

## Electronic Supporting Information

### The cubic $[\text{Ti}_8\text{F}_{36}]^{4-}$ anion found in the crystal structures of $\text{K}_4\text{Ti}_8\text{F}_{36}\cdot 8\text{HF}$ and $\text{Rb}_4\text{Ti}_8\text{F}_{36}\cdot 6\text{HF}$

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## Crystal growth of $\text{K}_4\text{Ti}_8\text{F}_{36}\cdot 8\text{HF}$ and $\text{Rb}_4\text{Ti}_8\text{F}_{36}\cdot 6\text{HF}$

In a general procedure, single crystals growths were carried out in a double T-shaped apparatus consisting of two tubes made from tetrafluoroethylen-hexafluoropropylene copolymer (FEP; Polytetra GmbH, Mönchengladbach, Germany) with diameters 19 and 6 mm, respectively. Both tubes were heat-sealed on the one end, connected with Teflon<sup>®</sup> T-shaped part and equipped with a Teflon<sup>®</sup> valve on another. Before use, reaction vessels were passivated with elemental fluorine at 0.7 bars for two hours. Anhydrous HF (Linde, 99.995 %) was treated with  $\text{K}_2\text{NiF}_6$  (Advance Research Chemicals, Inc.) for several hours prior to use.

Starting KF/RbF –  $\text{TiF}_4$  mixtures (89/106 mg of KF/RbF, 380/249 mg of  $\text{TiF}_4$  were loaded into the wider arm of the crystallization vessel in a dry-box. aHF (~4–8 ml) was then condensed onto the starting material at 77 K. The crystallization mixtures were brought up to ambient temperature and the samples partly dissolved. Clear solutions were decanted into the narrower arm. The evaporation of the solvent from these solutions was carried out by maintaining a temperature gradient corresponding to about 10 K between both tubes for one week. The effect of this treatment was to enable aHF to be slowly evaporated from narrower into wider tube leaving the crystals. Raman spectra of both salts were recorded on corresponding crystals still covered by saturated solutions of aHF. The Raman spectra were recorded on a Horiba Jobin-Yvon LabRam HR spectrometer using the 632.81 nm excitation line of a He-Ne laser with regulated power in the range 25 mW – 0.0025 mW.

Single crystals of  $\text{K}_4\text{Ti}_8\text{F}_{36}\cdot 8\text{HF}$  and  $\text{Rb}_4\text{Ti}_8\text{F}_{36}\cdot 6\text{HF}$  are stable at ambient temperature only in mother liquid. When last traces of aHF are removed, compounds start to release HF and decompose. For those, they were isolated on a special way. When there was only small amount of mother liquid still visible the cold perfluorinated oil (perfluorodecaline  $\text{C}_{10}\text{F}_{18}$ ; around 1-2 ml) was injected inside FEP tube to completely cover the crystals. The tube has been cut and a mixture of crystals and oil was transferred on a cold glass plate under microscope. Appropriate crystals were selected maintaining the temperature between 265–275 K and then transferred into the cold nitrogen stream of the diffractometer.

## Crystal structure determination

Single-crystal diffraction data were collected using a Rigaku AFC7 diffractometer (graphite monochromatized MoK $\alpha$  radiation) equipped with a Mercury CCD area detector at

200 K. The data were corrected for Lorentz, polarization and absorption effects and were processed using Rigaku CrystalClear software<sup>1</sup>. The structure was solved by direct methods using the program SIR-92<sup>2</sup> (teXan software from Molecular Structure Corporation<sup>3</sup>) and refined with SHELXL-97 software<sup>4</sup> implemented in the program package WinGX<sup>5</sup>. The positions of hydrogen atoms were found geometrically. The coordinates and the isotropic thermal parameter (Uiso) of the H atom were fixed before the final refinement (Uiso(H) was set at 1.2 times the equivalent isotropic thermal parameter of its F atom).

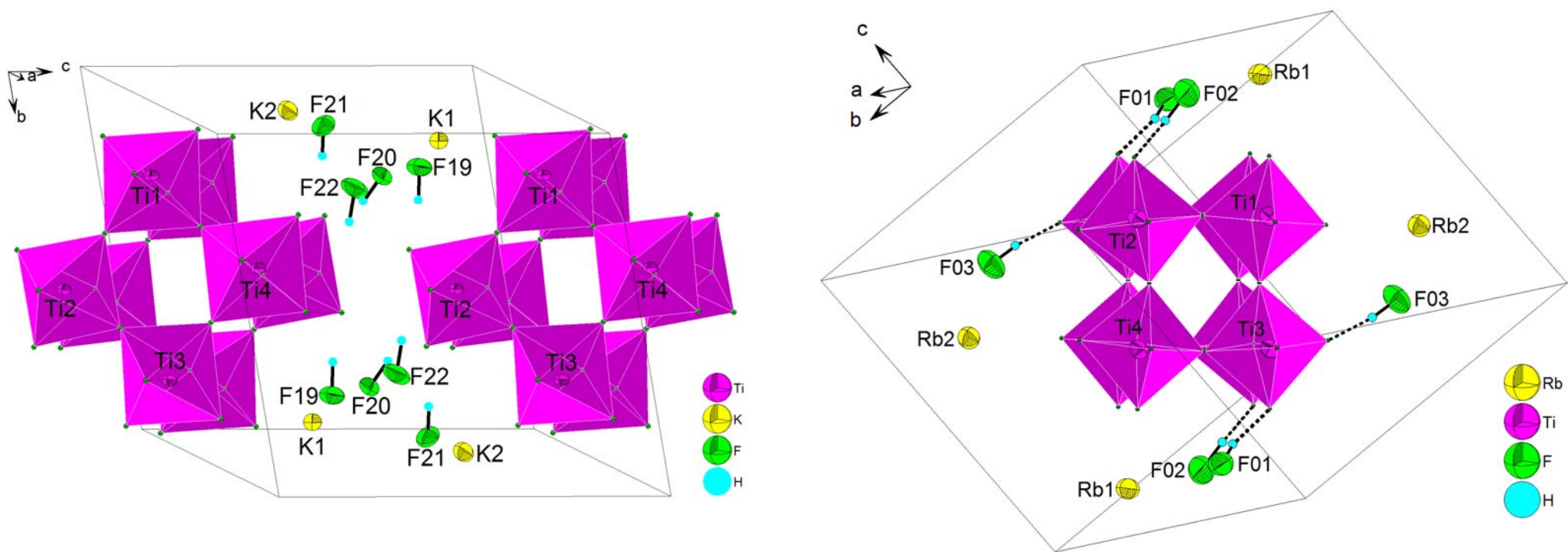
Collected data of Rb compound were of lower quality than for K salt. Unfortunately, all attempts to prepare better quality crystals of Rb compound have been so far unsuccessful. The figures were prepared using DIAMOND 3.1 software.<sup>6</sup>

- 1) Crystal Clear, Rigaku Corp., Woodland, Texas, 1999.
- 2) A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Cryst.* **1993**, *26*, 343–350.
- 3) teXan for Windows, version 1.06 ed., Molecular Structure Corporation, Woodland, Texas, 1999.
- 4) G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112–122.
- 5) L.J. Farrugia, *J. Appl. Cryst.*, **1999**, *32*, 837–838.
- 6) DIAMOND v3.1. 2004-2005 Crystal Impact GbR, Bonn, Germany.

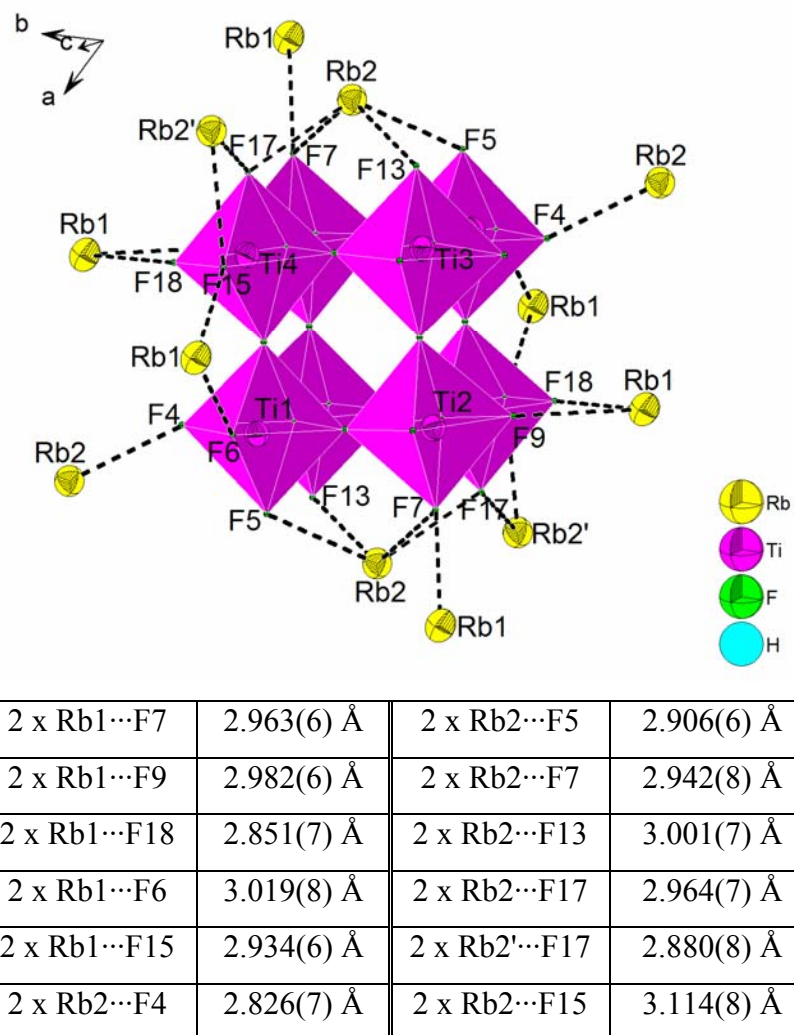
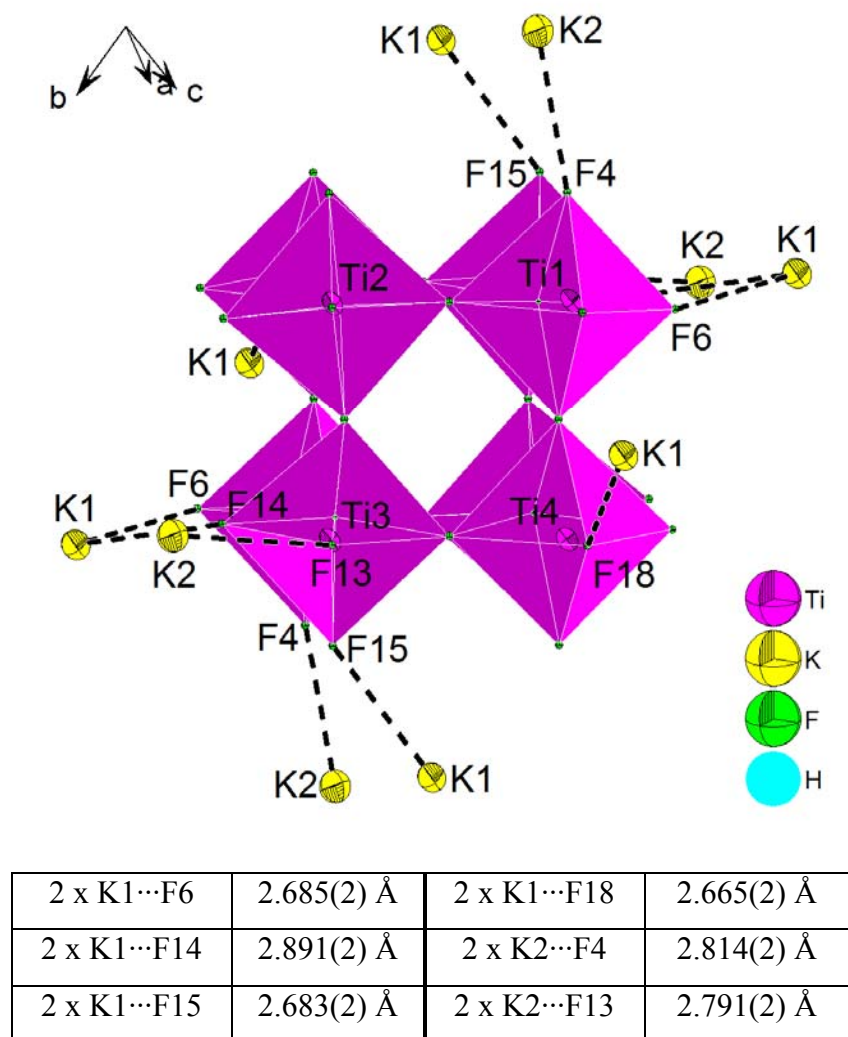
**Table S1.** Crystal Data and Refinement Results for  $K_4Ti_8F_{36} \cdot 8HF$  and  $Rb_4Ti_8F_{36} \cdot 6HF$  arising from  $K(Rb)F \cdot 2TiF_4 \cdot aHF$  Systems

Chemical formula	$K_4Ti_8F_{36} \cdot 8HF$	$Rb_4Ti_8F_{36} \cdot 6HF$
Fw (g/mol)	1383.42	1529.13
Space group	$P\bar{1}$	$P\bar{1}$
$a$ (Å)	10.2054(7)	10.1991(17)
$b$ (Å)	10.3448(1)	10.4191(5)
$c$ (Å)	10.5896(2)	10.5848(7)
$\alpha$ (°)	79.808(14)	89.68(6)
$\beta$ (°)	65.208(11)	66.41(5)
$\gamma$ (°)	60.889(11)	64.17(4)
$V$ (Å <sup>3</sup> )	886.21(14)	908.2(7)
$Z$	1	1
$D_{calc}$ (g/cm <sup>3</sup> )	2.593	2.796
$T$ (K)	200	200
$R_1^a$	0.0457	0.0724
$wR_2^b$	0.1203	0.215
GOF <sup>c</sup>	1.131	1.109
$\Delta\rho_{max,min}$ (e Å <sup>-3</sup> )	0.851/-0.747	2.844/-0.86

<sup>a</sup> $R_1$  is defined as  $\frac{\sum \left[ |F_o| - |F_c| \right]}{\sum |F_o|}$  for  $I > 2\sigma(I)$ . <sup>b</sup> $wR_2$  is defined as  $[\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$  for  $I > 2\sigma(I)$ . <sup>c</sup> GOF =  $[\sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p)]^{1/2}$ , where  $N_o$  = number of reflections and  $N_p$  = number of refined parameters.

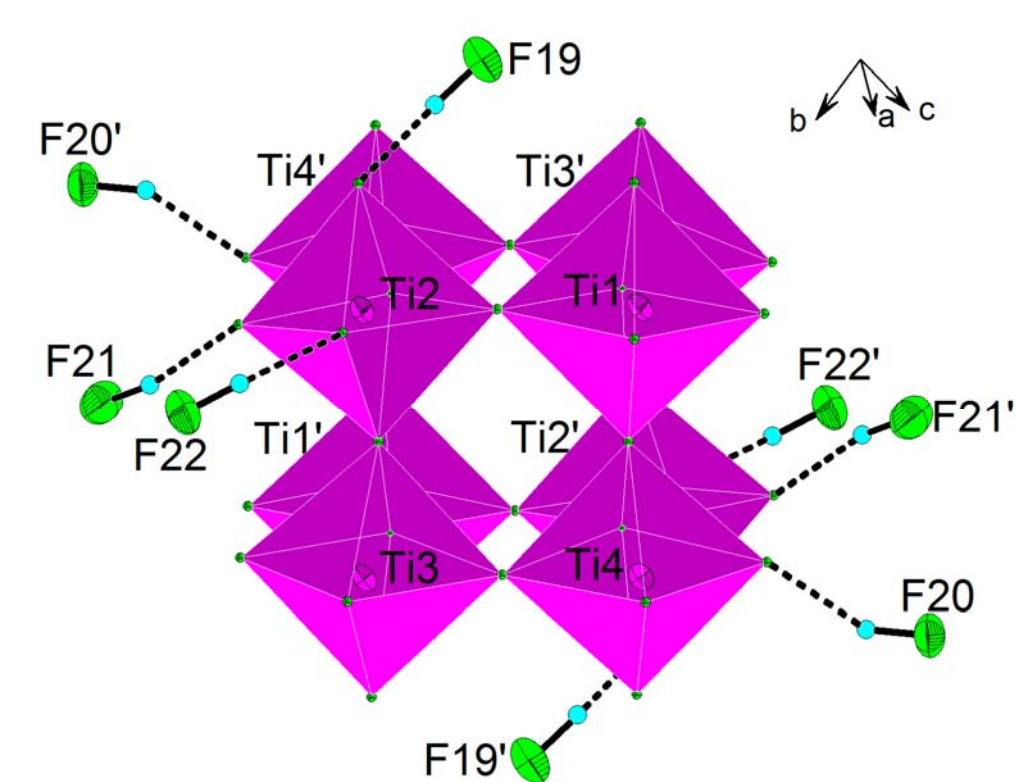


**Figure S1.** Unit cells of  $K_4Ti_8F_{36} \cdot 8HF$  (left) and  $Rb_4Ti_8F_{36} \cdot 6HF$  (right); ellipsoids are drawn at 50 % probability.

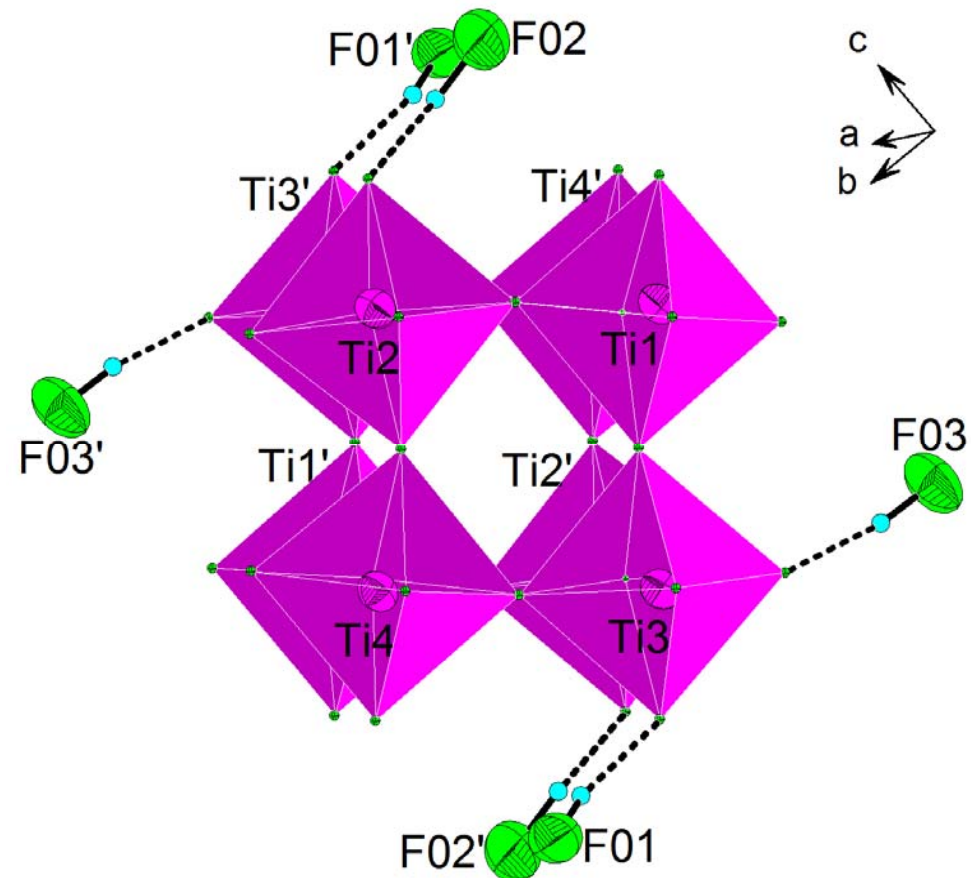


**Figure S2.** The A...F (A = K, Rb) interactions with single  $[\text{Ti}_8\text{F}_{36}]^{4-}$  anion in  $\text{K}_4\text{Ti}_8\text{F}_{36}\cdot 8\text{HF}$  (left) and  $\text{Rb}_4\text{Ti}_8\text{F}_{36}\cdot 6\text{HF}$  (right); ellipsoids are drawn at 50 % probability.



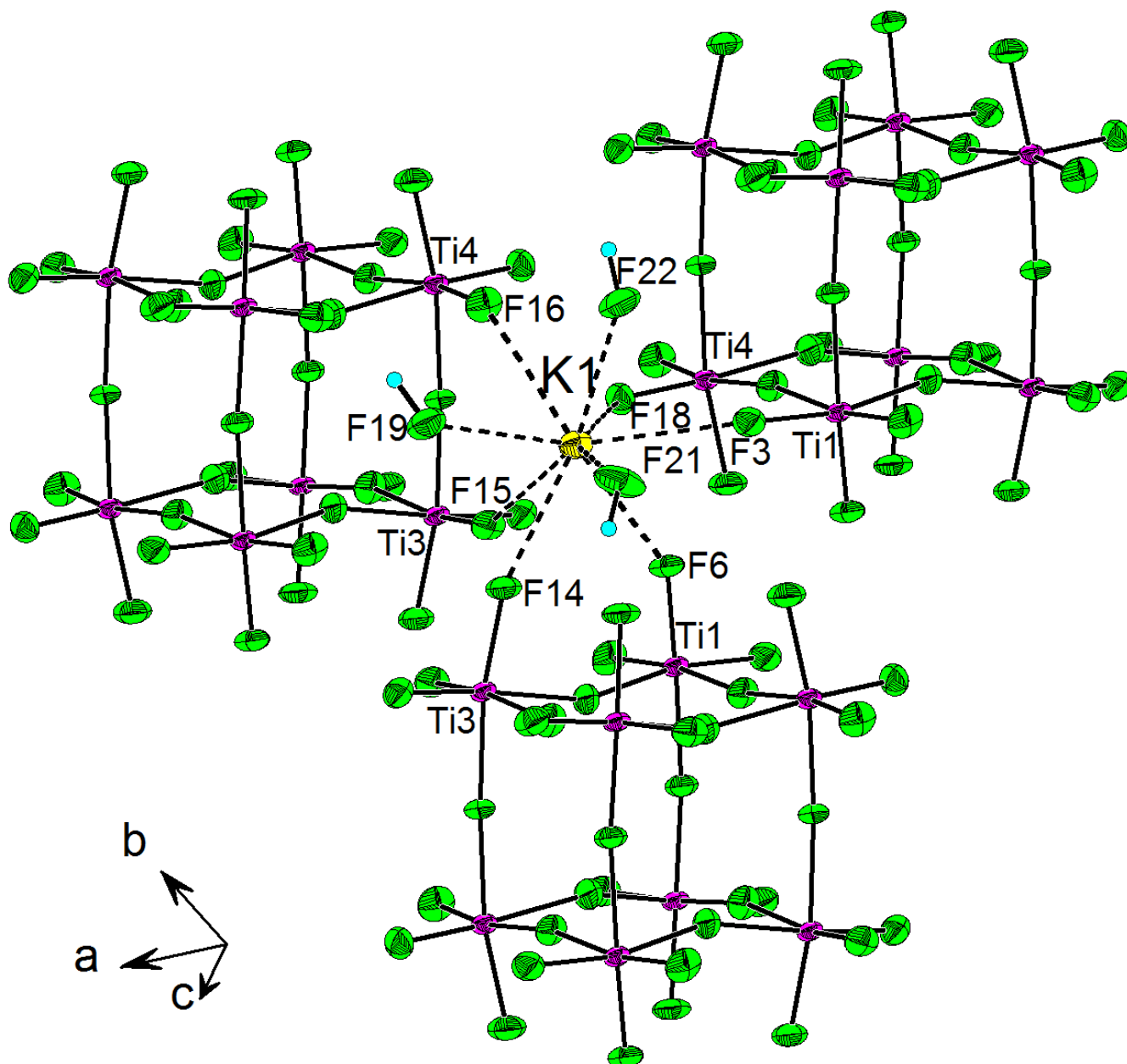


F–H...F	F – H [Å]	H...F [Å]	F...F [Å]	F – H...F [°]
F19–H...F10	0.93	1.677(10)	2.567(13)	158.68(15)
F19'–H...F10	0.93	1.677(10)	2.567(13)	158.68(15)
F20–H...F17	0.93	1.781(6)	2.525(17)	134.91(14)
F20'–H...F17	0.93	1.781(6)	2.525(17)	134.91(14)
F21–H...F9	0.93	1.667(11)	2.568(21)	162.07(18)
F21'–H...F9	0.93	1.667(11)	2.568(21)	162.07(18)
F22–H...F11	0.93	1.804(14)	2.577(18)	138.71(18)
F22'–H...F11	0.93	1.804(14)	2.577(18)	138.71(18)



F–H...F	F – H [Å]	H...F [Å]	F...F [Å]	F – H...F [°]
F01–H...F11	0.9778	1.653(13)	2.573(36)	155.09(52)
F01'–H...F11	0.9778	1.653(13)	2.573(36)	155.09(52)
F02–H...F8	1.0794	1.756(29)	2.548(33)	126.33(60)
F02'–H...F8	1.0794	1.756(29)	2.548(33)	126.33(60)
F03–H...F12	0.955	1.611(30)	2.555(34)	169.12(51)
F03'–H...F12	0.955	1.611(30)	2.555(34)	169.12(51)

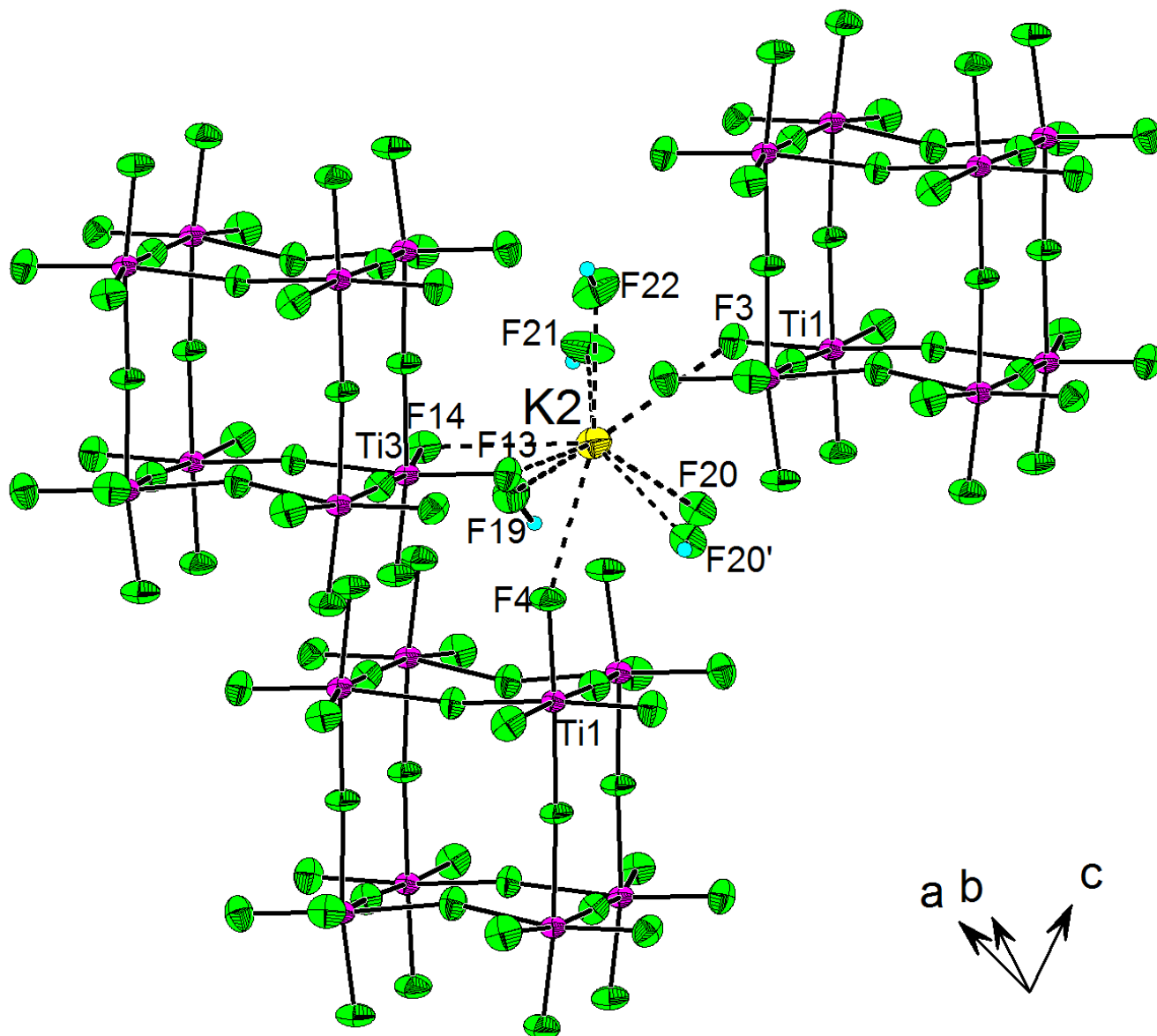
**Figure S3.** Hydrogen bonding between  $[\text{Ti}_8\text{F}_{36}]^{4-}$  anion and HF molecules in  $\text{K}_4\text{Ti}_8\text{F}_{36}\cdot 8\text{HF}$  (left) and  $\text{Rb}_4\text{Ti}_8\text{F}_{36}\cdot 6\text{HF}$  (right); ellipsoids are drawn at 50 % probability.



K1...F18(-Ti4)	2.665(2) Å	K1...F19(-H)	2.689(3) Å
K1...F3(-Ti1)	3.009(2) Å	K1...F21(-H)	2.659(3) Å
K1...F6(-Ti1)	2.685(2) Å	K1...F22(-H)	2.728(3) Å
K1...F14(-Ti3)	2.891(2) Å		
K1...F16(-Ti4)	3.028(2) Å		
K1...F15(-Ti3)	2.683(2) Å		

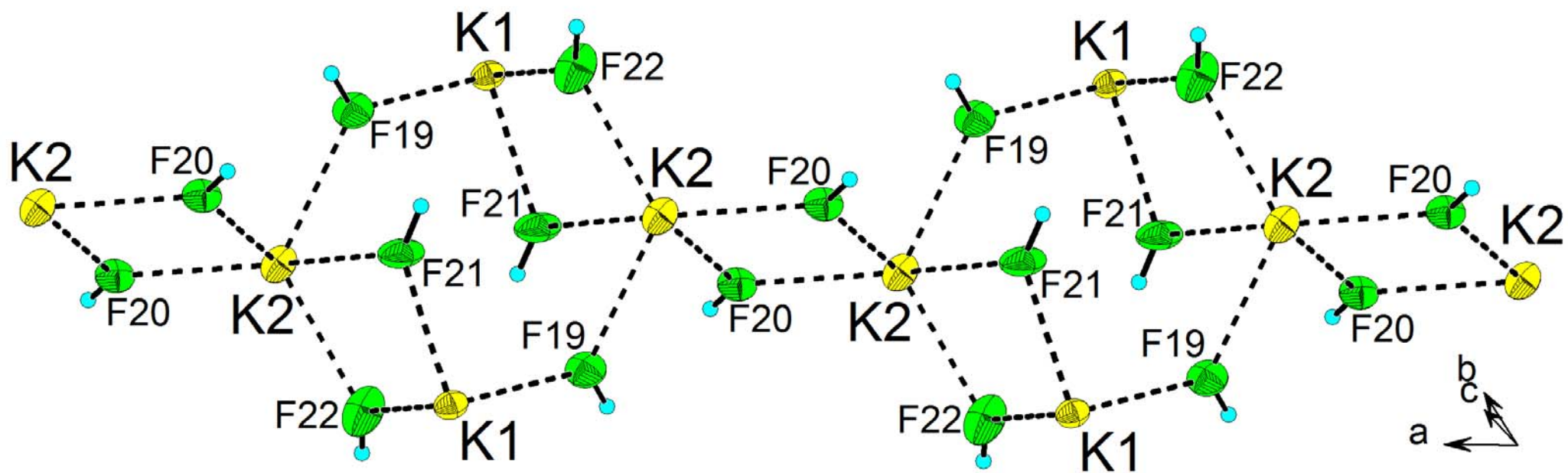
**Figure S4a.** The K1 atoms coordination in  $K_4Ti_8F_{36} \cdot 8HF$  (ellipsoids are drawn at 50 % probability).



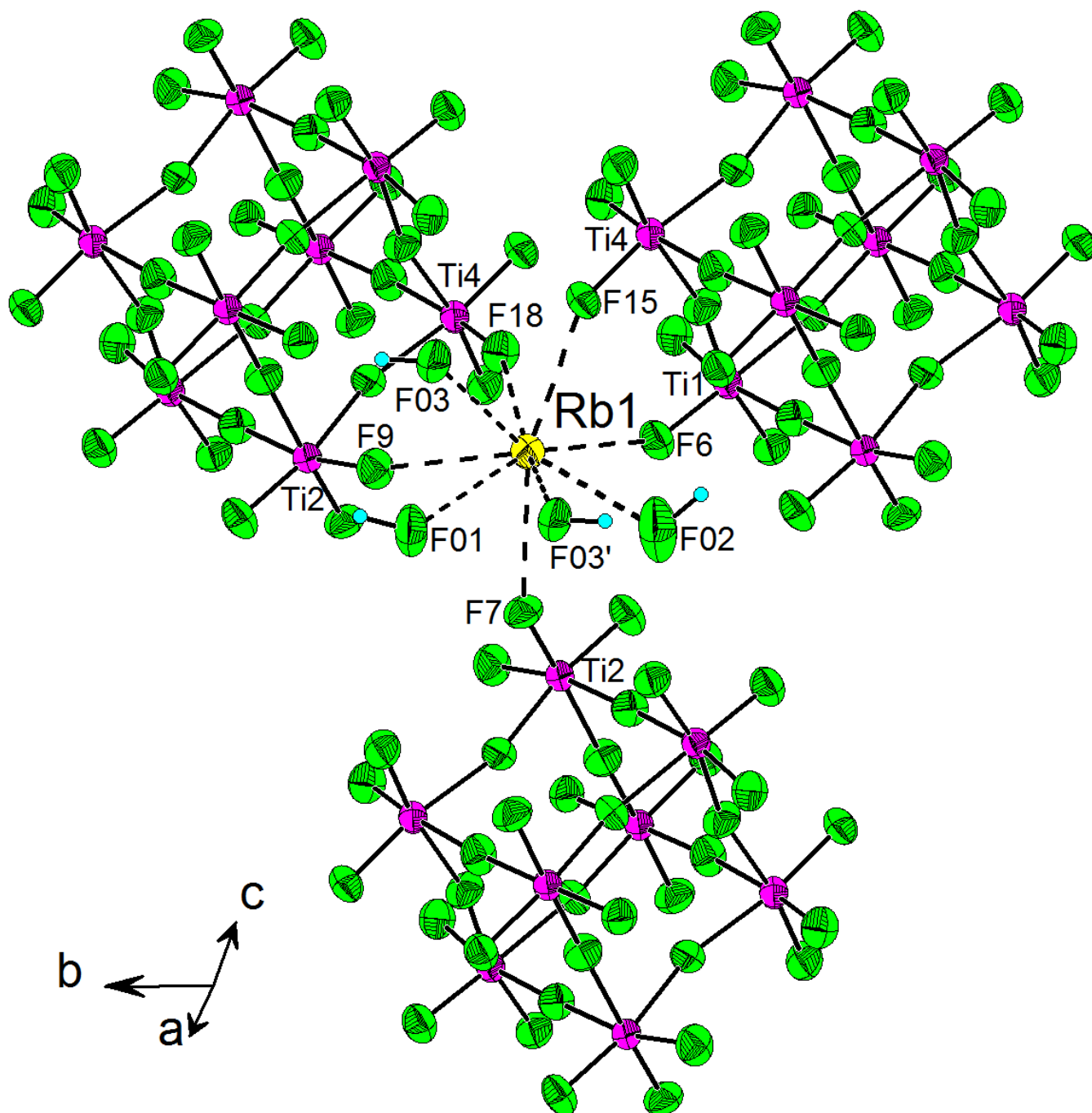


K2...F14(-Ti3)	2.959(2) Å	K2...F20(-H)	2.707(2) Å
K2...F13(-Ti3)	2.791(2) Å	K2...F20'(-H)	2.703(2) Å
K2...F4(-Ti1)	2.814(2) Å	K2...F21(-H)	2.752(3) Å
K2...F3(-Ti1)	3.042(2) Å	K2...F22(-H)	2.785(3) Å
K2...F19(-H)	2.845(3) Å		

**Figure S4b.** The K2 atoms coordination in  $K_4Ti_8F_{36} \cdot 8HF$  (ellipsoids are drawn at 50 % probability).

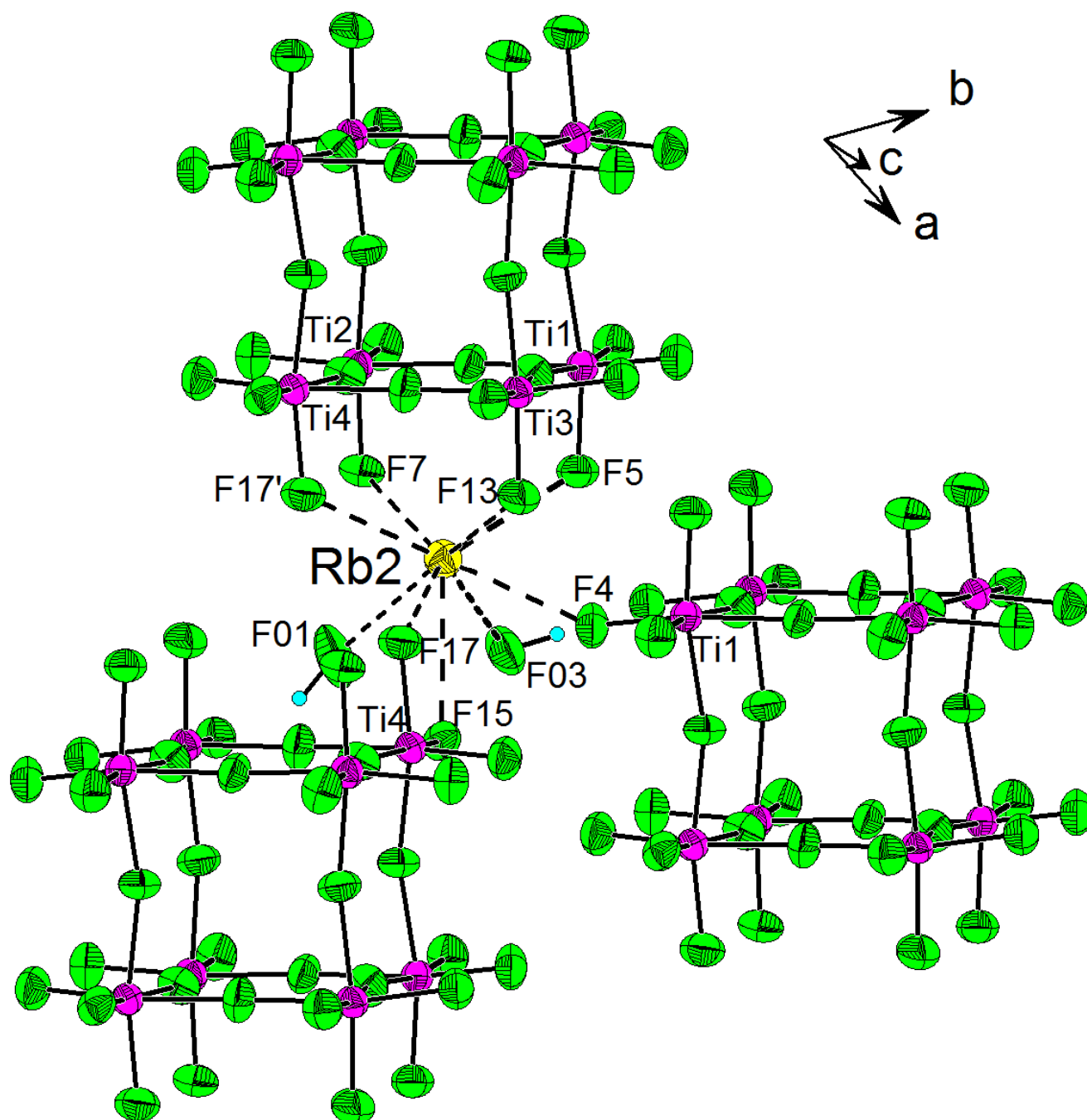


**Figure S5.** Interactions between K<sup>+</sup> cations and HF molecules in K<sub>4</sub>[Ti<sub>8</sub>F<sub>36</sub>]·8HF. For reasons of clarity K<sup>+</sup>...[Ti<sub>8</sub>F<sub>36</sub>] contacts and HF...[Ti<sub>8</sub>F<sub>36</sub>] hydrogen bonds are not shown (ellipsoids are drawn at 50 % probability).



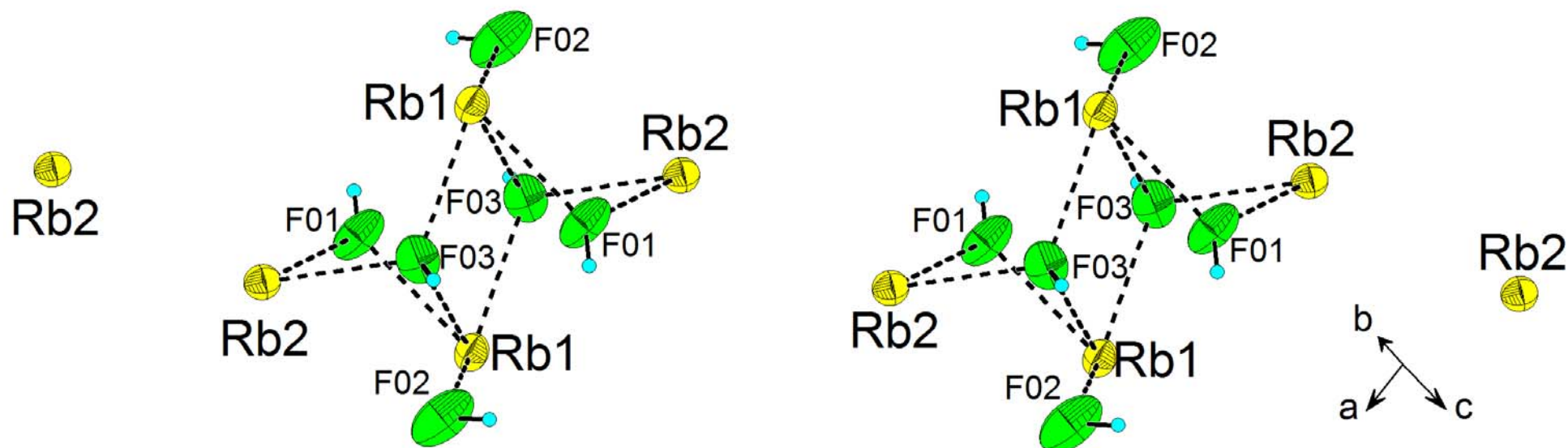
Rb1...F15(-Ti4)	2.934(6) Å	Rb1...F01(-H)	2.964(8) Å
Rb1...F6(-Ti1)	3.019(8) Å	Rb1...F02(-H)	2.843(9) Å
Rb1...F18(-Ti4)	2.851(7) Å	Rb1...F03(-H)	3.004(9) Å
Rb1...F9(-Ti2)	2.982(6) Å	Rb1...F03'(-H)	3.215(10) Å
Rb1...F7(-Ti2)	2.963(6) Å		

**Figure S6a.** The Rb1 atoms coordination in  $\text{Rb}_4\text{Ti}_8\text{F}_{36}\cdot 6\text{HF}$  (ellipsoids are drawn at 50 % probability).

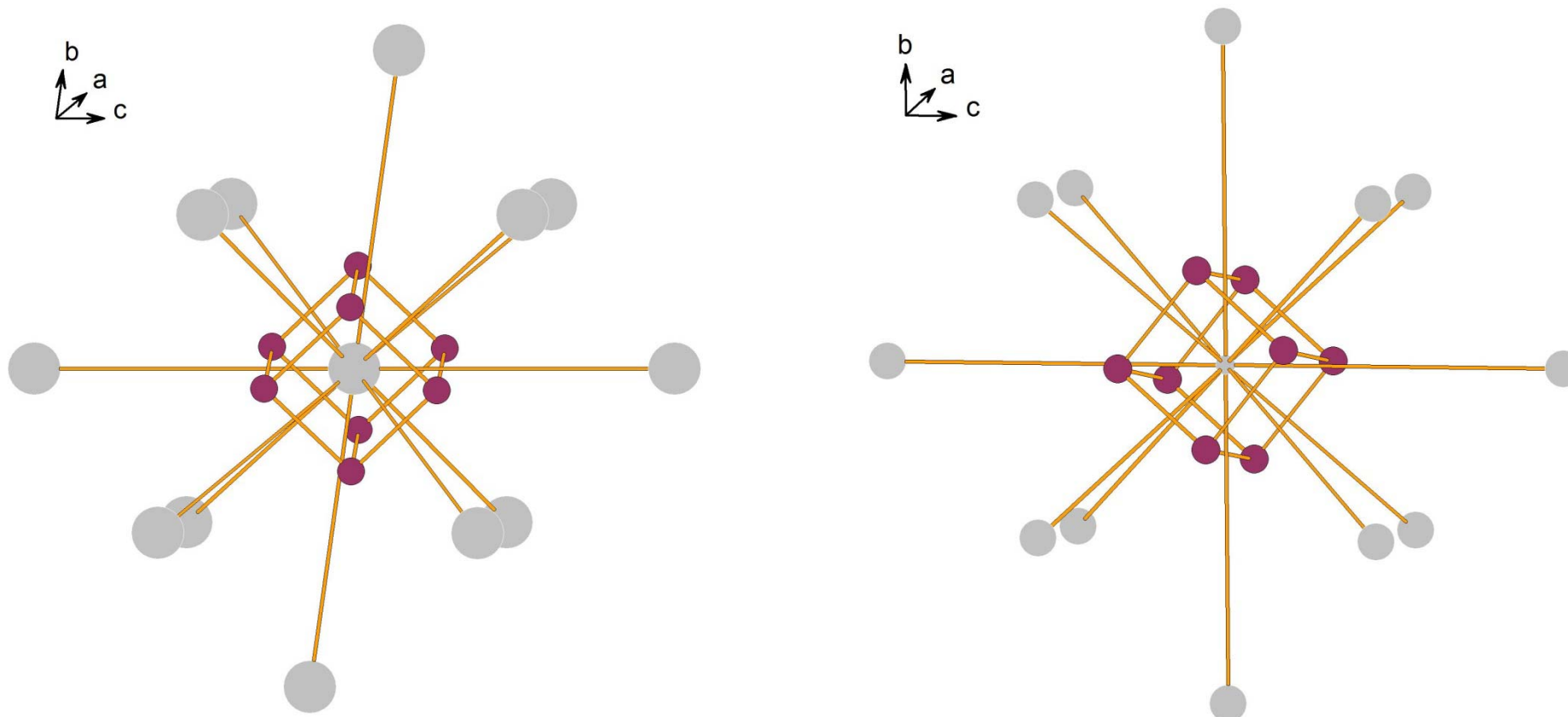


Rb2...F5(-Ti1)	2.906(6) Å	Rb2...F4(-Ti1)	2.826(7) Å
Rb2...F7(-Ti2)	2.942(8) Å		
Rb2...F13(-Ti3)	3.001(7) Å	Rb1...F01(-H)	2.889(8) Å
Rb2...F17'(-Ti4)	2.964(7) Å		
Rb2...F17(-Ti4)	2.880(8) Å	Rb1...F03(-H)	2.904(8) Å
Rb2...F15(-Ti4)	3.114(8) Å		

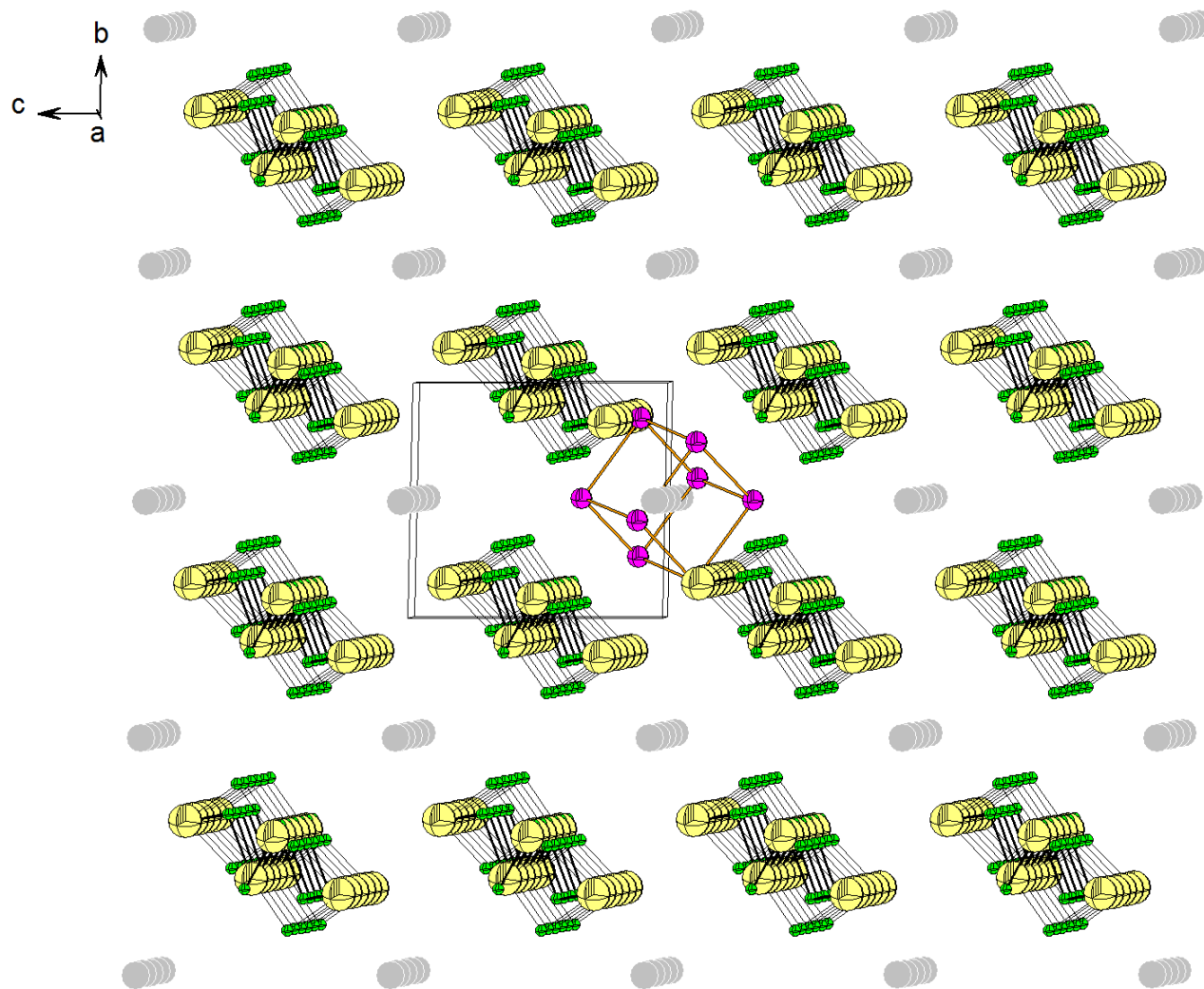
**Figure S6b.** The Rb2 atoms coordination in  $\text{Rb}_4\text{Ti}_8\text{F}_{36}\cdot 6\text{HF}$  (ellipsoids are drawn at 50 % probability).



**Figure S7.** Interactions between Rb<sup>+</sup> cations and HF molecules in Rb<sub>4</sub>[Ti<sub>8</sub>F<sub>36</sub>]·6HF. For reasons of clarity Rb<sup>+</sup>⋯[Ti<sub>8</sub>F<sub>36</sub>] contacts and HF⋯[Ti<sub>8</sub>F<sub>36</sub>] hydrogen bonds are not shown (ellipsoids are drawn at 50 % probability).

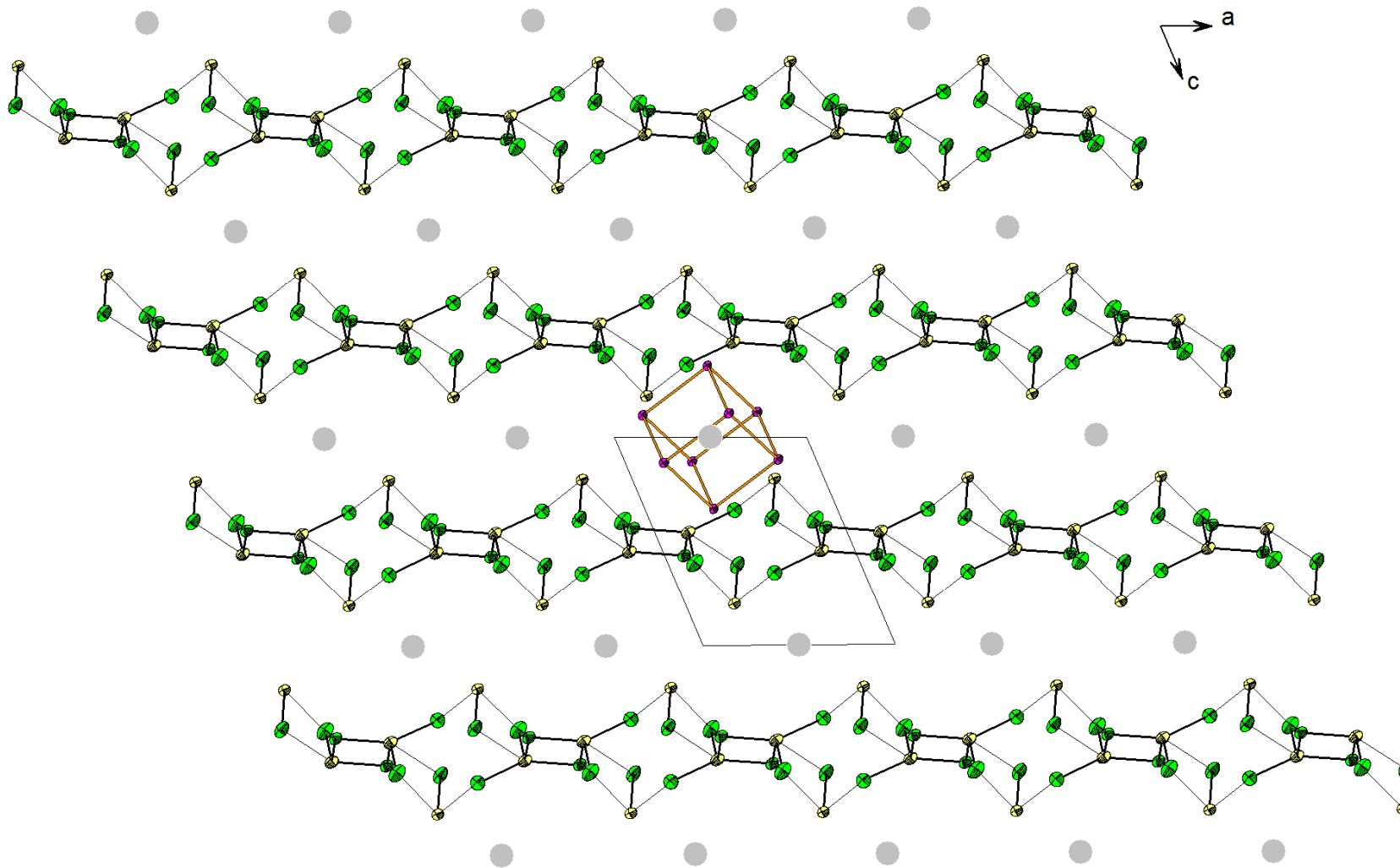


**Figure S8.** The array of  $[\text{Ti}_8\text{F}_{36}]^{4-}$  anions around selected cubic  $[\text{Ti}_8\text{F}_{36}]^{4-}$  anion in  $\text{K}_4\text{Ti}_8\text{F}_{36}\cdot 8\text{HF}$  (left) and  $\text{Rb}_4\text{Ti}_8\text{F}_{36}\cdot 6\text{HF}$  (right). Grey circles represent  $\text{Ti}_8\text{F}_{36}$  centroids.

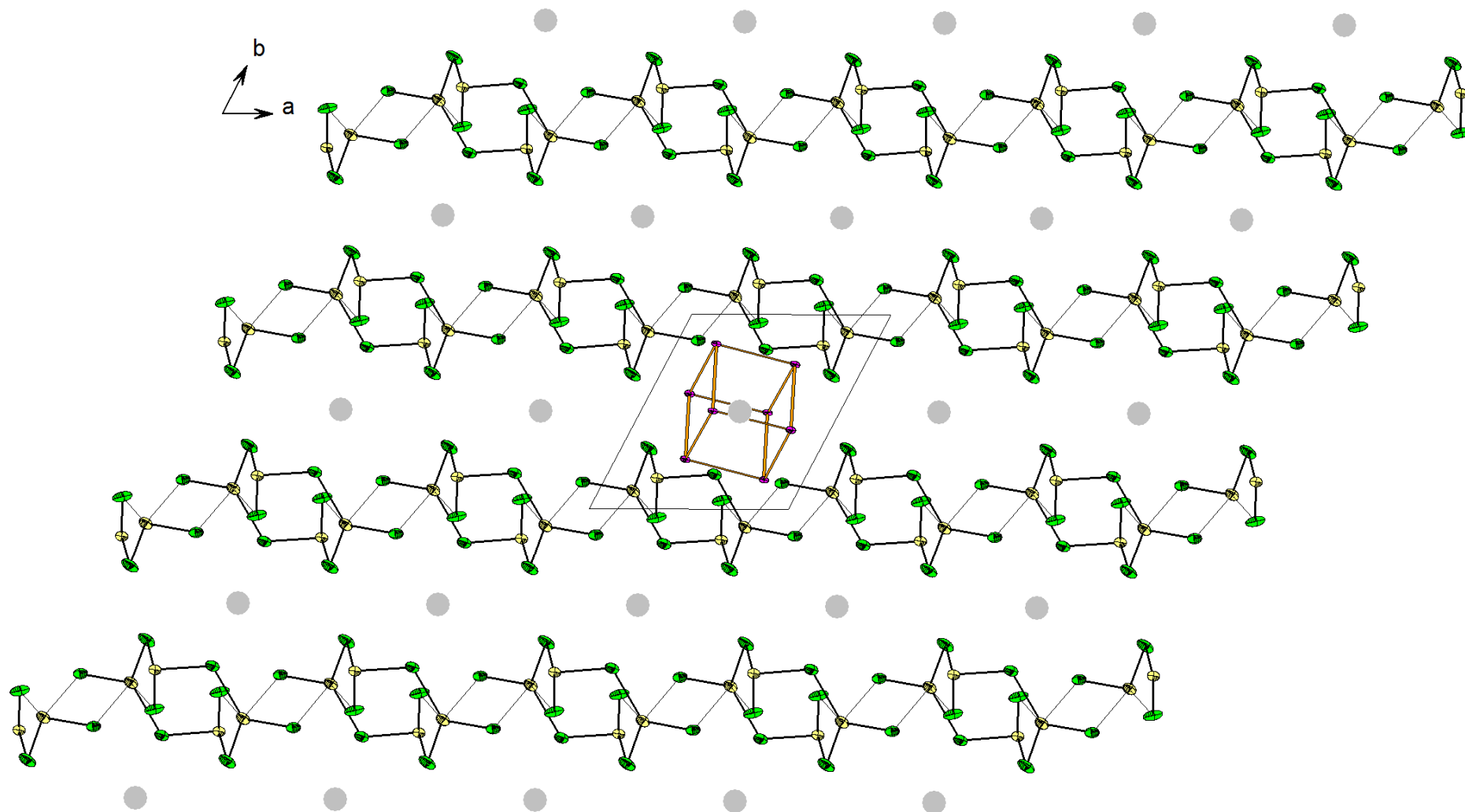


**Figure S9a.** Packing diagrams of  $K_4Ti_8F_{36} \cdot 8HF$ ; view along the  $a$ -axis; grey circles represent  $Ti_8F_{36}$  centroids; yellow circles = K cations; green circles = F atoms of HF molecules; for reasons of clarity H atoms are not shown; the violet cube shows the orientation of  $[Ti_8F_{36}]^{4-}$  anions; grey line = unit cell.

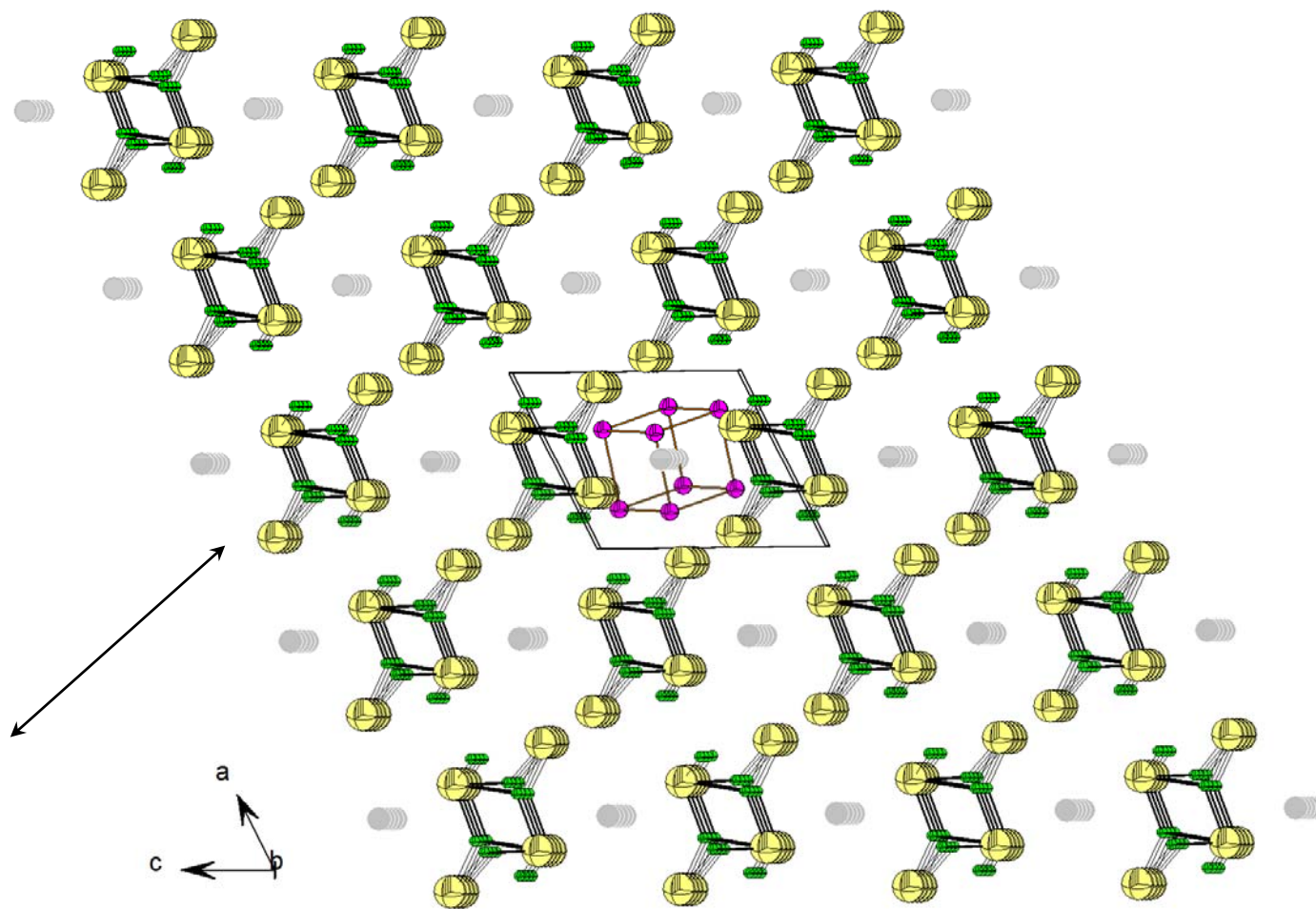




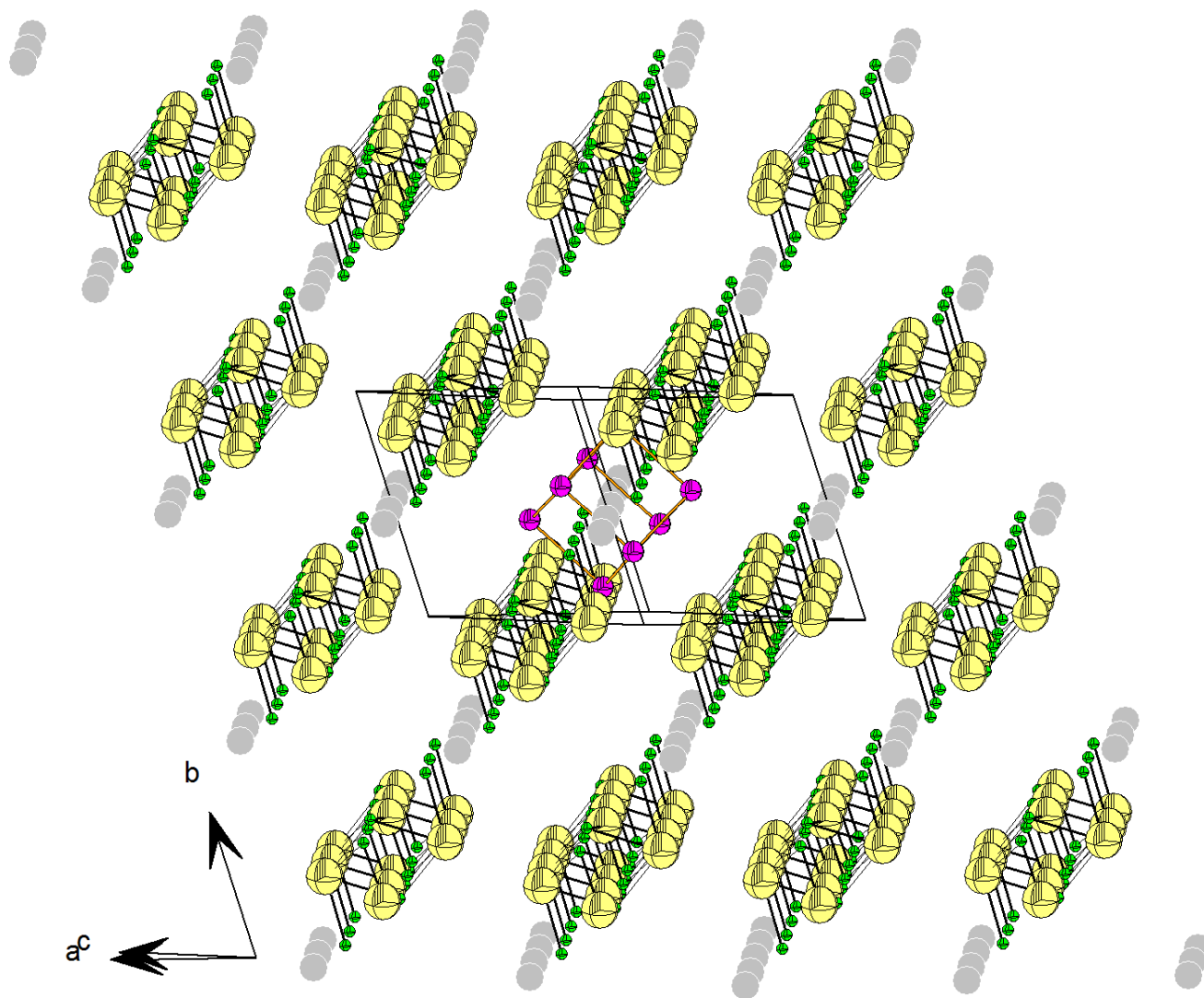
**Figure S9b.** Packing diagrams of  $\text{K}_4\text{Ti}_8\text{F}_{36}\cdot 8\text{HF}$ ; view along the *b*-axis; grey circles represent  $\text{Ti}_8\text{F}_{36}$  centroids; yellow circles = K cations; green circles = F atoms of HF molecules; for reasons of clarity H atoms are not shown; the violet cube shows the orientation of  $[\text{Ti}_8\text{F}_{36}]^{4-}$  anions; grey line = unit cell (ellipsoids are drawn at 50 % probability).



**Figure S9c.** Packing diagrams of  $\text{K}_4\text{Ti}_8\text{F}_{36}\cdot 8\text{HF}$ ; view along the *c*-axis; grey circles represent  $\text{Ti}_8\text{F}_{36}$  centroids; yellow circles = K cations; green circles = F atoms of HF molecules; for reasons of clarity H atoms are not shown; the violet cube shows the orientation of  $[\text{Ti}_8\text{F}_{36}]^{4-}$  anions; grey line = unit cell (ellipsoids are drawn at 50 % probability).



**Figure S10a.** Packing diagrams of  $\text{Rb}_4\text{Ti}_8\text{F}_{36} \cdot 6\text{HF}$ ; view along the  $b$ -axis; grey circles represent  $\text{Ti}_8\text{F}_{36}$  centroids; yellow circles = Rb cations; green circles = F atoms of HF molecules; for reasons of clarity H atoms are not shown; the violet cube shows the orientation of  $[\text{Ti}_8\text{F}_{36}]^{4-}$  anions; grey line = unit cell.



**Figure S10b.** Packing diagrams of  $\text{Rb}_4\text{Ti}_8\text{F}_{36} \cdot 6\text{HF}$ ; view along the  $b$ -axis; grey circles represent  $\text{Ti}_8\text{F}_{36}$  centroids; yellow circles =  $\text{Rb}$  cations; green circles =  $\text{F}$  atoms of  $\text{HF}$  molecules; for reasons of clarity  $\text{H}$  atoms are not shown; the violet cube shows the orientation of  $[\text{Ti}_8\text{F}_{36}]^{4-}$  anions; grey line = unit cell.

**Table S2.** List of the experimental strongest Raman bands (in-phase Ti–F<sub>terminal</sub> stretching frequencies) of various [Ti<sub>n</sub>F<sub>4n+x</sub>]<sup>x-</sup> anions and calculated charge/n(Ti) ratios

Wavenumber / cm <sup>-1</sup>	[Ti <sub>n</sub> F <sub>4n+x</sub> ] <sup>x-</sup> anion	Total charge x	Number of TiF <sub>6</sub> octahedra, n	Charge / [TiF <sub>6</sub> ] ratio x/n	Ref.
599-610	[TiF <sub>6</sub> ] <sup>2-</sup>	-2	1	-2	1,2
695	[Ti <sub>4</sub> F <sub>20</sub> ] <sup>4-</sup>	-4	4	-1	3
724	([TiF <sub>5</sub> ] <sup>-</sup> ) <sub>n</sub> <sup>a</sup>	-1	1	-1	4
741	[Ti <sub>5</sub> F <sub>23</sub> ] <sup>3-</sup>	-3	5	-0.6	3
742	[Ti <sub>4</sub> F <sub>19</sub> ] <sup>3-</sup>	-3	4	-0.75	5
745-747	[Ti <sub>4</sub> F <sub>18</sub> ] <sup>2-</sup>	-2	4	-0.5	6
755	[Ti <sub>8</sub> F <sub>36</sub> ] <sup>4-</sup>	-4	8	-0.5	This work
752-756	([Ti <sub>2</sub> F <sub>9</sub> ] <sup>-</sup> ) <sub>n</sub>	-1	2	-0.5	2,6
765	([Ti <sub>7</sub> F <sub>30</sub> ] <sup>2-</sup> ) <sub>n</sub>	-2	7	-0.29	7
770	[Ti <sub>3</sub> F <sub>13</sub> ] <sup>-</sup>	-1	3	-0.33	2
784	[Ti <sub>6</sub> F <sub>25</sub> ] <sup>-</sup>	-1	6	-0.17	2
807	TiF <sub>4</sub>	/	/	/	2

<sup>a</sup> The symbol "n" denotes polymeric infinite anions (chains, columns, layers, etc.)

- Ref.
- 1) W. von der Ohe, *J. Chem. Phys.* 1976, **65**, 3575.
  - 2) O. Christe, C.J. Schack, *Inorg. Chem.*, 1977, **16**, 353.
  - 3) I. M. Shlyapnikov, E.A. Goreshnik, H.P.A. Mercier, G.J. Schrobilgen, Z. Mazej, 20th International Symposium on Fluorine Chemistry, July 22, 2012, Kyoto, Japan, *Book of Abstracts* p. 112.
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  - 6) Z. Mazej and E. Goreshnik, *Inorg. Chem.*, 2009, **48**, 6918.
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