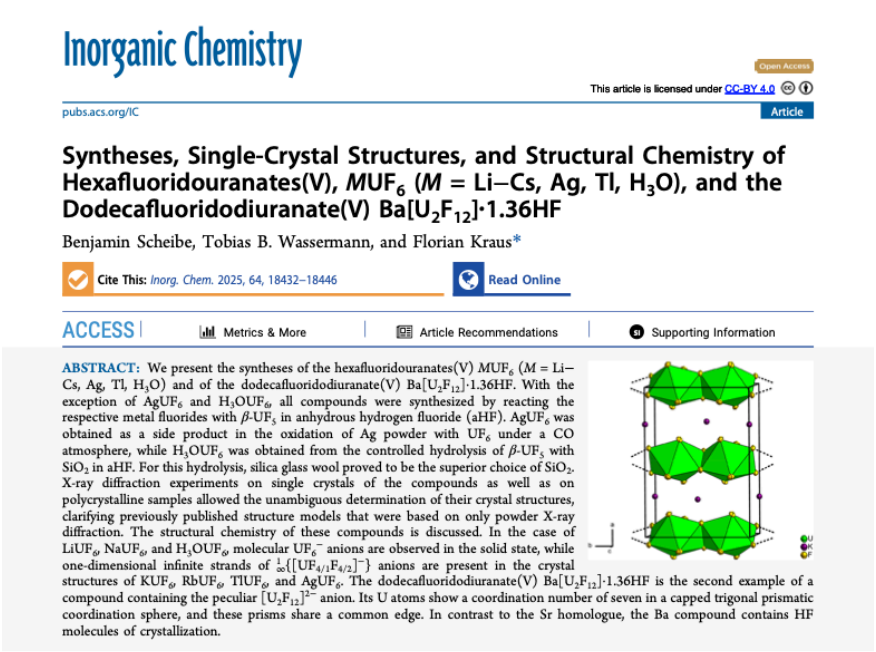
Synthesis & Structure of Hexafluoridouranates(V)

Lena-Marie Aßmann, Timo Wolf
Supervised by: Jun. Prof. Dr. Suta

28th November 2025

Where can I read about that?

Heinrich Heine Universität Düsseldorf



Inorganic Chemistry

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Article

Syntheses, Single-Crystal Structures, and Structural Chemistry of Hexafluoridouranates(V), MUF_6 (M = Li–Cs, Ag, Tl, H_3O), and the Dodecafluoridodiuranate(V) $Ba[U_2F_{12}]\cdot 1.36HF$

Benjamin Scheibe, Tobias B. Wassermann, and Florian Kraus*

Cite This: *Inorg. Chem.* 2025, 64, 18432–18446

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ABSTRACT: We present the syntheses of the hexafluoridouranates(V) MUF_6 (M = Li–Cs, Ag, Tl, H_3O) and of the dodecafluoridodiuranate(V) $Ba[U_2F_{12}]\cdot 1.36HF$. With the exception of $AgUF_6$ and H_3OUF_6, all compounds were synthesized by reacting the respective metal fluorides with β-UF_5 in anhydrous hydrogen fluoride (aHF). $AgUF_6$ was obtained as a side product in the oxidation of Ag powder with UF_6 under a CO atmosphere, while H_3OUF_6 was obtained from the controlled hydrolysis of β-UF_5 with SiO_2 in aHF. For this hydrolysis, silica glass wool proved to be the superior choice of SiO_2. X-ray diffraction experiments on single crystals of the compounds as well as on polycrystalline samples allowed the unambiguous determination of their crystal structures, clarifying previously published structure models that were based on only powder X-ray diffraction. The structural chemistry of these compounds is discussed. In the case of $LiUF_6$, $NaUF_6$, and H_3OUF_6, molecular UF_6^- anions are observed in the solid state, while one-dimensional infinite strands of $^1_\infty\{[UF_{4/1}F_{4/2}]^-\}$ anions are present in the crystal structures of KUF_6, $RbUF_6$, $TlUF_6$, and $AgUF_6$. The dodecafluoridodiuranate(V) $Ba[U_2F_{12}]\cdot 1.36HF$ is the second example of a compound containing the peculiar $[U_2F_{12}]^{2-}$ anion. Its U atoms show a coordination number of seven in a capped trigonal prismatic coordination sphere, and these prisms share a common edge. In contrast to the Sr homologue, the Ba compound contains HF molecules of crystallization.

[1] B. Scheibe, T. B. Wassermann, F. Kraus, *Inorg. Chem*. **2025**, *64*, 18432–18446.

What are Hexafluoridourantes(V)?

How to synthesize these compounds?

What is the structure of these compounds and

how are the structures connected?

Concepts / Methods

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Universität Düsseldorf

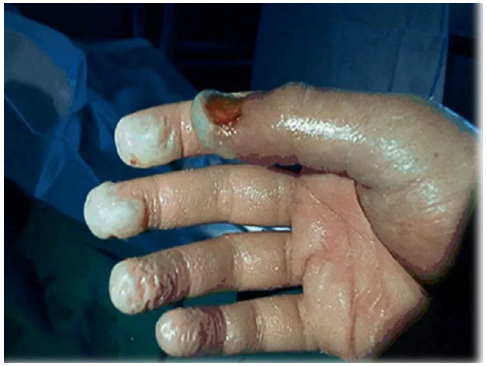
Working with anhydrous HF

Uranium-chemistry

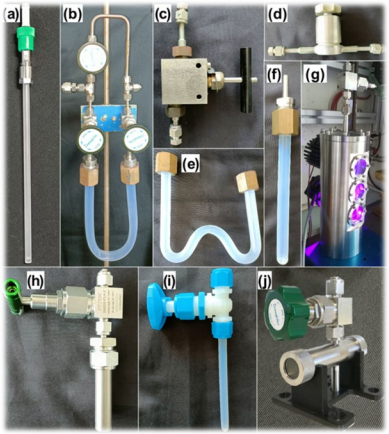
Working with anhydrous HF

$$4\ HF + SiO_2 \longrightarrow SiF_4 + 2\ H_2O$$

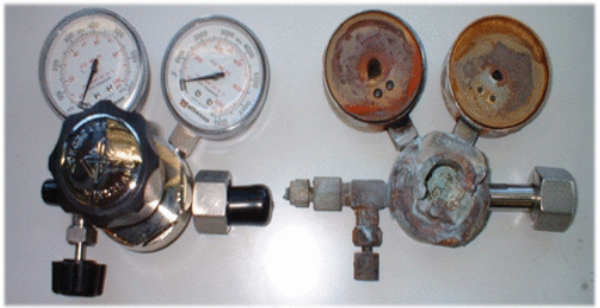
HF is very toxic!



Glass vessels can‘t be used!



Passivation & baking out is needed!



[2] M. Möbs, F. Kraus, *ACS Chem. Health Saf.* **2025**, *32*, 662–672.
[3] https://environnement.prevor.com/de/flusssaeure-und-fluoride-massnahmen-zur-begrenzung-der-exposition/, Last accessed: 19th November 2025

Concepts / Methods

Heinrich Heine
Universität Düsseldorf

Working with anhydrous HF

[II]

Uranium-chemistry

Alkali metals

[5] https://4.bp.blogspot.com/-ZaAMy38xBqU/W_aAPyr9FyI/AAAAAAAAAxA/-U_3th-3_UAswxsi9KvkYeKabKzFRGc2ACLcBGAs/s1600/alkali%2Bmetals.jpg , last accessed 23th November 2025

Synthesis of alkali metal Hexafluoridouranates(V) MUF$_6$

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Universität Düsseldorf

Synthesis of β-UF$_5$:

$$UF_6 + 0.5\ CO \xrightarrow{hv} \beta\text{-}UF_5 + 0.5\ COF_2$$

Properties: tetragonal symmetry, $I\bar{4}2d$ (No. 122)

Synthesis of MUF$_6$:

$$\beta\text{-}UF_5(s) + MF(solv) \xrightarrow[aHF(l)]{} MUF_6(solv)$$

M = Li - Cs

[6] G. W. Halstead, G. P. Eller, R. T. Paine, Inorganic Synthesis, Wiley VCH, New Jersey, 1982, pp 162−167.

Structural chemistry of $LiUF_6$

trigonal
$R\bar{3}$ (No. 148)

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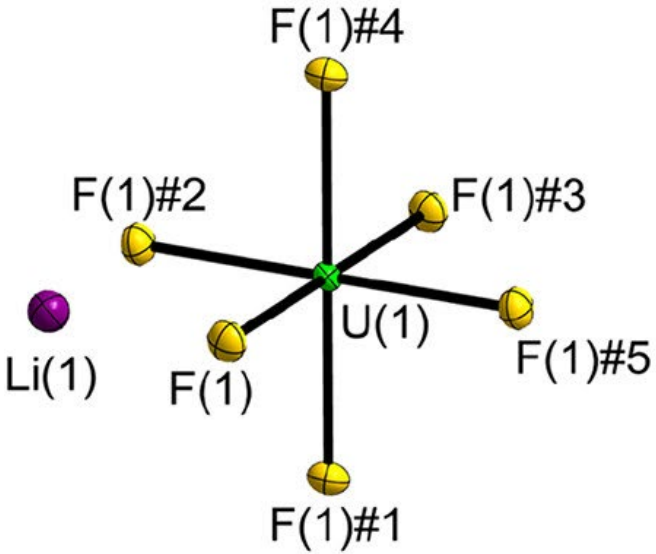

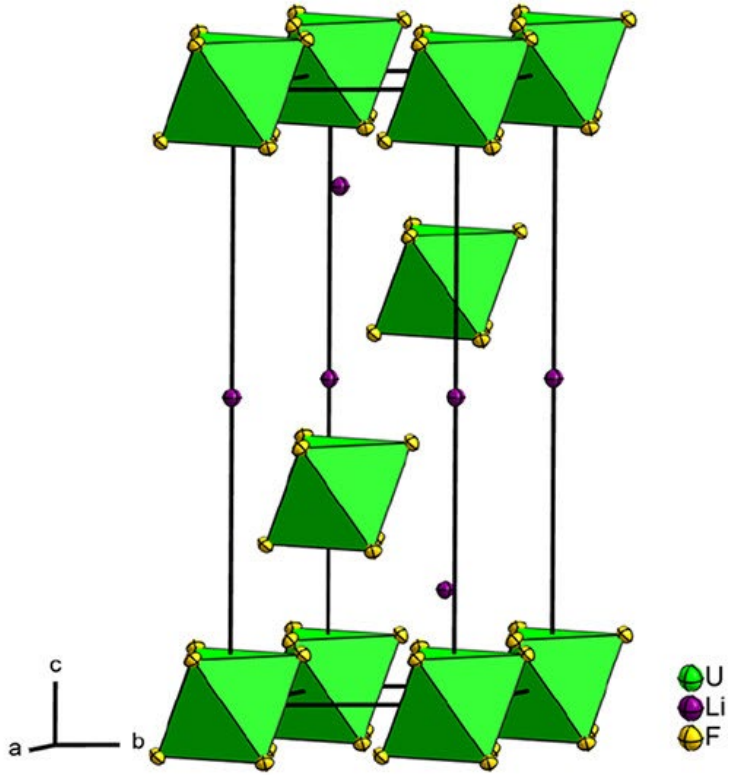

[1] B. Scheibe, T. B. Wassermann, F. Kraus, *Inorg. Chem.* **2025**, *64*, 18432–18446. Supporting Information

Structural chemistry of $NaUF_6$ & $CsUF_6$

trigonal
$R\bar{3}$ (No. 148)

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	$LiUF_6$	$NaUF_6$	$CsUF_6$
a [Å]	5.1902	5.4101	8.0284
b [Å]	14.265	15.746	8.4388
V [Å^3]	332.78	399.12	471.05
V/Z [Å^3]	110.93	133.04	157.02

	$LiUF_6$	$NaUF_6$	$CsUF_6$
d(U-F) [Å]	2.0624	2.0661	2.057
d(M-F) [Å]	2.0061	2.2768	
d(U-U) [Å]	5.1902	6.1078	5.1732

[1] B. Scheibe, T. B. Wassermann, F. Kraus, *Inorg. Chem.* **2025**, *64*, 18432–18446. Supporting Information

Structural chemistry of KUF_6

monoclinic
$C2/m$ (No. 12)

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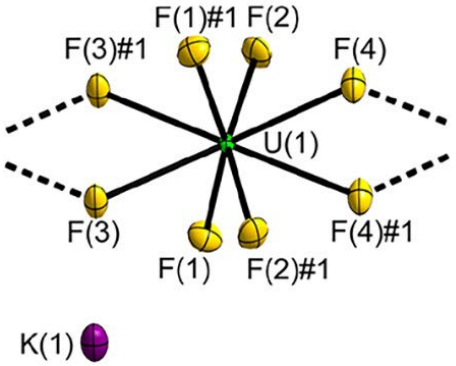

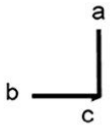

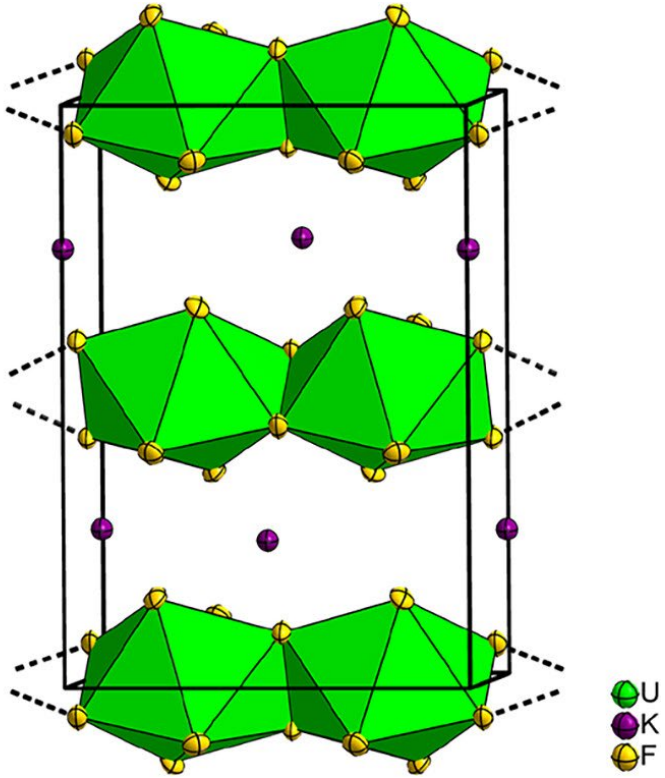

[1] B. Scheibe, T. B. Wassermann, F. Kraus, *Inorg. Chem.* **2025**, *64*, 18432–18446. Supporting Information

Structural chemistry of $RbUF_6$

monoclinic
$C2/m$ (No. 12)

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Universität Düsseldorf

	KUF_6	$RbUF_6$
a [Å]	11.442	11.797
b [Å]	8.0345	8.0167
c [Å]	5.5655	5.7272
β [°]	90.128	90.00
V [Å^3]	511.62	541.64
V/Z [Å^3]	127.905	135.41

	KUF_6	$RbUF_6$
d(U(1)-F(1)) [Å]	2.0633	2.0600
d(U(1)-F(2)) [Å]	2.0635	2.0573
d(U(1)-F(3)) [Å]	2.3400	2.3286
d(U(1)-F(4)) [Å]	2.3403	2.3286
d(U(1)-U(1)#1) [Å]	4.0102	4.0019
d(U(1)-U(1)#2) [Å]	4.0243	4.0148

[1] B. Scheibe, T. B. Wassermann, F. Kraus, *Inorg. Chem.* **2025**, *64*, 18432–18446. Supporting Information

Usage of alkali metal analogus

monoclinic
$C2/m$ (No. 12)

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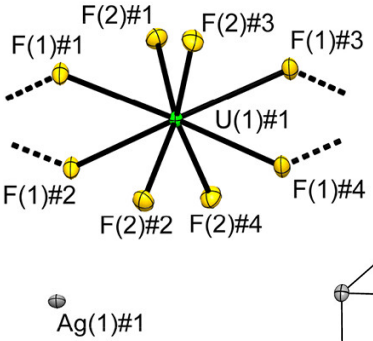
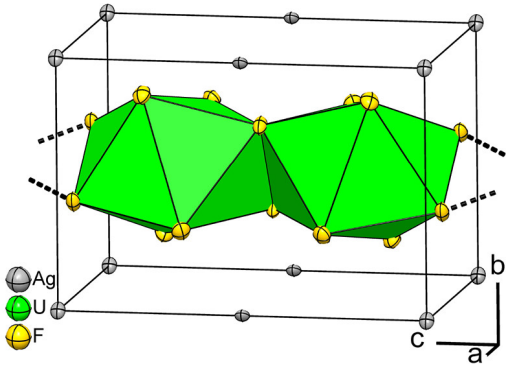
$AgUF_6$

Byproduct of a reaction

$$Ag + UF_6 \xrightarrow[aHF]{} AgUF_6$$





tetragonal
$P4_2/m$ (No. 84)

$TlUF_6$

1) Solid-state reaction

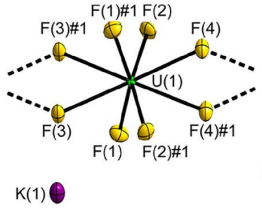
$$TlF_{(s)} + UF_{5(s)} \longrightarrow TlUF_{6(s)}$$

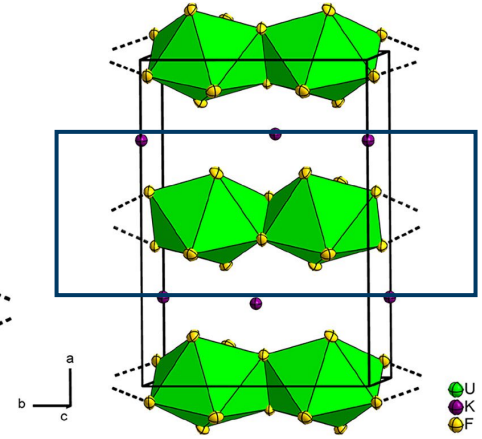
2) Preparation in solution

$$UF_{5(s)} + TlF_{(solv)} \xrightarrow[aHF]{} TlUF_{6(solv)}$$

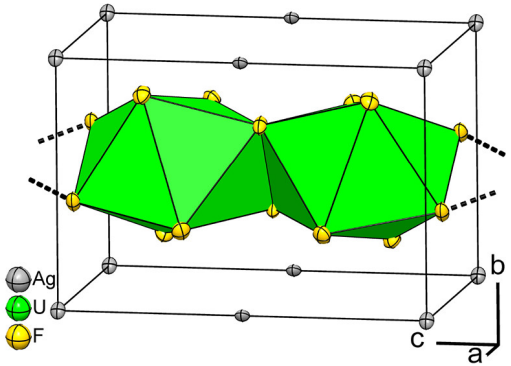
Isotypic to KUF_6!

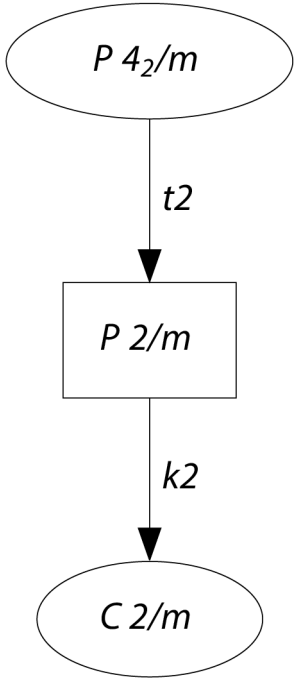
But: Shorter U-F-bond length, shorter U-U-distances

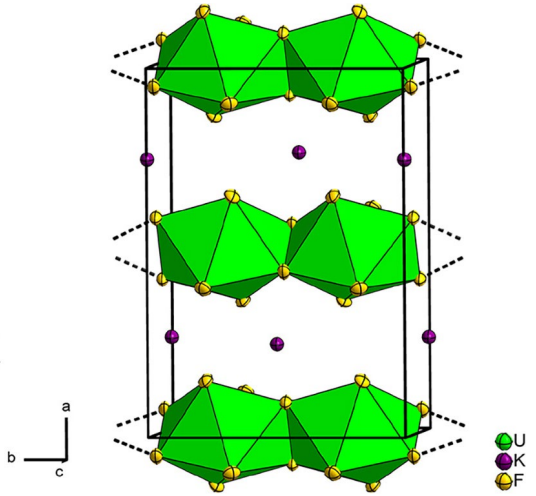




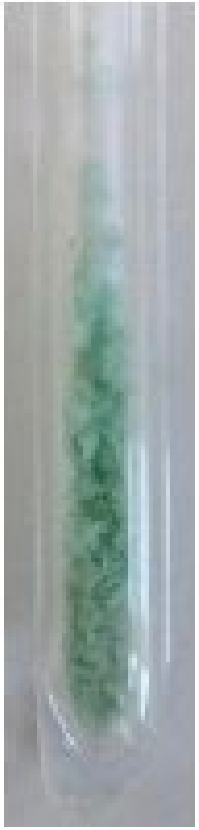
Relationship $AgUF_6$ & KUF_6

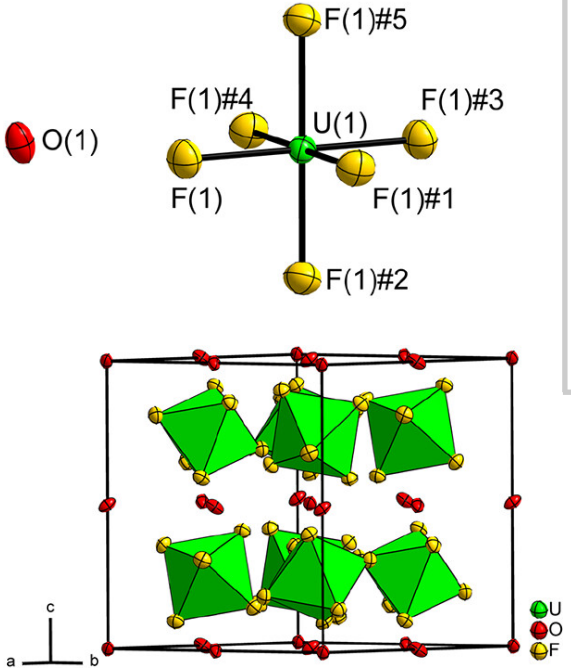






Structural chemistry



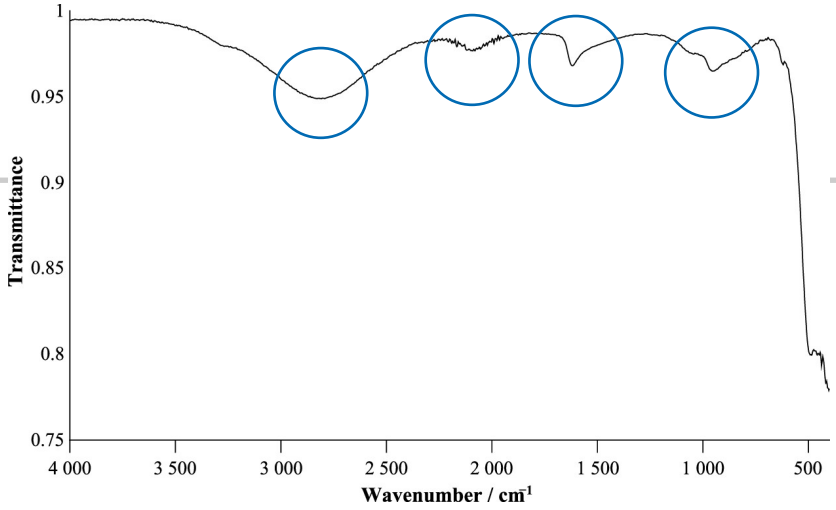


Cubic
$Ia\bar{3}$ (No. 206)

Synthesis of H_3OUF_6

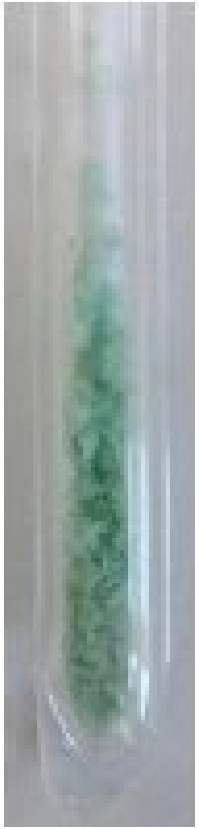
How to use water without usage of water?

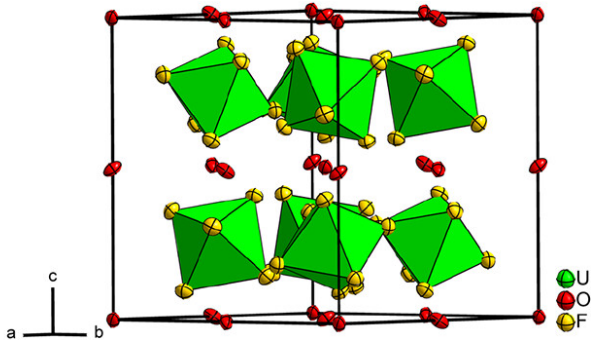
$$SiO_{2(s)} + 6\ HF \xrightarrow[aHF]{} 2\ H_3OF_{(solv)} + SiF_{4(g)}$$

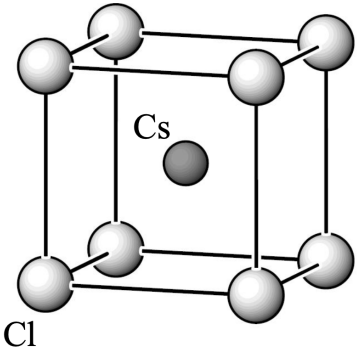


[1] B. Scheibe, T. B. Wassermann, F. Kraus, *Inorg. Chem.* **2025**, *64*, 18432–18446. Supporting Information

Structural chemistry







$P4/m\bar{3}2/m$ (Nr. 221)

CsCl

t2

$P2/m\bar{3}$ (Nr. 200)

k4

$2\boldsymbol{a}, 2\boldsymbol{b}, 2\boldsymbol{c}$

$-1/2, -1/2, -1/2$

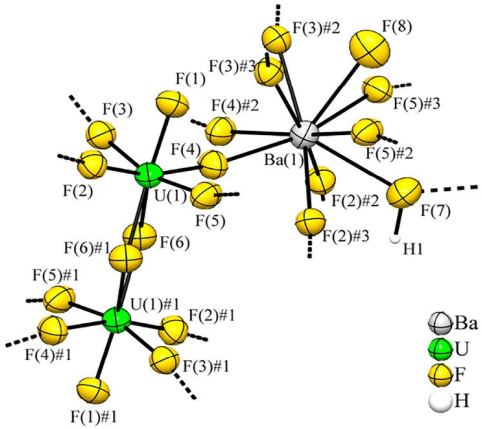
$I2_1/a\bar{3}$ (Nr. 206)

$KSbF_6$

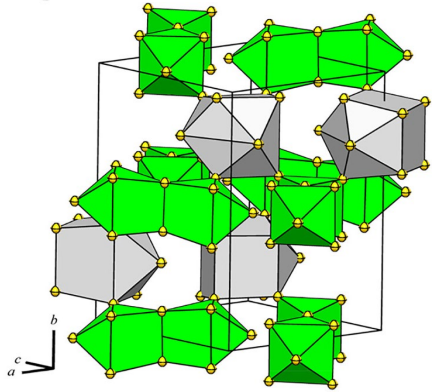
Cl: 1*b* $m\bar{3}m$	Cs: 1*a* $m\bar{3}m$
0 0 0	1/2 1/2 1/2
1*b* $m\bar{3}.$	1*a* $m\bar{3}.$
0 0 0	1/2 1/2 1/2
$1/2\,x + 1/4$	$1/2\,y + 1/4$, $1/2\,z + 1/4$
K: 8*a* $.\bar{3}.$	Sb: 8*b* $.\bar{3}.$
1/4 1/4 1/4	1/2 1/2 1/2

[7] U. Müller, *Anorganische Strukturchemie*, Vieweg & Teubner, **2008**.

Structural chemistry



orthorhombic
Pnma (No. 62)



Synthesis of $Ba[U_2F_{12}]\cdot 1.36\ HF$

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Universität Düsseldorf

Similar to the previous synthesis of $Sr[U_2F_{12}]$

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Universität Düsseldorf

Thank you for listening.
Are there any questions?

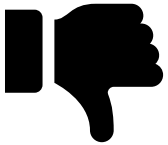
?

What is good & what is bad?

Unusual topic and synthesis methods

A lot of different structures

Nicely written & understandable without expertise



Structure of cubic $NaUF_6$?

More information on $CsUF_6$?

What's about other earth alkali metal U_2F_{12} compounds?

If we have sparked your interest:

Heinrich Heine Universität Düsseldorf

Videos about and with Florian Kraus & his group

The Most Dangerous Chemical Reaction – Fluorine Meets Cesium

by Advanced Tinkering

FluorLab

by Advanced Tinkering

Everything you ever wanted to know about the production and purification of alkali metals

by Advanced Tinkering

Wie GEFÄHRLICH ist Fluor? Das REAKTIVSTE Element der Welt!

by Elias Experiments

Or short videos by Florian Kraus himself! @FluorineIsGreat

https://thenounproject.com/icon/youtube-5288426/ last accessed 23 November 2025

Comparison of the structural data

Heinrich Heine
Universität Düsseldorf

	$LiUF_6$	$NaUF_6$	$CsUF_6$
crystal system	trigonal	trigonal	trigonal
space group	R-3	R-3	R-3
Z	3	3	3
a [Å]	5.1902	5.4101	8.0284
b [Å]	14.265	15.746	8.4388
V [Å^3]	332.78	399.12	471.05
V/Z [Å^3]	110.93	133.04	157.02

	$LiUF_6$	$NaUF_6$	$CsUF_6$
d(U-F) [Å]	2.0624	2.0661	2.057
d(M-F) [Å]	2.0061	2.2768	
d(U-U) [Å]	5.1902	6.1078	5.1732

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Comparison of the structural data

Heinrich Heine
Universität Düsseldorf

	KUF_6	$RbUF_6$	$TlUF_6$
crystal system	monoclinic	monoclinic	monoclinic
space group	C2/m	C2/m	C2/m
Z	4	4	4
a [Å]	11.442	11.797	11.895
b [Å]	8.0345	8.0167	7.9983
c [Å]	5.5655	5.7272	5.6787
β [°]	90.128	90.00	90.00
V [Å^3]	511.62	541.64	540.28
V/Z [Å^3]	127.905	135.41	135.07

	KUF_6	$RbUF_6$	$TlUF_6$
d(U(1)-F(1)) [Å]	2.0633	2.0600	2.0538
d(U(1)-F(2)) [Å]	2.0635	2.0573	2.0611
d(U(1)-F(3)) [Å]	2.3400	2.3286	2.3241
d(U(1)-F(4)) [Å]	2.3403	2.3286	2.3264
d(U(1)-U(1)#1) [Å]	4.0102	4.0019	3.9937
d(U(1)-U(1)#2) [Å]	4.0243	4.0148	4.0046
d(M(1)-F(1)) [Å]	2.6995	2.833	2.8394
d(M(1)-F(1)) [Å]	3.0950	3.1123	3.1410
d(M(1)-F(2)) [Å]	2.6897	2.8308	2.8311
d(M(1)-F(2)) [Å]	3.0902	3.1168	3.1485
d(M(1)-F(3)) [Å]	2.6762	2.7691	2.7962
d(M(1)-F(4)) [Å]	2.6886	2.7694	2.8052

[1] B. Scheibe, T. B. Wassermann, F. Kraus, *Inorg. Chem.* **2025**, *64*, 18432–18446. Supporting Information

Structural field diagram