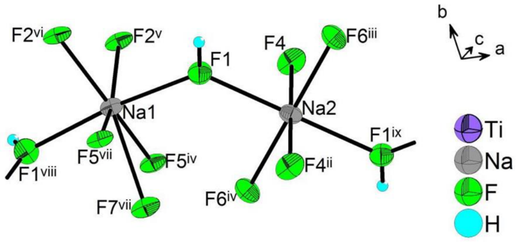

Figure 4. Coordination of Na^+ cations by fluorine atoms belonging to $([TiF_5]^-)_\infty$ anions and HF molecules in the crystal structure of $Na[TiF_5]\cdot HF$. Symmetry codes: (ii) 1.5 − *x*, 0.5 − *y*, 1 − *z*; (iii) *x*, 1 − *y*, 0.5 + *z*; (iv) 1.5 − *x*, −0.5 + *y*, 0.5 − *z*; (v) 1.5 − *x*, 0.5 + *y*, 0.5 − *z*; (vi) −0.5 + *x*, 0.5 + *y*, *z*; (vii) −0.5 + *x*, −0.5 + *y*, *z*; (viii) 1 − *x*, *y*, 0.5 − *z*; (ix) 1.5 − *x*, 0.5 − *y*, 1 − *z*.

$K[TiF_5]\cdot HF$, $Rb[TiF_5]\cdot HF$, and $K[TiF_5]$. Potassium and rubidium pentafluoridotitanates(IV) crystallize from HF solutions as the solvates $K[TiF_5]\cdot HF$ and $Rb[TiF_5]\cdot HF$, and further removal of volatiles in dynamic vacuum leads to release of HF, i.e., to $K[TiF_5]$ and $Rb[TiF_5]$.

The crystal structures of $K[TiF_5]\cdot HF$ and $Rb[TiF_5]\cdot HF$ are isotypic (Table 1). The anionic parts are $[TiF_5]^-$ zigzag single chains made of TiF_6 octahedra connected via cis vertices. The main building units of the anionic chains, the TiF_6 octahedra, which are constructed from one crystallographically independent titanium atom that is coordinated by six crystallographically unique fluorine atoms, are slightly distorted. The lengths of the bonds between Ti and F_t atoms are in the ranges 1.795(3)−1.859(3) Å for $K[TiF_5]\cdot HF$ and 1.791(4)−1.862(4) Å for $Rb[TiF_5]\cdot HF$. The longest Ti−F bonds are those between the Ti atom and the F_b atoms that bridge two octahedra (1.9605(7) and 1.9630(14) Å in $KTiF_5\cdot HF$ and 1.9639(12) and 1.968(2) Å in $Rb[TiF_5]\cdot HF$).

Contrary to the planar chains of $([TiF_5]^-)_\infty$ anions, as described for $[H_3O][TiF_5]$,[15] and the almost planar chains in the crystal structures of $[NH_4][TiF_5]$[16] and $Na[TiF_5]\cdot HF$, those in $K[TiF_5]\cdot HF$ and $Rb[TiF_5]\cdot HF$ have a considerably different conformation (Figure 5). Each TiF_6 octahedron is connected with two adjacent TiF_6 units via bridging F1 and F6 fluorine atoms, which are at cis positions of the single octahedron. The observed Ti1−F1−Ti1 angles are 180.0° for both the potassium and rubidium salts, while the Ti1−F6−Ti1 angles are 148.5(2)° and 147.2(3)° for $K[TiF_5]\cdot HF$ and $Rb[TiF_5]\cdot HF$, respectively.

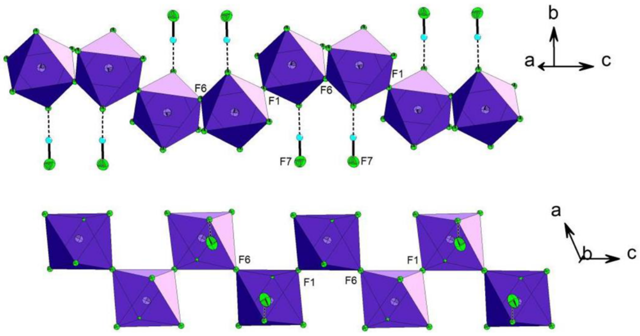

Figure 5. Structure of the $([TiF_5]^-)_\infty$ anions in $Rb[TiF_5]\cdot HF$ and hydrogen bonding between HF molecules and polymeric anions (a similar structure and coordination motif are found in $K[TiF_5]\cdot HF$).

HF molecules form strong hydrogen bonds with polymeric anions with the same motif, as in $Na[TiF_5]\cdot HF$, but with a different orientation, namely, each TiF_6 octahedron interacts with one HF molecule, which is oriented along the *b* axis perpendicular to the middle plane of the chain. The (Ti−)F4··· (H−)F7 distances are 2.471(5) and 2.451(6) Å in the potassium and rubidium salts, respectively.

The alkali metal cations in the crystal structures of $A[TiF_5]\cdot HF$ (A = K, Rb) also have very similar coordination. There is only one crystallographically independent A^+ cation in the crystal structure of $A[TiF_5]\cdot HF$. It is coordinated by nine fluorine atoms with K···F [Rb···F1] distances ranging from 2.696(3) to 3.020(4) Å [2.792(4) to 3.167(4) Å], resulting in ∑BV = 0.893 for K^+ [∑BV = 0.853 for Rb^+]. Each K^+ [Rb^+] cation is coordinated by two HF molecules, with K1···F7 [Rb1···F7] distances equal to 2.735(4) and 2.905(4) Å [2.845(4) and 2.950(5) Å]. Similar to the $Na[TiF_5]\cdot HF$ compound, A^+ cations are linked to chains via HF molecules (Figure 6).

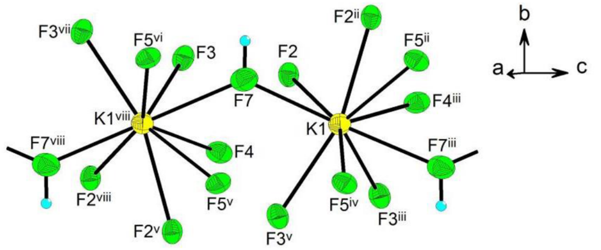

Figure 6. Coordination of K^+ cations by fluorine atoms belonging to $([TiF_5]^-)_\infty$ anions and by HF molecules in the crystal structure of $K[TiF_5]\cdot HF$. Symmetry codes: (ii) $0.5 - x, 0.5 - y, 1 - z$; (iii) $x, -y, 0.5 + z$; (iv) $-0.5 + x, -0.5 + y, z$; (v) $0.5 - x, -0.5 + y, 0.5 - z$; (vi) $-0.5 + x, 0.5 - y, -0.5 + z$; (vii) $0.5 - x, 0.5 - y, -z$; (viii) $x, -y, -0.5 + z$.

The zigzag $([TiF_5]^-)_\infty$ chains are closely packed in the crystal structures of $K[TiF_5]\cdot HF$ and $Rb[TiF_5]\cdot HF$, forming a slightly distorted hexagonal arrangement. The packing of anions, cations, and HF molecules is presented in Figure S8.

Crystals of $A[TiF_5]\cdot HF$ (A = K, Rb) rapidly lose HF in an air-free environment at 25 °C. They are stable at ambient temperature only in the mother liquor. Continuous removal of volatiles from $A[TiF_5]\cdot HF$ leads to the formation of $A[TiF_5]$ phases. In only one of the several repeated crystallizations, a few single crystals of $KTiF_5$ were also grown (Table 1). Its crystal structure consists of $([TiF_5]^-)_\infty$ zigzag single chains, similar to those determined in the crystal structure of $[NH_4][TiF_5]$. There are two crystallographically independent Ti ions in the structure of the discussed compound. All of the positions of fluorine atoms bound to Ti1 are split, resulting in two orientations of TiF_6 octahedra tilted with respect to each other by about 15°. Three F atoms coordinated to Ti2 are also split (Figure 7).

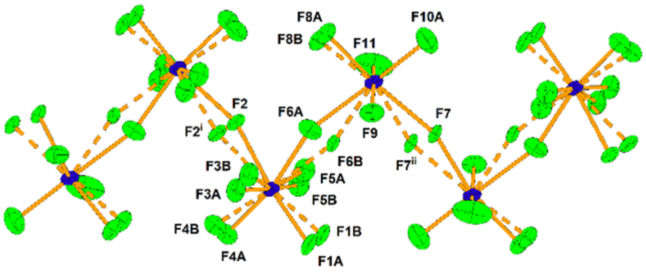

Figure 7. Part of the $([TiF_5]^-)_\infty$ chain in the crystal structure of $K[TiF_5]$. Thermal ellipsoids are drawn at the 50% probability level.

$Cs[TiF_5]$. Cesium pentafluoridotitanate crystallizes from saturated HF solution in an orthorhombic unit cell with four formula units per cell. Its crystal structure contains infinite $([TiF_5]^-)_\infty$ single chains of corner-sharing TiF_6 octahedra (Figure 8) and cesium cations. The $([TiF_5]^-)_\infty$ chains are more symmetric than all of the previously described compounds containing such chains, i.e., $[H_3O][TiF_5]$,[15] $[NH_4][TiF_5]$,[16] $Na[TiF_5]\cdot HF$, $K[TiF_5]\cdot HF$, $Rb[TiF_5]\cdot HF$, $K[TiF_5]$, and $[XeF_5][TiF_5]$.[14] Each TiF_6 unit is made of one crystallographically independent titanium atom situated on a mirror plane and coordinated by six fluorine atoms, four of which are crystallographically independent. All of the positions of terminal fluorine atoms are split, showing orientational disordering of TiF_6 octahedra. This results in two orientations of $([TiF_5]^-)_\infty$ chains that are slightly tilted with respect to each other. Such disorder is understandable taking into account the large ionic radius of Cs^+ ions and the presence of a lot of space between cesium centers. The formed TiF_6 octahedra lie in the same plane and are slightly distorted. The observed $Ti{-}F_t$ bond lengths between titanium atoms and terminal fluorine atoms range from 1.687(11) to 1.904(6) Å and are shorter than bonds between the Ti and bridging fluorine atoms (1.972(2) and 1.982(2) Å).

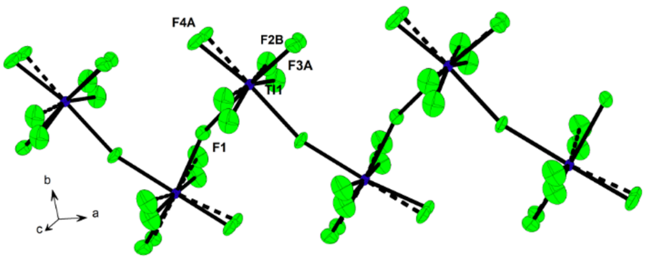

Figure 8. Structure of the $([TiF_5]^-)_\infty$ anions in $Cs[TiF_5]$.

The anions in the crystal structure of $Cs[TiF_5]$ are closely packed, forming a hexagonal array (Figure S9).

Crystal Structures Containing $([Ti_2F_9]^-)_\infty$ Double-Chain-like Anions. The $([Ti_2F_9]^-)_\infty$ perfluoridotitanate anions in the form of zigzag double chains made of TiF_6 octahedra were previously determined in the crystal structures of $Cs[Ti_2F_9]$[9] and $[H_3O][Ti_2F_9]$[9] and in the recently characterized α and β phases of the imidazolium nonafluoridodititanate(IV) compound $[C_3H_5N_2][Ti_2F_9]$ ($[ImH][Ti_2F_9]$).[8] Each TiF_6 octahedron shares fluorine atoms at *fac* positions with three neighboring octahedra, forming $([Ti_2F_9]^-)_\infty$ double chains of cis-connected octahedra. The conformations of the anions in $[H_3O][Ti_2F_9]$, $Cs[Ti_2F_9]$, and $[ImH][Ti_2F_9]$ differ (Figure S10). In the case of the cesium salt, the TiF_6 octahedra belonging to the one individual chain are slightly rotated in view of another chain, while in the $[H_3O]^+$ salt those octahedra are eclipsed. The $Ti{-}F_b{-}Ti$ angles within the single zigzag chain are 166.4(2)°, 156.3(4)°, and 149.54(8)°/152.1(1)° for $[H_3O][Ti_2F_9]$, $Cs[Ti_2F_9]$, and α-/β-$[ImH][Ti_2F_9]$, respectively. The $Ti{-}F_b{-}Ti$ angles between the two single chains forming the double chain are 143.7(2)°, 149.3(6)°, and 162.27(8)°/163.1(2)° for the $[H_3O]^+$, Cs^+, and α-/β-$[ImH]^+$ salts, respectively.

$Na[Ti_2F_9]\cdot HF$. Sodium nonafluoridodititanate(IV) crystallizes from saturated HF solution as the solvate $Na[Ti_2F_9]\cdot HF$. The anionic part of the crystal structure of $Na[Ti_2F_9]\cdot HF$ is similar to those determined in $[H_3O][Ti_2F_9]$, $Cs[Ti_2F_9]$, and α-/β-$[ImH][Ti_2F_9]$, i.e., zigzag $([Ti_2F_9]^-)_\infty$ double chains (Figure 9). The asymmetric unit of the anion consists of six atoms: one Ti atom and five F atoms. The $Ti{-}F_b$ bond lengths between

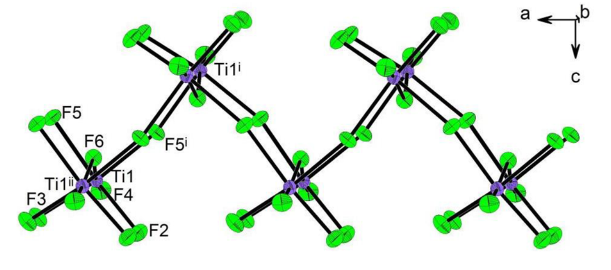

Figure 9. $([Ti_2F_9]^-)_\infty$ anion in the crystal structure of $Na[Ti_2F_9]\cdot HF$. Thermal ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $-0.5 + x, y, 0.5 - z$; (ii) $x, 0.5 - y, z$.

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the titanium and bridging fluorine atoms (1.963(2)−1.974(1) Å) are elongated in comparison with the Ti−F$_t$ bonds between the titanium and terminal fluorine atoms (1.768(2)−1.787(2) Å). The Ti−F$_b$−Ti angles within individual single chains are equivalent and equal to 158.7(1)°. The Ti−F$_b$−Ti angles in which the titanium atoms belong to the two neighboring single chains of the dimer are equal to 141.4(1)°, which is close to corresponding angles in $[H_3O][Ti_2F_9]$[15] and more acute than those in α-/β-[ImH]$[Ti_2F_9]$.[8] The nearest-neighbor TiF_6 octahedra belonging to two individual chains are in an eclipsed conformation relative to each other.

Contrary to the $[Ti_2F_9]^-$ salts of Cs^+, $[H_3O]^+$, and α-/β-$[ImH]^+$, the $Na[Ti_2F_9]\cdot HF$ compound includes HF molecules incorporated into its crystal structure. It is the first observed example of hydrogen-bonding interactions between HF molecules and a polymeric $([Ti_2F_9]^-)_\infty$ anion. Each TiF_6 unit of the anion is involved in hydrogen bonding with one HF molecule via a (Ti−)F4···F1(−H) hydrogen bond, which causes elongation of the Ti−F4 bond. Each HF molecule forms a bifurcated hydrogen bond to two adjacent F4 anions in the *ab* plane (F4···F1 distance = 2.869(4) Å, F4···H−F1 angle = 133.78°).

There is one crystallographically independent sodium atom in the crystal structure. It is coordinated by seven fluorine atoms with Na···F distances ranging from 2.330(4) to 2.398(2) Å, leading to ∑BV = 0.917 for Na. Six fluorine atoms coordinated to the Na^+ cation belong to three different $([Ti_2F_9]^-)_\infty$ anions, and the remaining F atom belongs to the HF molecule. Since Na^+ cations are coordinated both to HF molecules and F4 atoms of anions, infinite chains including Na^+ cations and oriented along the *a* axis (i.e., along the polymeric anions) could be distinguished (Figure 10). The polymeric $([Ti_2F_9]^-)_\infty$ anions are closely packed to form a slightly distorted hexagonal array, similar to the packing of $([Ti_2F_9]^-)_\infty$ anions in β-[ImH]$[Ti_2F_9]$[8] and $Cs[Ti_2F_9]$[9] (Figure 11).

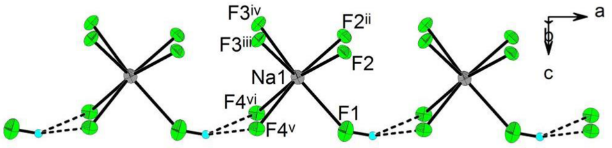

Figure 10. Coordination of Na^+ cations by fluorine atoms belonging to $([Ti_2F_9]^-)_\infty$ anions and HF molecules in the crystal structure of $Na[Ti_2F_9]\cdot HF$. Symmetry codes: (ii) *x*, 0.5 − *y*, *z*; (iii) −1 + *x*, *y*, *z*; (iv) −1 + *x*, 0.5 − *y*, *z*; (v) 1 − *x*, 1 − *y*, 1 − *z*; (vi) 1 − *x*, −0.5 + *y*, 1 − *z*.

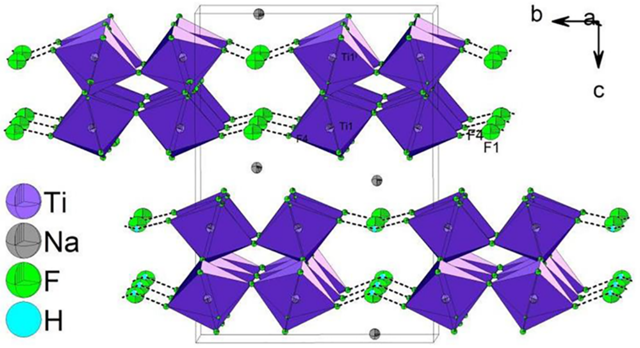

Figure 11. Unit cell and packing of anions, cations, and HF molecules in the crystal structure of $Na[Ti_2F_9]\cdot HF$. Thermal ellipsoids are drawn at the 50% probability level.

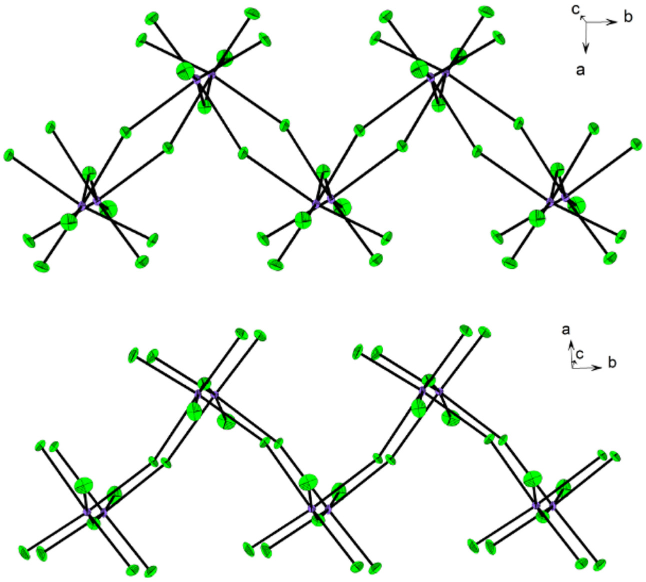

Figure 12. Geometry of the $([Ti_2F_9]^-)_\infty$ anions in the crystal structure of $Rb[Ti_2F_9]$. The upper structure shows the anion containing the crystallographically unique Ti1 and Ti2 atoms;the lower structure shows the anion containing Ti3 and Ti4. Thermal ellipsoids are drawn at the 50% probability level.

Rb[Ti$_2$F$_9$]. The single-crystal structure of $Rb[Ti_2F_9]$ consists of infinite $([Ti_2F_9]^-)_\infty$ anions in two different conformations (Figure 12) and two crystallographically unique rubidium cations, one of which is disordered, occupying two positions with occupancies 81% and 19%.

One $([Ti_2F_9]^-)_\infty$ anion, namely, that constructed from Ti1 and Ti2 atoms, has a gauche conformation of pairs of TiF_6 octahedra belonging to the two individual chains of the double chain, as in the anions in the crystal structures of $Cs[Ti_2F_9]$[9] and α-[ImH]$[Ti_2F_9]$.[8] The second anion, built from Ti3 and Ti4 atoms, has an eclipsed conformation of those pairs of TiF_6 octahedra, similar to the anions in the crystal structures of $[H_3O][Ti_2F_9]$,[9] β-[ImH]$[Ti_2F_9]$,[8] and $Na[Ti_2F_9]\cdot HF$. The Ti−F bond lengths are in the 1.762(2)−2.005(2) Å range, which is typical for fluoridotitanate(IV) compounds. The packing of Rb^+ cations and $([Ti_2F_9]^-)_\infty$ anions is shown in Figure S11.

Crystal Structures Containing $([Ti_4F_{19}]^{3-})_\infty$ Columnlike Anions. The crystal structure determination of $Cs_3[Ti_4F_{19}]$ revealed a new type of fluoridotitanate(IV) anion, $[Ti_4F_{19}]^{3-}$. Like the polymeric $([Ti_2F_9]^-)_\infty$ anions (Figure 12), the polymeric $([Ti_4F_{19}]^{3-})_\infty$ anion is also constructed from two zigzag chains comprising TiF_6 units. However, in $([Ti_4F_{19}]^{3-})_\infty$ every second connection between a TiF_6 unit of one chain and a TiF_6 unit of the second chain is missing (Figure 13).

The length distributions of Ti−F$_t$ and Ti−F$_b$ bonds fall into the 1.768(3)−1.833(4) and 1.958(3)−2.006(3) Å ranges, respectively. The Ti−F$_b$−Ti angles within the zigzag single chains are 155.7(2)°, and the Ti−F$_b$−Ti angles between the two single chains are 151.6(3)°.

The crystal structure of $Cs_3[Ti_4F_{19}]$ contains the anion that can be expressed by general formula $[Ti_4F_{19}]^{3-}$. A similar formula is valid for $[XeF_5]_3[Ti_4F_{19}]$.[14] However, there is one large difference between these two $[Ti_4F_{19}]^{3-}$ anions. The $[Ti_4F_{19}]^{3-}$ anion in $[XeF_5]_3[Ti_4F_{19}]$ is an oligomeric species

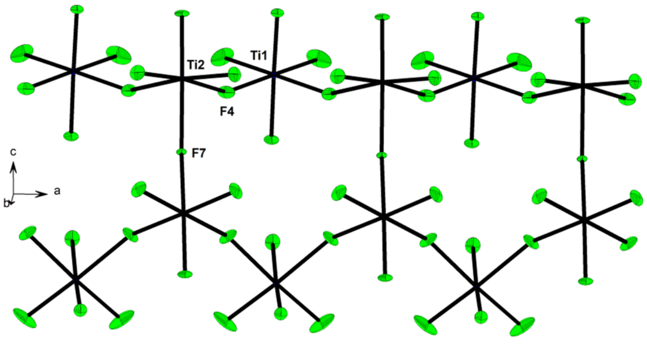

Figure 13. $([Ti_4F_{19}]^{3-})_\infty$ anion in the crystal structure of $Cs_3[Ti_4F_{19}]$. Thermal ellipsoids are drawn at the 50% probability level.

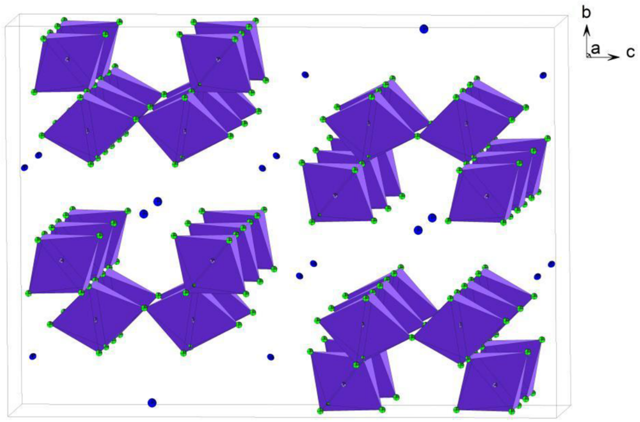

Figure 14. Unit cell and packing of $([Ti_4F_{19}]^{3-})_\infty$ anions and Cs^+ cations in the crystal structure of $Cs_3[Ti_4F_{19}]$.

made of four TiF_6 units sharing some vertices (Table S1), whereas the $[Ti_4F_{19}]^{3-}$ anion in $Cs_3[Ti_4F_{19}]$ forms a polymeric infinite column (Figures 13 and 14). Therefore, to distinguish oligomeric from polymeric species, the use of $([Ti_4F_{19}]^{3-})_\infty$ is more appropriate for description of the latter. Although many fluoridotitanate(IV) anions are known, this is the first case that two different geometries (0-D and 1-D) have been structurally determined for the same general formula of the anion.

Crystal Structures Containing a Three-Dimensional $([Ti_6F_{27}]^{3-})_\infty$ Anionic Framework. Long-lasting crystallization and decomposition of $K_4[Ti_8F_{36}]\cdot8HF$ and $Rb_4[Ti_8F_{36}]\cdot6HF$ crystals resulted in growth of cube-shaped crystals ($a \approx 17$ Å; Table 1) of $([Ti_6F_{27}]^{3-})_\infty$ salts. For Rb, only a few crystals of this phase were detected, and the rest of the crystals were those of $Rb[Ti_2F_9]$. The $([Ti_6F_{27}]^{3-})_\infty$ anionic part is a 3-D network consisting of TiF_6 octahedra, which is a unique case. As already mentioned in the Introduction, all previous known crystal structures of fluoridotitanate(IV) anions contain monomeric $[TiF_6]^{2-}$ or oligomeric fluoridotitanate(IV) anions (0-D) or polymeric species (1-D and 2-D).

Unfortunately, there is a problem with charge balance, i.e., a deficit of A^+ (A = K, Rb) cations. Additionally, long-lasting crystallization could lead to diffusion of some water through the FEP walls of the reaction vessel, resulting in the formation of $[H_3O]^+$ in superacidic aHF.[36] Instead of pure A^+ (A = K, Rb) salts, we can have mixed-cation $A^+/[H_3O]^+$ salts. Later, the same type of anion $([Ti_6F_{27}]^{3-})_\infty$ was determined in $[H_3O]_3[Ti_6F_{27}]$, where only $[H_3O]^+$ cations are present. However, the problem with missing positive charge remains (i.e., 0.25 $[H_3O]^+$). The explanation could be that the missing amount of $[H_3O]^+$ cations is distributed over more crystallographic sites where the occupancy of each site is too small for $[H_3O]^+$ to be located. The total potential solvent area volume, determined with PLATON software,[37] is 785.9 Å^3 (15.4% of the unit cell volume). The two largest voids (119.8 Å^3) are located at 0.25 0.25 0.25 and −0.25 0.75 0.75 positions. If we take into account that a hydrogen-bonded H_2O molecule occupies ~40 Å^3 it may be expected that missing H_3O^+ cations are distributed inside these relatively large cavities.

The anionic part of the crystal structure $([Ti_6F_{27}]^{3-})_\infty$ is well-refined and represents the first example of a 3-D framework built of TiF_6 units. Its structure can be described as built from nonplanar tetrameric Ti_4F_{20} units constructed from four octahedra, each sharing two cis vertices. Each Ti_4F_{20} unit is further linked to four other Ti_4F_{20} units in such way that each TiF_6 octahedron of the tetrameric ring is linked to one tetrameric unit (Figure 15). In other words, each titanium atom is coordinated to three bridging fluorine atoms and three terminal ones. Bridging and terminal atoms are situated on *fac* positions of each TiF_6 octahedron.

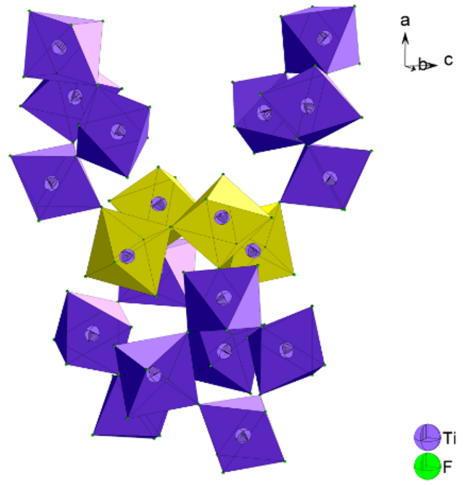

Figure 15. Part of the 3-D fluoridotitanate(IV) $([Ti_6F_{27}]^{3-})_\infty$ anion.

Distortion of the tetrameric Ti_4F_{20} rings leads to the formation of a 3-D array (Figure 15). In the crystal structure of the $([Ti_6F_{27}]^{3-})_\infty$ anion, two types of channels exist (Figure 16). They are occupied by cations and also probably by molecules of the solvent.

■ CONCLUSIONS

A systematic study of reactions between AF (A = Li, Na, K, Rb, Cs) and TiF_4 in aHF (where the starting molar ratio of reactants ranged from $n(AF):n(TiF_4) = 3:1$ to $n(AF):n(TiF_4) = 1:3$) resulted in the formation of $A_2[TiF_6]$, $A_2[TiF_6]\cdot HF$, $A[TiF_5]$, $A[TiF_5]\cdot HF$, $A_3[Ti_4F_{19}]$, $A[Ti_2F_9]$, $A[Ti_2F_9]\cdot HF$, and $A_3[Ti_6F_{27}]$ types of compounds. Their crystal structure determination revealed that they consist of monomeric $[TiF_6]^{2-}$ anions (0-D), polymeric $([TiF_5]^-)_\infty$ chains (1-D), $([Ti_4F_{19}]^{3-})_\infty$ columns (1-D), $([Ti_2F_9]^-)_\infty$ double chains (1-D), or a $([Ti_6F_{27}]^{3-})_\infty$ three-dimensional network (3-D).

Although many crystal structures of fluoridotitanate(IV) anions have been reported (Table S1), this is the first time that it has been observed that two compounds, i.e., $Cs_3[Ti_4F_{19}]$ and $[XeF_5]_3[Ti_4F_{19}]$,[12] contain anions with the same formula but different geometries. The $[Ti_4F_{19}]^{3-}$ anion in $[XeF_5]_3[Ti_4F_{19}]$ is

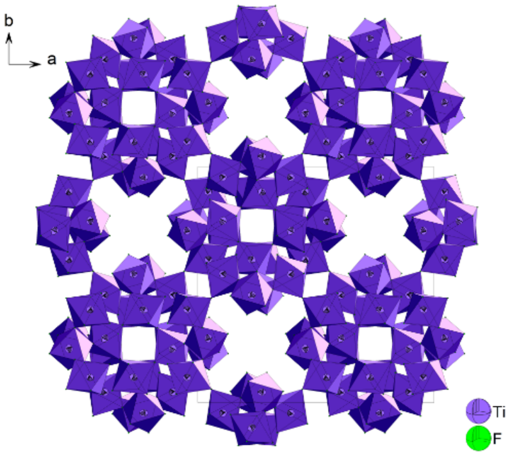

Figure 16. 3-D anionic framework in the crystal structure of $[Ti_6F_{27}]^{3-}$ salts.

an oligomeric species made of four TiF_6 units, while $([Ti_4F_{19}]^{3-})_\infty$ in $Cs_3[Ti_4F_{19}]$ is polymeric and has the geometry of an infinite column resembling the $([Ti_2F_9]^-)_\infty$ double-chain-like anion. In comparison to the latter, there are fewer contacts between TiF_6 groups in the $([Ti_4F_{19}]^{3-})_\infty$ anion.

The crystal structure of $Cs[TiF_5]$ is built of Cs^+ cations and infinite $([TiF_5]^-)$ chainlike anions. Its Raman spectrum (Table S4 and Figure S12) matches the reported Raman spectrum of "$Cs_2[Ti_2F_{10}]$",[27] which was claimed to consist of discrete $[Ti_2F_{10}]^{2-}$ anions and Cs^+ cations. The present research revealed that the reported $Cs_2[Ti_2F_{10}]$ is in fact $Cs[TiF_5]$.

The $([Ti_6F_{27}]^{3-})_\infty$ anion represents the first example of a 3-D framework built of TiF_6 octahedra. To date only examples of 0-D ($[Ti_2F_{10}]^{2-}$,[4,5] $[Ti_2F_{11}]^{3-}$,[6−8] $[Ti_4F_{18}]^{2-}$,[9−11] $[Ti_4F_{19}]^{3-}$,[12] $[Ti_4F_{20}]^{4-}$,[8] $[Ti_5F_{23}]^{3-}$,[8] $[Ti_8F_{36}]^{4-}$,[13] and $[Ti_{10}F_{45}]^{5-}$ [14]), 1-D {$([TiF_5]^-)_\infty$,[14−16] $([Ti_2F_9]^-)_\infty$,[8,9] $([Ti_3F_{13}]^-)_\infty$,[14] $([Ti_7F_{30}]^{2-})_\infty$,[17] and $([Ti_9F_{38}]^{2-})_\infty$[18]}, and 2-D {$([Ti_8F_{33}]^-)_\infty$}[18,19] geometries have been known.

Since Ti^{4+} has no unpaired electrons (d^0 electron configuration), its compounds are diamagnetic, and consequently, no exciting magnetic properties are present. It would be interesting to research whether other transition metal cations with unpaired electrons, e.g., V^{4+} (d^1 electron configuration) or Mn^{4+} (d^3 electron configuration), also demonstrate such rich structural diversity of corresponding perfluoridometalate(IV) compounds. Besides the well-known $[VF_6]^{2-}$ salts,[38] the only other known example of a fluoridovanadate(IV) anion is the infinite $([VF_5]^-)_\infty$ chain determined in $[H_3N(CH_2)_2NH_2][VF_5]$.[39] For fluoridomanganate(IV) anions there are more examples: the monomeric $[MnF_6]^{2-}$ anion,[40] the polymeric infinite $([MnF_5]^-)_\infty$ chainlike anion (like $([TiF_5]^-)_\infty$),[40] the discrete octameric $[Mn_8F_{36}]^{4-}$ oligomer[40] (whose ringlike geometry is completely different from the cube-shaped geometry of $[Ti_8F_{36}]^{4-}$ anion[13]), and the polymeric $([Mn_2F_9]^-)_\infty$ double chain [similar to $([Ti_2F_9]^-)_\infty$] observed in O_2MnF_9.[41] Magnetic properties have recently been reported for $A[Cr^{IV}F_5]$ compounds (A = K, Rb, Cs).[42] The other known example of a fluoridochromate(IV) anion (Cr^{4+}; d^2 electron configuration) is dimeric $[Cr_2F_{11}]^{3-}$.[43]

■ EXPERIMENTAL SECTION

Reagents. LiF (The British Drug Houses Ltd.), NaF (Merck, 99%), KF (Ventron, 99.9%), RbF (Sigma-Aldrich, 99.8%), and CsF (Alfa Aesar, 99.99%) were used as supplied. Titanium tetrafluoride was synthesized by the reaction of $TiCl_3$ (Sigma-Aldrich, 99.999%) with elemental F_2 in aHF. The purity of TiF_4 was confirmed using Raman spectroscopy and elemental chemical analysis.

CAUTION! *Anhydrous HF and some fluorides are highly toxic and must be handled in a well-ventilated hood, and protective clothing must be worn all the time!*

Synthetic Apparatus. Because of the high hygroscopicity of TiF_4 and fluoridotitanate(IV) compounds, all manipulations with them were carried out under anhydrous conditions. Nonvolatile materials were handled in an M. Braun glovebox in an argon atmosphere, where the quantity of water did not exceeded 0.5 ppm. Volatile compounds, such as aHF and F_2, were handled on a vacuum line constructed from nickel and polytetrafluoroethylene (PTFE).

Vessels used for syntheses and single-crystal growth were manufactured from tetrafluoroethylene−hexafluoropropylene block copolymer (FEP) (Polytetra GmbH, Germany) tubes. The reaction vessel was composed of a tube (16 mm i.d. × 19 mm o.d.) that was heat-sealed at one end and equipped with a PTFE valve at the other flared end. The crystallization vessel consisted of two FEP tubes (one 16 mm i.d. × 19 mm o.d. and the other 4 mm i.d. × 6 mm o.d.). Each tube was heat-sealed at one end and attached via a linear PTFE connector to a connecting PTFE T-part at 90° (see the Supporting Information for ref 36). A PTFE valve was attached to the T-part at a 180° angle with respect to the 19 mm o.d. tube. All of the PTFE details were covered by brass parts with threads that prevented deformation of those details and simplified their connections to each other and to the vacuum system. Magnetic stirring bars, isolated by PTFE, were put inside the reaction vessels. The temperature gradient between the two arms of the crystallization vessels was maintained by cooling the wider arm of the vessel in a Huber Ministat 230 (to −33 °C) or Thermo Fisher Scientific EK 90 (to −60 °C) cryostat.

Prior to use, all of the reaction and crystallization vessels were dried under dynamic vacuum and passivated with elemental F_2 (Solvay Fluor and Derivate GmbH, 99.98%) at 1 bar for 2 h. Anhydrous HF (Linde AG, 99.995%) was treated with K_2NiF_6 (Advance Research Chemicals Inc., 99.9%) for at least several hours before use and was usually kept in FEP vessels above K_2NiF_6.

Synthesis and Crystal Growth. TiF_4 (0.6 g), suspected to be contaminated by traces of moisture, was washed with 20 mL of aHF. Solid product (100 mg) recovered from the decanted solution was redissolved in 6 mL of aHF. Single crystals of $[H_3O]_3[Ti_6F_{27}]$ and $[H_3O][Ti_2F_9]$[9] were grown from the corresponding solutions. Titanium tetrafluoride and alkali metal fluoride (AF, A = Li, Na, K, Rb, Cs) were loaded into the reaction vessel in a glovebox. Around 4−8 mL of aHF was condensed onto the mixture of reagents at 77 K. The obtained mixture was warmed to ambient temperature and mixed for several days. In the case of significant amounts of undissolved residue, an additional portion of aHF was added. Finally, after the reaction seemed to be completed, aHF was pumped away, and the obtained product was dried under a high vacuum.

Single Crystals Prepared in the Crystallization Vessels. In this case, a ternary alkali metal−Ti(IV) fluoride compound or nAF/TiF_4 mixture was loaded inside the wider arm of the crystallization vessel in a glovebox. Then aHF was condensed onto the sample at 77 K, and the vessel was warmed to ambient temperature. When the sample was completely or in some cases partly dissolved, clear solution was decanted into the narrower arm. In order to achieve evaporation of the solvent from the narrower arm, a temperature gradient between the two arms of the crystallization vessel was maintained. The gradient was 10 K at the beginning of the process and later was slowly increased to 50 K and in some cases even up to 80 K. Finally, crystals grown in the narrower arm were isolated by two different methods. The first method consisted of pumping away volatiles at ambient temperature, drying the crystals under dynamic vacuum, and transferring them to a glovebox. The second method was applied in order to isolate crystals that are stable at ambient temperature only in the mother liquor (mainly HF solvate compounds). For this, a small portion (1−2 mL) of cold perfluorinated oil (perfluorodecaline, $C_{10}F_{18}$; ABCR or Fluorochem Ltd., both 98%) was injected inside the narrower FEP tube to cover the crystals when there was still some mother liquor visible. After that, crystals covered with oil were transferred to a cold glass plate under a microscope.

Characterization Methods. *Raman Spectroscopy.* Raman spectra with a resolution of 0.5 cm^{-1} were recorded at room temperature on a Horiba Jobin Yvon LabRam-HR spectrometer equipped with an Olympus BXFM-ILHS microscope. Samples were excited by the 632.8 nm emission line of a He−Ne laser with regulated power in the range 20−0.0020 mW, which gives 17−0.0017 mW focused on a 1 μm spot through a 50× microscope objective on the top surface of the sample.

Single crystals or powdered material were mounted in the glovebox in previously vacuum-dried quartz capillaries, which were initially sealed with Halocarbon 25-5S grease (Halocarbon Corp.) inside the glovebox and later heat-sealed in an oxygen−hydrogen flame outside the glovebox. In some cases Raman spectra were recorded through the wall of the crystallization vessel on single crystals still covered with mother liquor. Raman spectra of $A[TiF_5]$ (A = Na, K, Rb, Cs), $A[TiF_5]\cdot HF$ (A = Na, K), $Na[Ti_2F_9]$, $Na[Ti_2F_9]\cdot HF$, and $Rb[Ti_2F_9]$ are given in Tables S4 and S5 and Figures S12 and S13.

Chemical Analysis. The total content of fluoride ions was determined by direct potentiometry using a fluoride-ion-selective electrode after decomposition of samples by fusion with $NaKCO_3$.[44,45] The content of titanium was determined by back-titration with EDTA after removal of fluorine from the sample.[46] The contents of alkali metals were determined by flame atomic emission spectroscopy.

Single-Crystal X-ray Diffraction Analysis. Crystals were immersed in perfluorodecalin (ABCR, 98%) inside a glovebox, selected under a microscope, and mounted on the goniometer head of the diffractometer in a cold nitrogen stream created by an Oxford Cryojet cooling system. Some single crystals were put in previously vacuum-dried quartz capillaries. Although up to 15 crystals from the same batch were screened, the presence of other crystal phases cannot be definitively ruled out.

Single-crystal data for Rb_2TiF_6, $K[TiF_5]$, $Na[TiF_5]\cdot HF$, $K[TiF_5]\cdot HF$, $Rb[TiF_5]\cdot HF$, and $Na[Ti_2F_9]\cdot HF$ were collected on a Rigaku AFC7S diffractometer equipped with a Mercury CCD area detector using graphite-monochromatized Mo Kα radiation. The data were processed using Rigaku Crystal Clear software.[47] The crystal structures were solved by direct methods using SIR-92[48] as implemented in teXan software[49] and refined with SHELXL-97 software[50] as implemented in the program package WinGX.[51] Single-crystal data for Li_2TiF_6, $Cs[TiF_5]$, $Cs_3[Ti_4F_{19}]$, $Rb[Ti_2F_9]$, and $[H_3O]_3[Ti_6F_{27}]$ were collected on a Gemini A diffractometer equipped with an Atlas CCD detector using graphite-monochromated Mo Kα radiation. The collected diffraction data were processed with the CrysAlis PRO program.[52] The crystal structures were solved by the charge-flipping method using the SUPERFLIP program[53] and refined with SHELXL-2013[54] using OLEX crystallographic software.[55]

Hydrogen atoms in the structures of $[H_3O]_3[Ti_6F_{27}]$, $K[TiF_5]\cdot HF$, $Na[TiF_5]\cdot HF$, and $Rb[TiF_5]\cdot HF$ were placed on ideal positions and refined as riding atoms with relative isotropic displacement parameters. The position of the hydrogen atom in $Na_2Ti_2F_9\cdot HF$ was found in the Fourier map and refined using geometrical restrictions. Figures were prepared using the program DIAMOND 4.4.[56]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02890.

Structural data for TiF_4 and compounds containing monomeric $[TiF_6]^{2-}$, oligomeric $[Ti_nF_{4n+x}]^{x-}$ (0-D), and polymeric (1-D, 2-D, 3-D) $([Ti_nF_{4n+x}]^{x-})_\infty$ anions; stoichiometries used to synthesize and crystallize the alkali metal fluoridotitanates(IV) and phases detected in the isolated solids after the reactions and/or crystallizations of the various nAF/TiF_4/aHF (A = Li, Na, K, Rb, Cs) mixtures; bond-valence parameters of selected bonds used within the present research; Raman spectra of the products of reactions between AF (A = Li, Na, K, Rb, Cs) and TiF_4 in different molar ratios; figures showing geometries of previously known $([TiF_5]^-)_\infty$ and $([Ti_2F_9]^-)_\infty$ anions and packing of anions, cations, and HF molecules in the crystal structures of $Na[TiF_5]\cdot HF$, $K[TiF_5]\cdot HF$, $CsTiF_5$, and $Rb[Ti_2F_9]$ (PDF)

Accession Codes

CCDC 1586180−1586190 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: igorshlyapnikov@yandex.ru.
*E-mail: zoran.mazej@ijs.si.

ORCID

Zoran Mazej: 0000-0003-3085-7323

Notes

The authors declare no competing financial interest.

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