Strukturna arhitektura ternarnih titanovih(IV) fluoridov

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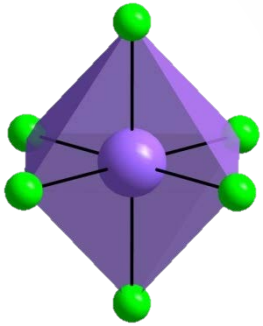
Poli[perfluoridotitanatne(IV)] spojine

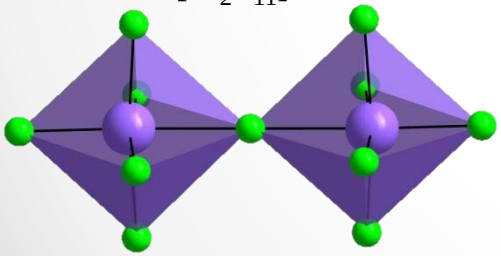
Ti atomi so koordinirani z 6 atomi fluora F

Dolžine Ti–F vezi: 1.70 – 2.00 Å

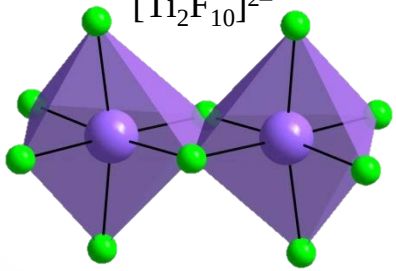


Oligomerni in polimerni anioni – skupni F atomi

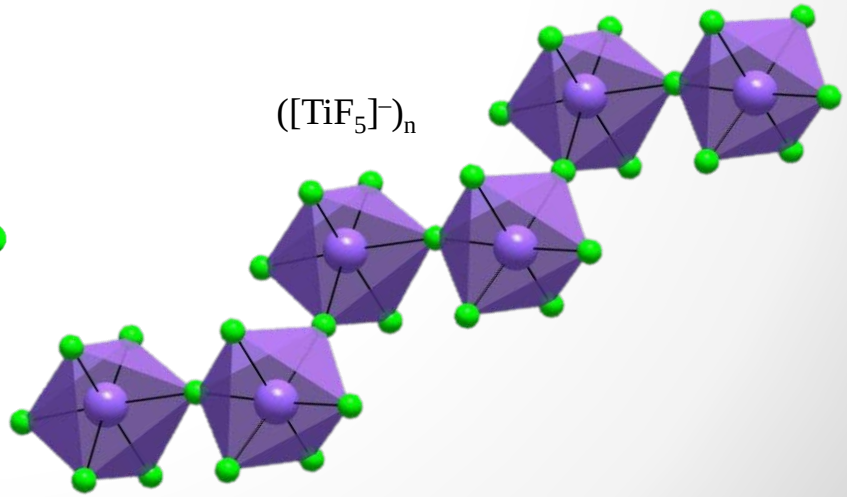
$[Ti_2F_{11}]^{3-}$



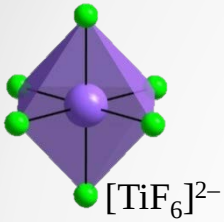
$[Ti_2F_{10}]^{2-}$



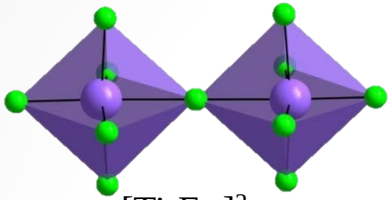
$([TiF_5]^-)_n$



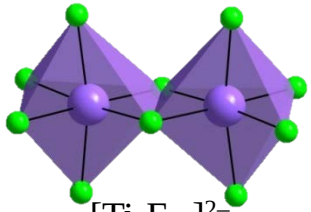
Strukturno okarakterizirane poli[perfluoridotitanatne(IV)] spojine



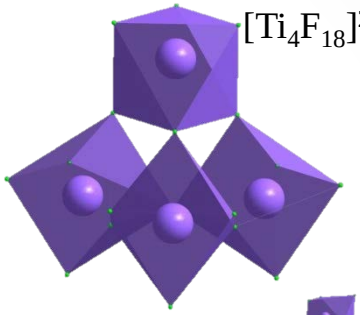
$[TiF_6]^{2-}$



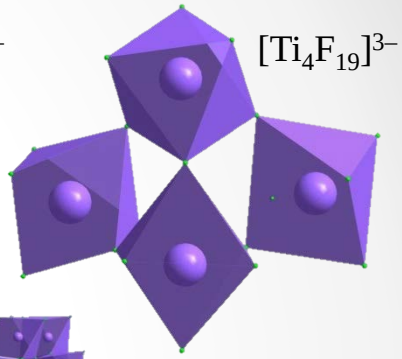
$[Ti_2F_{11}]^{3-}$



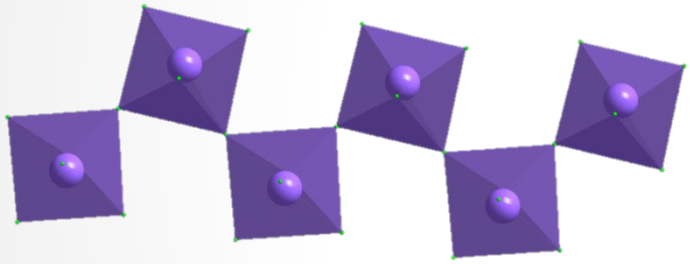
$[Ti_2F_{10}]^{2-}$



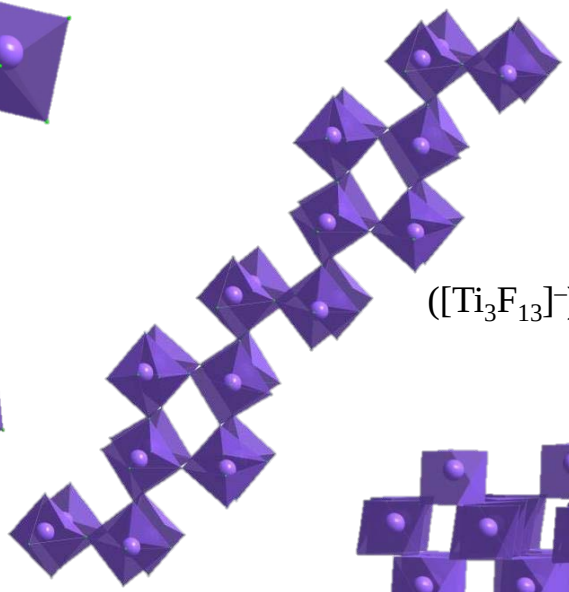
$[Ti_4F_{18}]^{2-}$



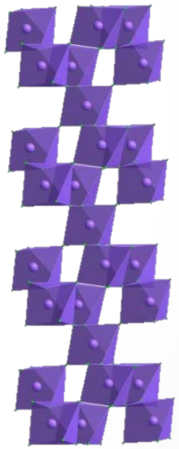
$[Ti_4F_{19}]^{3-}$



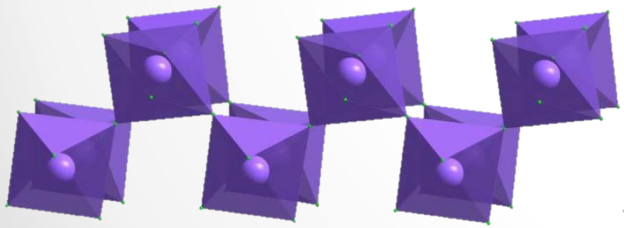
$([TiF_5]^-)_n$



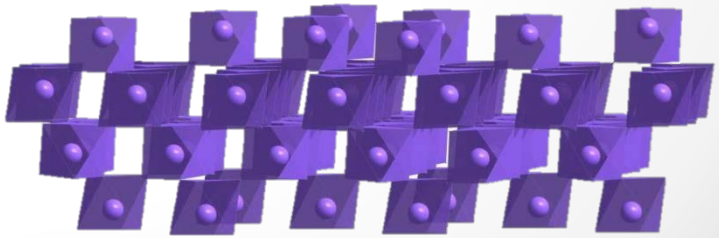
$([Ti_3F_{13}]^-)_n$



$([Ti_7F_{30}]^{2-})_n$



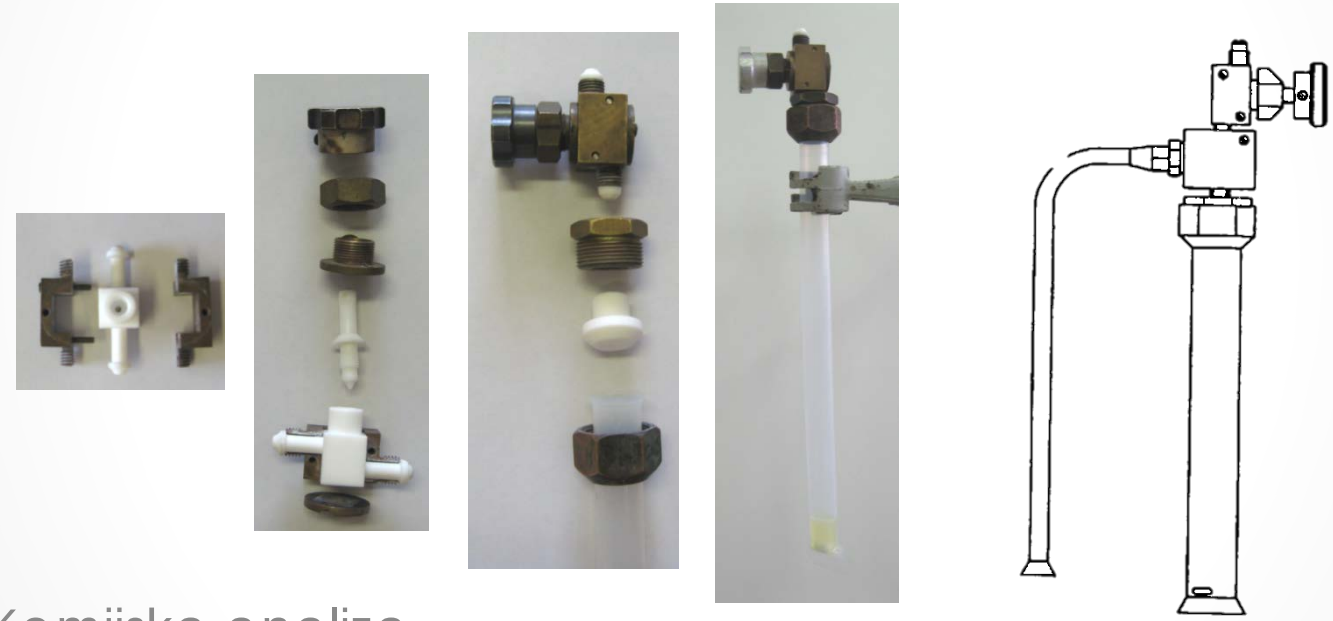
$([Ti_2F_9]^-)_n$



$([Ti_8F_{33}]^-)_n$

Sinteza in karakterizacija poli[perfluoridotitanatnih(IV)] spojin

1. $yA + xTiF_4 + (y+n)HF \rightarrow [AH]_y[Ti_xF_{4x+y}](\cdot nHF)$
2. $yAF + xTiF_4 (+ nHF) \rightarrow A_y[Ti_xF_{4x+y}](\cdot nHF)$



- Kemijska analiza
- Ramanska spektroskopija
- Rentgentska analiza (na monokristalih, praškovna)

Sinteza poli[perfluoridotitanatnih(IV)] spojin

- Alkali metals fluorides – TiF_4 – HF
- 1H-imidazole – TiF_4 – HF
- Guanidine hydrochloride – TiF_4 – HF
- 1,2-diaminoethane – TiF_4 – HF
- 1,3,5-triazine-2,4,6-triamine – TiF_4 – HF

Sinteza poli[perfluoridotitanatnih(IV)] spojin

$2\ AF + TiF_4 \rightarrow A_2TiF_6$ (Li_2TiF_6, Na_2TiF_6, K_2TiF_6, $K_2TiF_6 \cdot HF$, Rb_2TiF_6, Cs_2TiF_6)

$AF + TiF_4\ (+ HF) \rightarrow ATiF_5(\cdot HF)$ ($NaTiF_5(\cdot HF)$, $KTiF_5(\cdot HF)$, $RbTiF_5(\cdot HF)$, $CsTiF_5$)

$AF + 2\ TiF_4\ (+ HF) \rightarrow ATi_2F_9(\cdot HF)$ ali $\mathbf{A_4Ti_8F_{36} \cdot nHF}$

($NaTi_2F_9 \cdot HF$, $K_4Ti_8F_{36} \cdot 8HF$, $Rb_4Ti_8F_{36} \cdot 6HF$, $CsTi_2F_9$)

Sinteza poli[perfluoridotitanatnih(IV)] spojin

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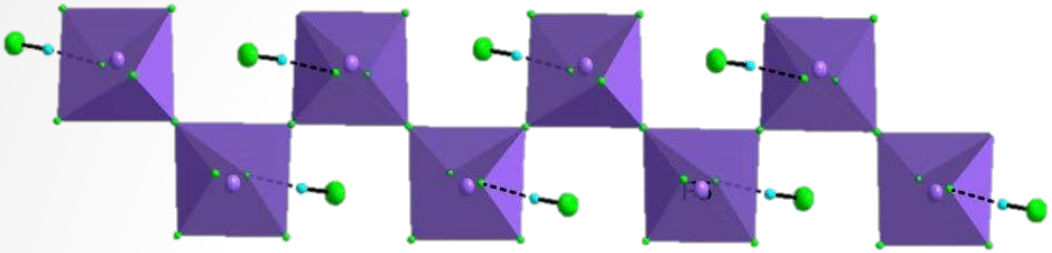
($NaTi_2F_9 \cdot HF$, $K_4Ti_8F_{36} \cdot 8HF$, $Rb_4Ti_8F_{36} \cdot 6HF$, $CsTi_2F_9$)

$ATiF_5 \cdot HF$

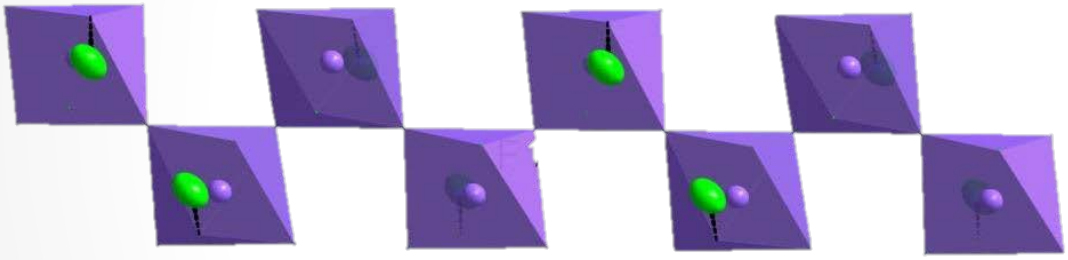
$AF + TiF_4 \ (+ HF) \rightarrow ATiF_5(\cdot HF)$

In bulk	Crystals with HF	Crystals without HF
$NaTiF_5$	$NaTiF_5 \cdot HF$	---
$KTiF_5$	$KTiF_5 \cdot HF$	$KTiF_5$
$RbTiF_5$	$RbTiF_5 \cdot HF$	*in progress*
$CsTiF_5$	---	$CsTiF_5$

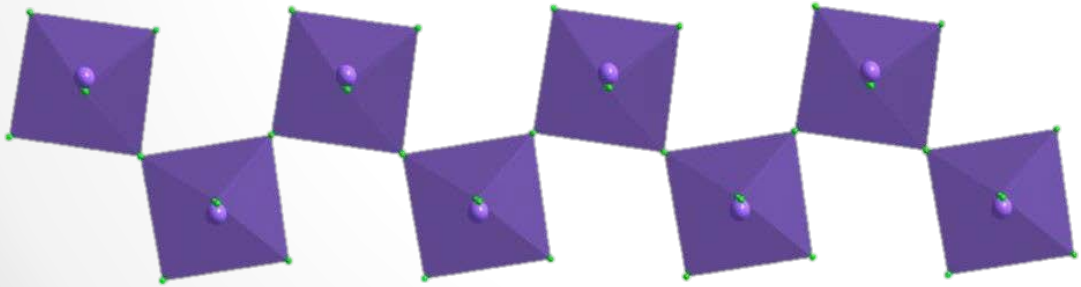
$ATiF_5 \cdot HF$



$NaTiF_5 \cdot HF$

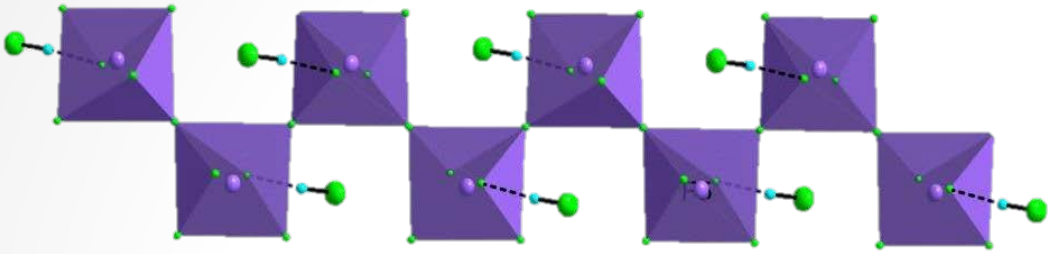


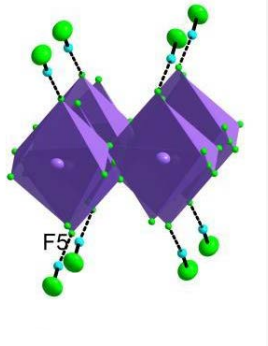
$KTiF_5 \cdot HF$
$RbTiF_5 \cdot HF$



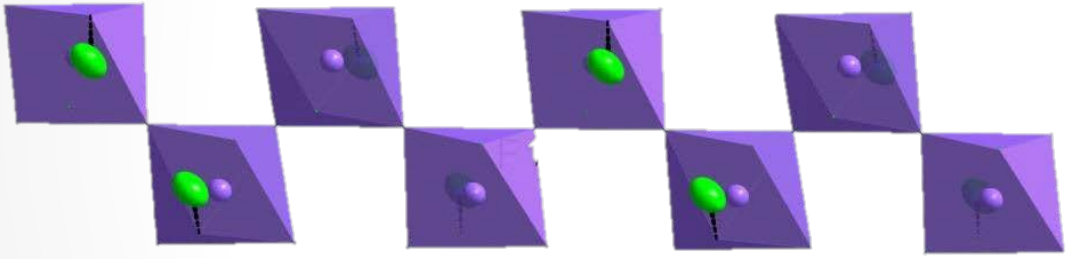
$CsTiF_5$

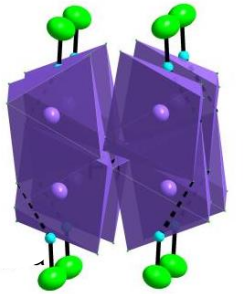
$ATiF_5 \cdot HF$



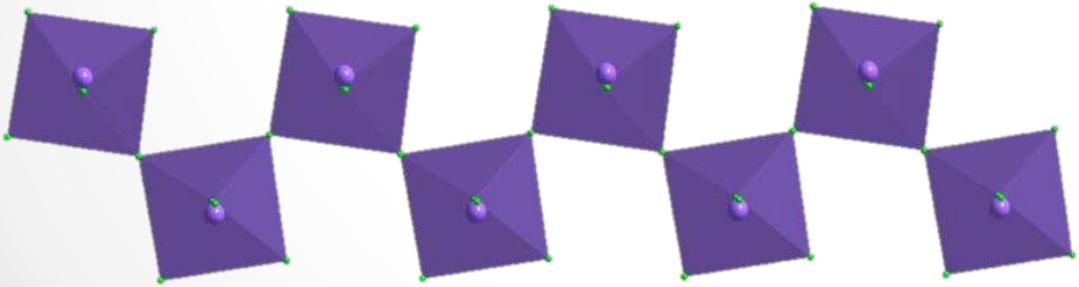


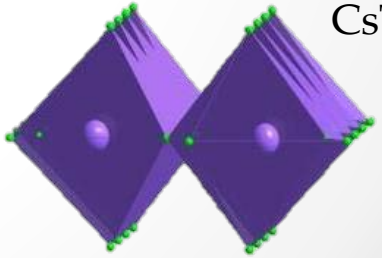
$NaTiF_5 \cdot HF$





$KTiF_5 \cdot HF$
$RbTiF_5 \cdot HF$





$CsTiF_5$

Sinteza poli[perfluoridotitanatnih(IV)] spojin

$2\ AF + TiF_4 \rightarrow A_2TiF_6$ (Li_2TiF_6, Na_2TiF_6, K_2TiF_6, $K_2TiF_6 \cdot HF$, Rb_2TiF_6, Cs_2TiF_6)

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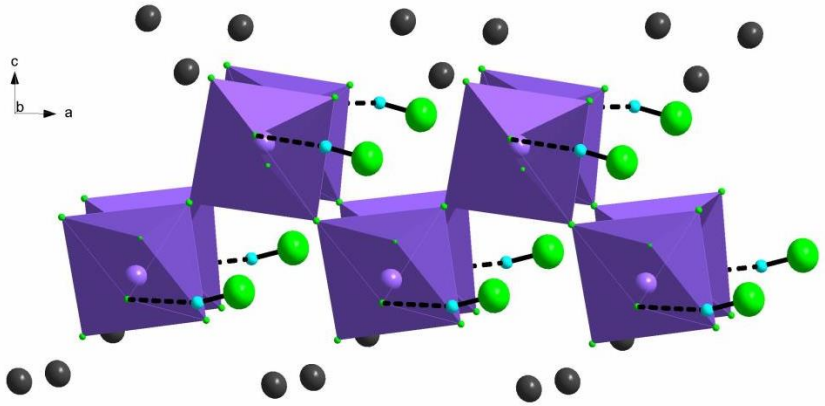
$AF + 2\ TiF_4\ (+ HF) \rightarrow ATi_2F_9(\cdot HF)$ ali $\mathbf{A_4Ti_8F_{36} \cdot nHF}$

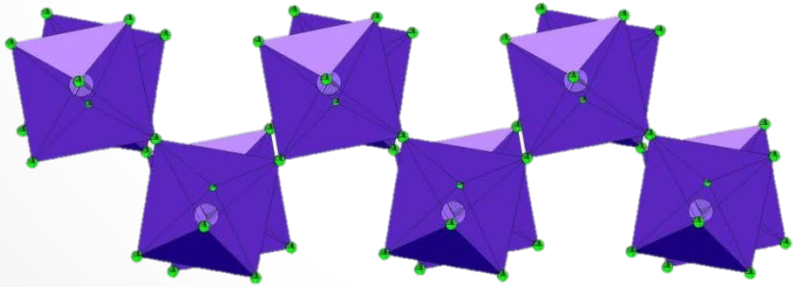
($NaTi_2F_9 \cdot HF$, $K_4Ti_8F_{36} \cdot 8HF$, $Rb_4Ti_8F_{36} \cdot 6HF$, $CsTi_2F_9$)

$NaTi_2F_9 \cdot HF$ in $CsTi_2F_9$

$AF + 2TiF_4 \ (+ HF) \rightarrow ATi_2F_9(\cdot HF)$



$NaTi_2F_9 \cdot HF$

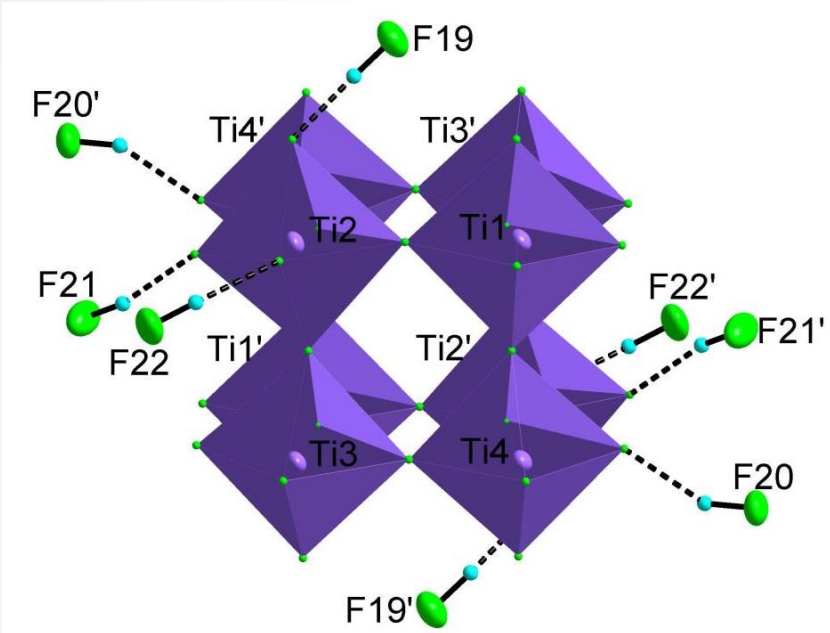


$CsTi_2F_9$*

*Z. Mazej, E. Goreshnik, *Inorg. Chem.*, **2009**, *48*, 6918-6923.

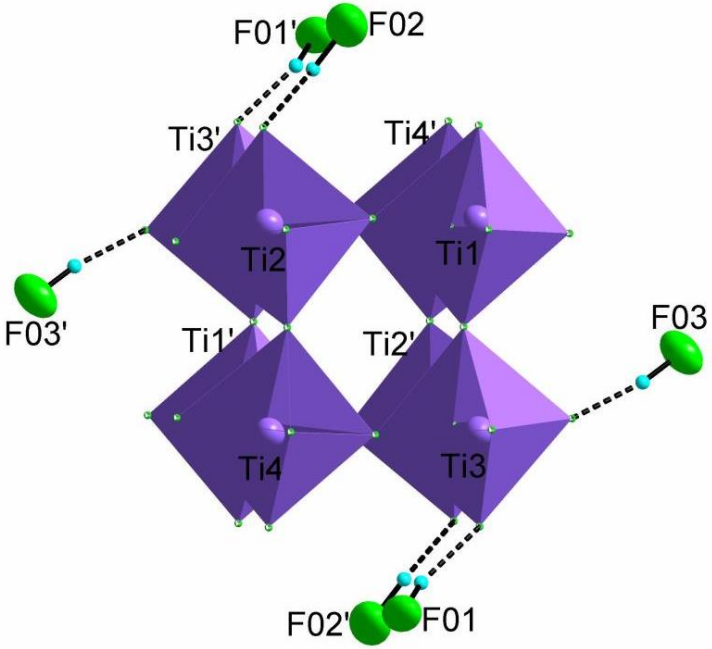
$K_4Ti_8F_{36}\cdot 8HF$ in $Rb_4Ti_8F_{36}\cdot 6HF$

$4\ KF + 8\ TiF_4 + 8\ HF \rightarrow K_4Ti_8F_{36}\cdot 8HF$



Space group	P−1
a (Å)	10.2054(7)
b (Å)	10.3448(1)
c (Å)	10.5896(2)
α (°)	79.81(1)
β (°)	65.21(1)
γ (°)	60.89(1)
V (Å³)	886.2(1)
Z	1
T (K)	200

$4\ RbF + 8\ TiF_4 + 6\ HF \rightarrow Rb_4Ti_8F_{36}\cdot 6HF$



Space group	P−1
a (Å)	10.199(1)
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c (Å)	10.5848(7)
α (°)	89.68(6)
β (°)	66.41(5)
γ (°)	64.17(4)
V (Å³)	908.2(7)
Z	1
T (K)	200

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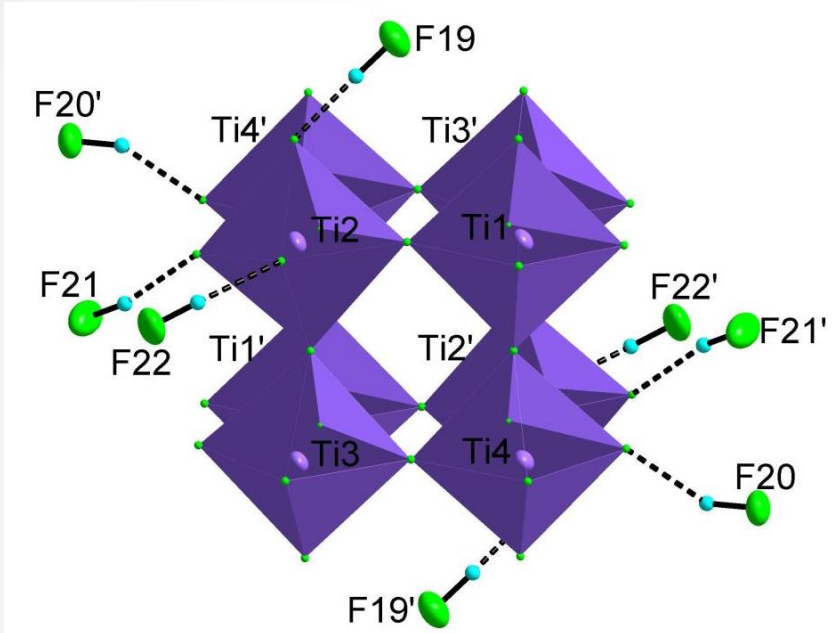
Chem. Comm., **2013**, *49*, 2703-2705

$K_4Ti_8F_{36}\cdot 8HF$ in $Rb_4Ti_8F_{36}\cdot 6HF$

$4\ KF + 8\ TiF_4 + 8\ HF \rightarrow K_4Ti_8F_{36}\cdot 8HF$



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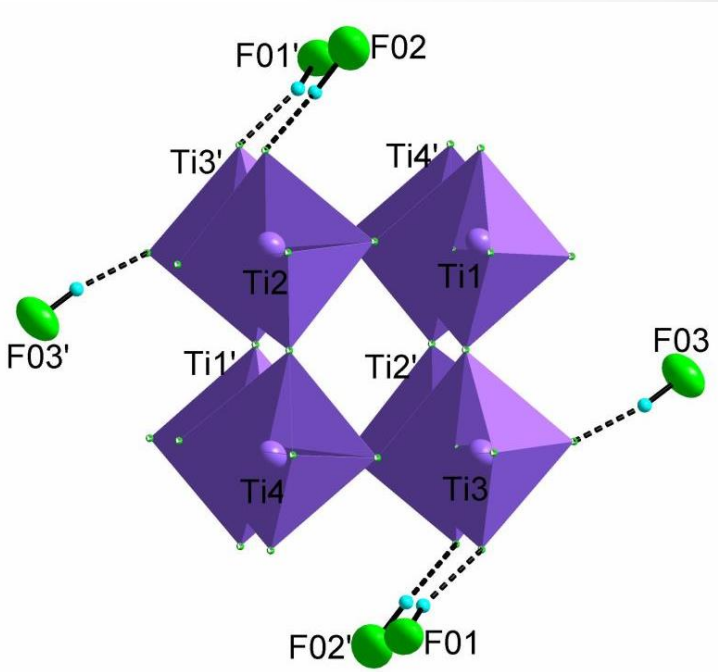
$4\ RbF + 8\ TiF_4 + 6\ HF \rightarrow Rb_4Ti_8F_{36}\cdot 6HF$



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γ (°)	64.17(4)
V (Å³)	908.2(7)
Z	1
T (K)	200

I.M. Shlyapnikov, E.A. Goreshnik, Z. Mazej
Chem. Comm., **2013**, *49*, 2703-2705

$K_4Ti_8F_{36}\cdot 8HF$ in $Rb_4Ti_8F_{36}\cdot 6HF$

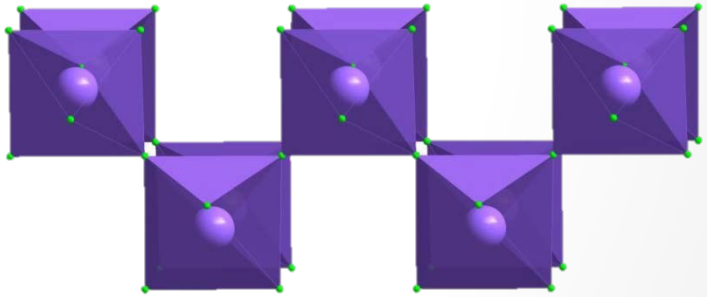
$K_4Ti_8F_{36}\cdot 8HF \rightarrow$ „$K_3[Ti_6F_{27}]$“

$Rb_4Ti_8F_{36}\cdot 6HF \rightarrow$ „$RbTi_2F_9\cdot HF$“

$K_4Ti_8F_{36}\cdot 8HF$ in $Rb_4Ti_8F_{36}\cdot 6HF$

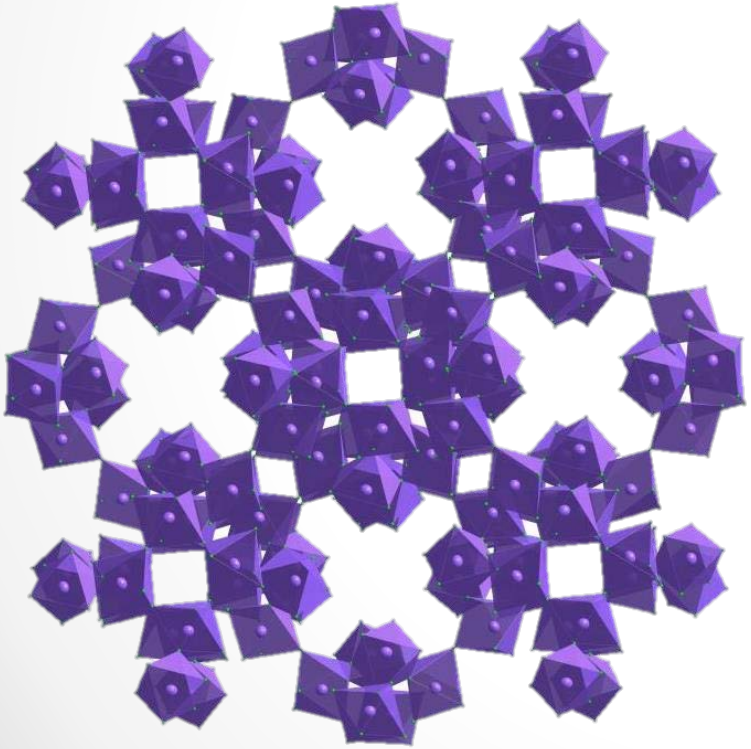
$K_4Ti_8F_{36}\cdot 8HF \rightarrow$ „$K_3[Ti_6F_{27}]$“

$Rb_4Ti_8F_{36}\cdot 6HF \rightarrow$ „$RbTi_2F_9\cdot HF$“

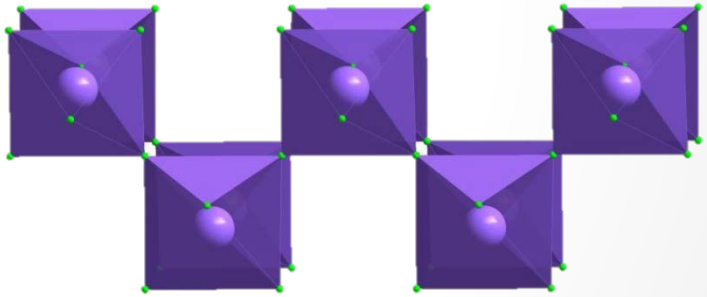


$K_4Ti_8F_{36}\cdot 8HF$ in $Rb_4Ti_8F_{36}\cdot 6HF$

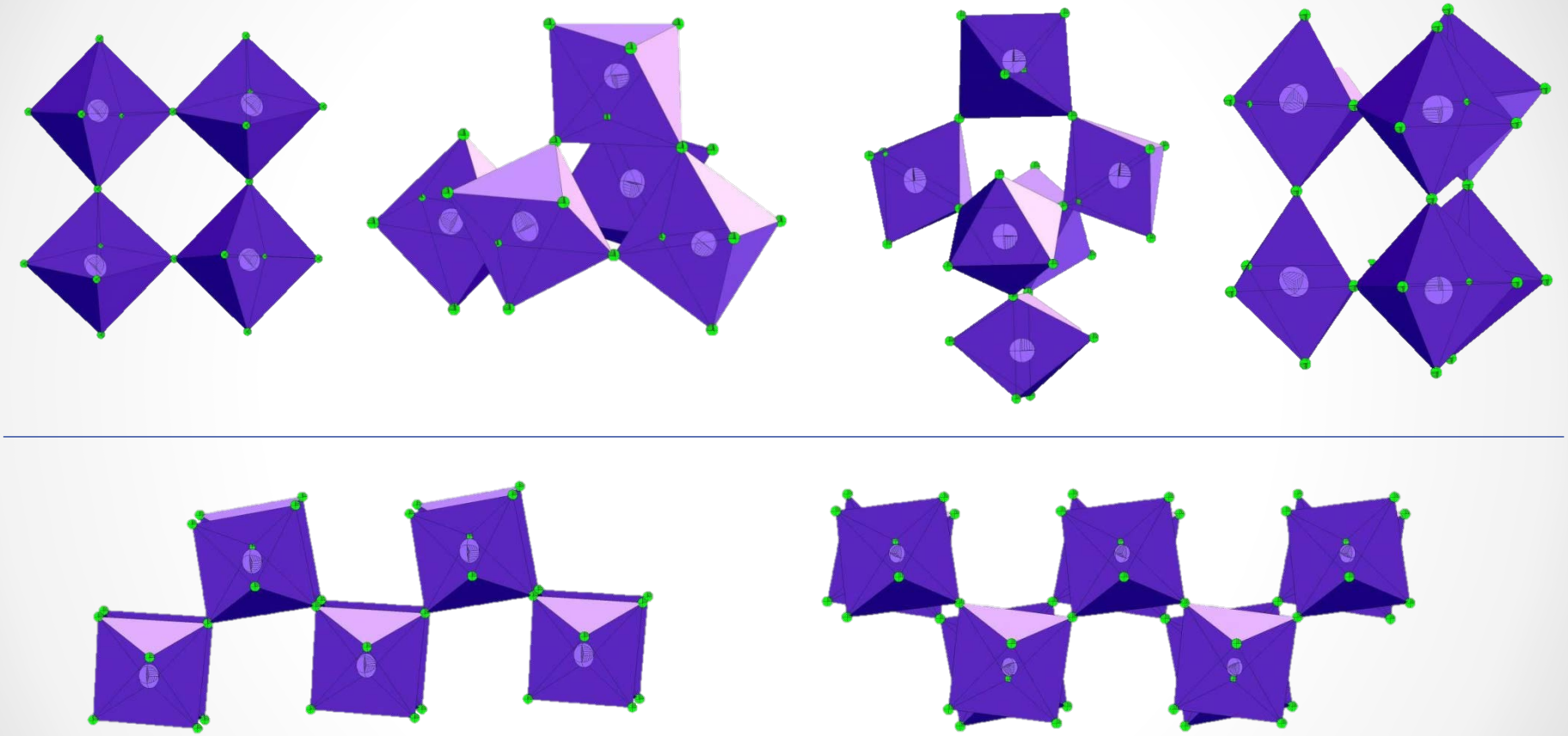
$K_4Ti_8F_{36}\cdot 8HF \rightarrow$ „$K_3[Ti_6F_{27}]$“



$Rb_4Ti_8F_{36}\cdot 6HF \rightarrow$ „$RbTi_2F_9\cdot HF$“

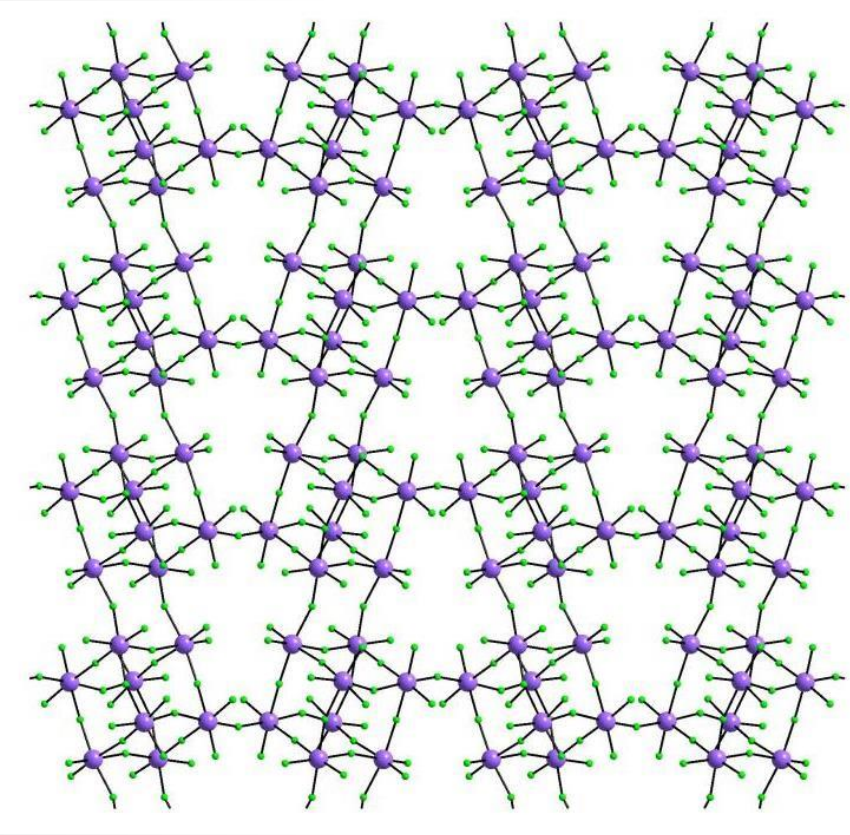


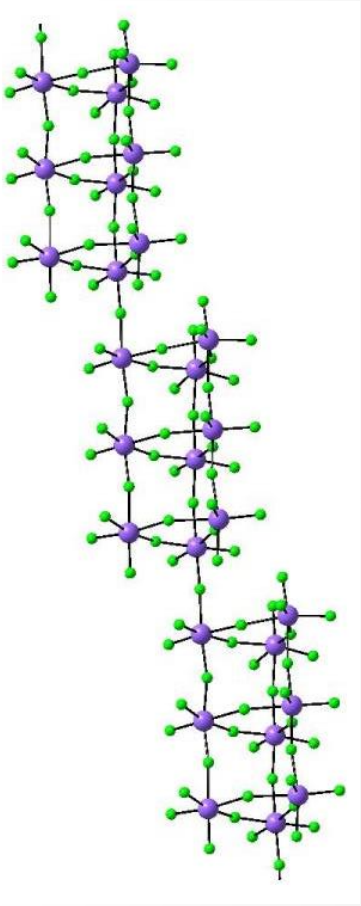
Druge zanimive poli[perfluoridotitanatne(IV)] spojine



I.M. Shlyapnikov, H.P.A. Mercier, E.A. Goreshnik, G.J. Schrobilgen, Z. Mazej *Inorg. Chem.*, **2013**, *52*, 8315-8326

Druge zanimive poli[perfluoridotitanatne(IV)] spojine





K. Radan, E. Goreshnik, B. Žemva *Angew. Chem. Int. Ed.*, **2014**, *53*, 13715–13719.

Zaključek

- Sintetiziranih 19 novih perfluoridotitanatnih spojin, ki vsebujejo doslej neznane fluoridotitanatne anione.

- Molsko razmerje reaktantov in vgradnja molekul HF v kristalno strukturo bistveno vplivata na nastanek različnih fluoridotitanatnih anionov.

Zahvale

- Javna Agencija za Raziskovalno Dejavnost RS

- dr. Zoran Mazej
- doc. dr. Gašper Tavčar
- doc. dr. Evgeny Goreshnik
- dr. Hélène P.A. Mercier
- prof. dr. Gary J. Schrobilgen
- doc. dr. Maja Ponikvar-Svet
- Mira Zupančič
- Robert Moravec
- Kristian Radan

- Vsi sodelavci odseka za Anorgansko Kemijo in Tehnologijo instituta „Jožef Stefan“.

Ramanska spektroskopija

Wavenumber / cm^{-1}	$[Ti_nF_{4n+x}]^{x-}$ anion	Total charge *x*	Number of TiF_6 octahedra, *n*	Charge /$[TiF_6]$ ratio *x*/*n*
599-610	$[TiF_6]^{2-}$	-2	1	-2
695	$[Ti_4F_{20}]^{4-}$	-4	4	-1
724	$([TiF_5]^-)_n$	-1	1	-1
741	$[Ti_5F_{23}]^{3-}$	-3	5	-0.6
742	$[Ti_4F_{19}]^{3-}$	-3	4	-0.75
745-747	$[Ti_4F_{18}]^{2-}$	-2	4	-0.5
755	$[Ti_8F_{36}]^{4-}$	-4	8	-0.5
752-756	$([Ti_2F_9]^-)_n$	-1	2	-0.5
765	$([Ti_7F_{30}]^{2-})_n$	-2	7	-0.29
770	$[Ti_3F_{13}]^-$	-1	3	-0.33
784	$[Ti_6F_{25}]^-$	-1	6	-0.17
807	TiF_4	/	/	/