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ARTICLE

Facile Syntheses of pure Uranium(III) Halides: UF_3, UCl_3, UBr_3, and UI_3

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Dedicated to Professor Hartmut Bärnighausen on the Occasion of his 85th Birthday

Abstract. Herein we describe a convenient lab scale synthesis for pure and solvent-free binary uranium(III) halides UCl_3, UBr_3, and UI_3. This is achieved by the reduction of the respective uranium(IV) halides with elemental silicon in borosilicate ampoules at moderate temperature. The silicon tetrahalides SiX_4 formed as a side product are utilized for the removal of excess starting material via a chemical vapor transport reaction. The syntheses introduced herein avoid the need for pure metallic uranium and are based on uranium(IV) halides synthesized from UO_2 and the respective aluminum halides and purified by chemical vapor transport. These uranium(III) halides are obtained in single crystalline form. A similar reaction yields UF_3 as a microcrystalline powder. However, no beneficial transport reaction occurs with this halide. Also, a higher temperature has to be applied and steel ampoules have to be used. The identities and purity of the products were checked by powder X-ray diffraction as well as IR spectroscopy. The synthesis of UI_3 enabled its crystal structure determination on single crystals for the first time. UI_3 crystallizes in the $PuBr_3$ structure type with space group type *Cmcm* and $a = 4.3208(9)$, $b = 13.923(3)$, $c = 9.923(2)$ Å, $V = 596.9(2)$ Å^3, and $Z = 4$ at $T = 100$ K.

Introduction

Thanks to the regained popularity of uranium chemistry a variety of remarkable compounds has been discovered in recent years.[1–23] UI_3 is widely used as a starting material for organometallic uranium chemistry, but usually in the form of its organic solvent adducts, like $[UI_3(THF)_4]$ and the more stable $[UI_3(1,4\text{-dioxane})_{1.5}]$.[24,25] For the synthesis of chlorides, $[UCl_3(Py)_4]$ is utilized as a starting material, since a convenient synthesis is available.[26] All these compounds have in common, that their coordinating solvent molecules often cannot be removed to yield the neat binary halides. In solid state chemistry, where comparatively harsh, high-temperature conditions are usually applied, decomposition of organic ligands could lead to the formation of undesired oxides or carbides of uranium, which will be reported elsewhere. But also for the investigation of the coordination of weak ligands, the absence of competing ligands is favorable. A straightforward non solid-state chemical synthesis for neat UI_3 in ethyl ether has been developed, but such UI_3 always contains some percent of unavoidable organic impurities which may not be desired.[27] These could be removed by extraction with THF, which, however, introduces THF as a ligand.

The halides of uranium(III) and uranium(IV) are known to chemists since *Péligot* synthesized UCl_4 in 1842 and reduced it with hydrogen to obtain UCl_3.[28] Various methods for their syntheses have been discovered over time which are either more or less sophisticated and still often lead to impure products or use nowadays (at least in the European Union) hardly accessible materials like uranium metal or UH_3.[29] In our recently published report, we summarized the most important methods currently in use for their synthesis and added a novel method for the preparation of highly pure and solvent-free UCl_4, UBr_4, and UI_4.[30] But still we found a convenient synthesis for the uranium(III) halides to be lacking. An overview of common syntheses, properties, and spectroscopic data of U^{III} compounds is given in a review by *J. Drożdżyński*.[31]

UF_3 is usually produced by the reduction of UF_4 with rigorously purified hydrogen inside a stainless steel tube. The temperature required for this reaction is rather high (around 1000 °C) and side reactions easily occur. The presence of moisture, oxygen, and oxygen atom containing materials, like corundum or silica boats, has to be excluded thoroughly, otherwise uranium oxides will be formed. Even UF_4 made from UO_2 in a stream of HF usually contains too much moisture for the preparation of oxide-free UF_3.[29] A suitable reaction for small scale batches is the reduction of UF_4 with aluminum in an inductively heated graphite crucible. At a temperature of 900 °C AlF is formed, which sublimes off the nonvolatile UF_3 in the applied high vacuum.[32]

Although much more convenient than the reduction of UF_4, the reaction of UCl_4 with hydrogen also requires a special apparatus and an exact control of reaction conditions if a complete reaction is to be achieved. At the required temperature of 500–580 °C, sintering and inclusion of UCl_4 easily occurs in the formed UCl_3.[29,33]

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The reduction of UBr_4 with hydrogen again requires a high temperature of 700 °C for complete reaction and leads to the formation of side products: Either oxide contamination or reduction to products of lower bromide content occurs.[29]

Alternatively to the reduction of the uranium(IV) halides, UCl_3 and UBr_3 are conveniently formed by reaction of UH_3 with HCl or HBr, respectively, but this requires the availability of pure uranium metal for the preparation of the highly pyrophoric UH_3, as well as the purification of the applied gases and thus a rather complex apparatus.[29]

UI_3 is synthesized by passing a stream of iodine over uranium metal at a pressure of ca. 10^{-5} mbar inside a furnace with four different temperature zones.[29] If UI_4 is available, UI_3 should be easily produced by heating the UI_4 in a vacuum or in a dry stream of inert gas. However, we found this method to be less suitable than expected.

Regarding uranium(III) halides, only the purification of UCl_3 by chemical vapor transport with iodine has been reported.[29] No other purification processes for uranium(III) halides have been established to the best of our knowledge. Starting their syntheses from pure starting materials is thus essential as nonvolatile impurities often cannot be removed. Based on our report on the synthesis of the pure uranium(IV) halides UCl_4, UBr_4, and UI_4,[30] we present herein a route to the uranium(III) halides utilizing these tetrahalides as starting materials and using an ampoule technique that practically excludes the introduction of impurities.

Results and Discussion

It is known that various metals are capable of reducing uranium(IV).[29,31] However, the alkali metals, calcium, magnesium as well as aluminum were reported to fully reduce U^{IV} halides to uranium metal.[29] Also, in most cases, the byproducts are hardly removable. Metals forming volatile halides are more suitable. An example for such a metal is hot zinc, which was reported to reduce UCl_4 vapors to UCl_3 upon contact, releasing volatile $ZnCl_2$.[29,31] We opted for silicon, as it is cheap and available in very high purity. It is well known to form volatile or easily sublimeable halides (subl.p.: SiF_4: –95.0 °C,[34] b.p. $SiCl_4$: 57.1 °C,[35] $SiBr_4$: 154.7 °C,[35] SiI_4: 287.5 °C[36]). SiI_4 was reported to decompose to the elements upon heating under vacuum.[37] Under the conditions applied here, we did not observe this reaction. In fact, SiI_4 presumably only decomposes partially to Si_2I_6, which can be sublimed at 350 °C in a vacuum without further decomposition and it only decomposes to the elements if it is melted.[36]

With the exception of UF_4, silicon is able to reduce uranium(IV) halides to the respective U^{III} halides at moderate temperatures of 350 to 450 °C according to Equation (1). This low temperature allows for the use of easy-to-handle borosilicate glass ampoules.

$$4\ UX_4 + Si \rightarrow 4\ UX_3 + SiX_4\ (X = F, Cl, Br, I) \quad (1)$$

UF_4 also can be reduced by silicon [Equation (1)], however higher temperatures are needed (700–800 °C). Naturally, borosilicate glass, but also fused silica, proved to be unsuitable for this synthesis. These glasses either melt or are heavily attacked by hot uranium fluorides. Even complete conversion to UO_2 was observed in some cases. We also tried using nickel and platinum ampoules, which led to incomplete reduction, probably due to the formation of silicides. Steel (316L, 1.4435) proved to be a cheap and well suitable material.

Like the aluminum halides, the silicon halides appear to act as transport agents for the uranium tetrahalides. The allegedly formed gas phase complexes seem to induce very smooth reactions, because the reduction of UX_4 (X = Cl, Br, I) with Si actually changes from a solid-solid reaction in the beginning into a solid-gas reaction. Thus, even large crystals of UX_4 of several millimeters edge length were completely converted into the also crystalline reduction products UX_3 (Figure 1). Furthermore, the reaction offers the opportunity to apply an excess of UX_4, which, after the reaction is completed, can be removed by placing the ampoule into a temperature gradient. The excess UX_4 is then transported out of the reaction zone and can easily be recovered. This measure ensures the complete reaction of the added silicon, as otherwise, weighing errors could lead to an irremovable silicon impurity in the products.

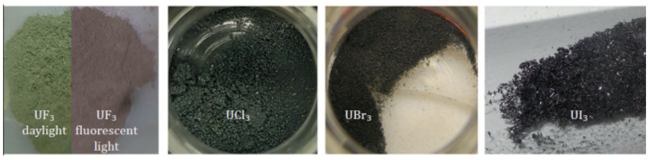

Figure 1. From left to right: photos of UF_3, black UCl_3, dark-brown UBr_3, and black UI_3, synthesized by reduction of the tetrahalides with silicon. Alexandrite effect of UF_3 with green color under daylight or a white LED (left) and purple color under fluorescent light (right).

We did not observe any chemical vapor transport with UF_3 and SiF_4. Therefore, the starting materials have to be present in the exact stoichiometric ratio and the impurities described above cannot be removed. However, SiF_4 is a gas at room temperature, so the removal of this byproduct is much easier than that of AlF in the reduction with aluminum.[32] Albeit, silicon will not melt under the applied conditions, which implies mixing problems that may lead to incomplete reactions due to limited diffusion in the solid state. We also tried to reduce β-UF_5 to UF_3 using silicon. Although this reaction is possible in principle, the results were not reproducible. Between 150 and 190 °C UF_5 disproportionates in a vacuum to UF_6 and black uranium(IV/V) fluorides, and to UF_4 at 280 °C.[38] The reactivity of UF_6 restricts the choice of ampoule materials such that we were not able to find a suitable material for the handling of UF_6 and silicon at the same time. Thus, side reactions occurred with the ampoules.

Powder X-ray diffraction analyses show good crystallinity of the products as well as the absence of crystalline impurities like the starting materials or the oxides, except for the case of

UF_3, where a slight impurity of UF_4 was detected (Figure 2, Figure 3, Figure 4, and Figure 5). Le Bail fitting resulted in the refined cell parameters listed in Table 1. Due to the strong X-ray absorption of the samples, capillaries had to be only loosely filled to obtain a powder X-ray diffraction pattern. However, the intensity of the reflections is still reduced, so the amorphous contribution of the glass capillaries is somewhat overrepresented in the diffraction experiment. This is avoided by dilution of the sample with diamond powder, which, nevertheless, leads to other problems, like overlapping reflections (Figure S1, Supporting Information).

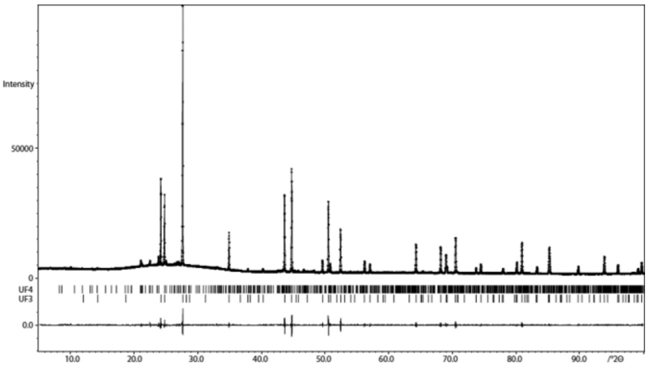

Figure 2. Powder X-ray diffraction pattern of UF_3 with Le Bail fitting, considering a UF_4 impurity. The calculated reflection positions are represented by lines below the observed and calculated powder pattern.[39,43] The difference curve is plotted underneath. Profile *R* factors: $R_p = 2.41\,\%$, $wR_p = 3.7\,\%$, GOF = 2.11.

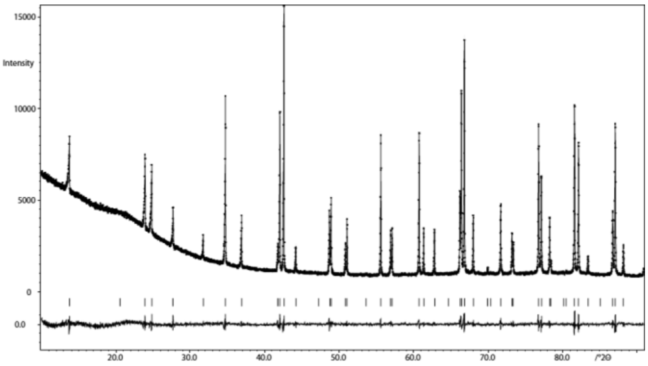

Figure 3. Powder X-ray diffraction pattern of UCl_3 with Le Bail fitting. The calculated reflection positions are represented by lines below the observed and calculated powder pattern.[40] The difference curve is plotted underneath. Profile *R* factors: $R_p = 2.35\,\%$, $wR_p = 3.19\,\%$, GOF = 1.46.

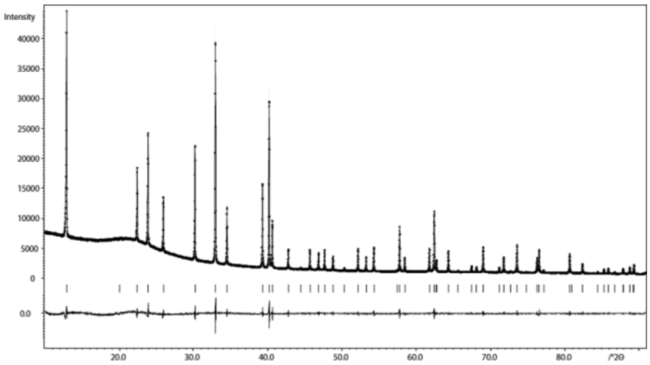

Figure 4. Powder X-ray diffraction pattern of UBr_3 with Le Bail fitting. The calculated reflection positions are represented by lines below the observed and calculated powder pattern.[41] The difference curve is plotted underneath. Profile *R* factors: $R_p = 2.73\,\%$, $wR_p = 3.58\,\%$, GOF = 1.87.

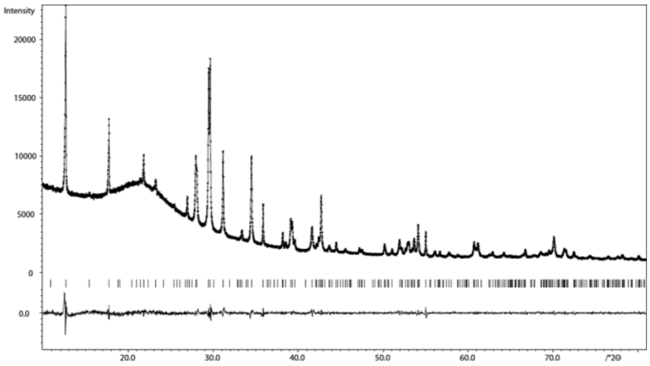

Figure 5. Powder X-ray diffraction pattern of UI_3 with Le Bail fitting. The calculated reflection positions are represented by lines below the observed and calculated powder pattern.[42] The difference curve is plotted underneath. Profile *R* factors: $R_p = 1.85\,\%$, $wR_p = 2.62\,\%$, GOF = 1.51.

Nevertheless, some of the ATR-IR spectra (Figure S2, Supporting Information) show a minor bump at around 1080 cm^{-1}, which could be attributed to the Si–O stretching band.[44] This might derive from small amounts of adsorbed SiO_2 from the hydrolysis of the formed silicon halides.

Probably due to the fragile nature of the lath-like single crystals of UI_3, no crystal structure based on single crystals has been reported till now. Two powder neutron diffraction

Table 1. Cell parameters of the uranium(III) halides at room temperature.

This work	UF_3	UCl_3	UBr_3	UI_3
Pearson Symbol	hP24	hP8	hP8	oC16
a /Å	7.18593(6)	7.44382(3)	7.94448(3)	4.3339(2)
b /Å				13.9996(5)
c /Å	7.35284(8)	4.32298(2)	4.44382(3)	9.9993(3)
Reference	UF_3 [39]	UCl_3 [40]	UBr_3 [41]	UI_3 [42]
a /Å	7.179	7.4439(3)	7.942(2)	4.334(6)
b /Å				14.024(18)
c /Å	7.345	4.3243(3)	4.441(2)	10.013(13)

Table 2. Reported cell parameters of UI_3.

T /K	Type	a /Å	b /Å	c /Å	Source
293	Powder	4.328(5)	14.011(16)	10.005(11)	[45]
293	Powder	4.334(6)	14.024(18)	10.013(13)	[42]
4.2	Powder	4.324(6)	13.933(18)	9.942(13)	[42]
293	Powder	4.3339(2)	13.9996(5)	9.9993(3)	this work
100	Single crystal	4.3208(9)	13.923(3)	9.923(2)	this work

structure analyses on UI_3 have been published so far, both describing the UI_3 crystal structure as the $PuBr_3$ structure type with the space group type *Cmcm*. The sample investigated in the first report contained some UO_2 impurity that decreased the data quality as overlapping reflections had to be discarded.[45] In the second study, a single-crystalline region was used for the determination of the starting structure model which was refined against powder neutron data.[42] Crystals grown via the synthesis presented here were of such quality that we were able to determine the crystal structure via single-crystal X-ray diffraction and gain more precise structural data.

We confirm that UI_3 crystallizes in the orthorhombic $PuBr_3$ structure type with space group type *Cmcm* and $a = 4.3208(9)$, $b = 13.923(3)$, $c = 9.923(2)$ Å, $V = 596.9(2)$ Å^3, and $Z = 4$ at $T = 100$ K, which is consistent with previously reported values (Table 2).[42,45] Crystallographic data is listed in Table 4. However it seems noteworthy, that the inspection of the reciprocal layer ($h0l$), calculated from the raw data, revealed several weak reflections violating the extinction condition for the c-glide operation (Figure S3, Supporting Information). Ten of these reflections have a relative intensity $I_o / \sigma(I_o) > 3$. Based on the comparison of the ratios I_{h0l} / I_{2h0l} for several reflections, we can exclude that they arise from a $\lambda/2$ contribution of the Mo-K_α radiation. Therefore, we refined the obtained structural model in the four maximal subgroups of *Cmcm* containing no c-glide plane, namely $Amm2$, $C222_1$, $C2/m$, and $P2_1/m$. In all cases however, no improvement of the R-values relative to those obtained for the refinement in space group *Cmcm* was observed. Moreover, in all cases, shifts less than 1 pm were enough to restore the *Cmcm* symmetry.

The crystal structure contains three crystallographic independent atoms. The atoms U and I1 are situated on the $4c$ position with site symmetry $m2m$. Atom I2 is located on position $8f$ (site symmetry $m.$).

The structure can be assembled from distorted trigonal UI_6 prisms [I2–I2: 3.6792(10) and I1–I2: 4.2752(11) Å], which are condensed via their triangular faces, forming columns running parallel to the a axis. Slabs according to the Niggli formula $^{2}_{\infty}[UI1_{2/2}I2_{6/3}]$ are formed by connection of these columns parallel to (010) through additional U–I contacts. Neighboring columns are mapped onto each other by the twofold screw axis parallel to the a axis running through x, ¼, 0. Thus, neighboring columns are shifted by x = ½ relative to each other. The resulting slabs consist of a central layer of uranium atoms covered on both sides by slightly corrugated layers of iodine atoms. While the uranium layers have the topology of a 3^6 net, the iodine layers are composed of rectangles and triangles with I1 lying on a 3^6 vertex and I2 on a $3^3.4^2$ vertex.

Due to the additional U–I contacts, the trigonal prism around the uranium atom is actually bicapped over two of its rectangular faces with atomic distances U–I1 = 3.1447(7) Å and U–I2 = 3.2449(6) Å for the atoms forming the prism and U–I2 = 3.4048(8) Å for the capping atoms (Figure 6). The atomic distances are in good accordance to the reported ones (Table 3).

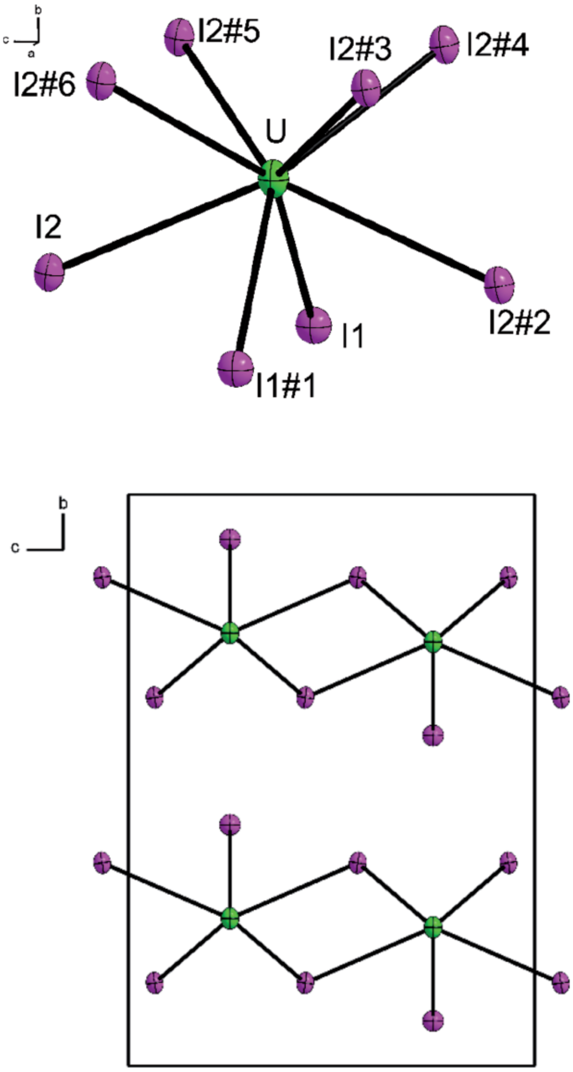

Figure 6. Crystal structure of UI_3. Top: Surrounding of the U atom. Bottom: Projection along the a axis. Displacement ellipsoids are shown at a 95 % probability level at 100 K. Symmetry operations for generating equivalent atoms: #1: $x + 1, y, z$; #2: $-x, y, -z + 1/2$; #3: $-x + 1/2, -y + 1/2, z - 1/2$; #4: $-x - 1/2, -y + 1/2, z - 1/2$; #5: $x - 1/2, -y + 1/2, -z + 1$; #6: $x + 1/2, -y + 1/2, -z + 1$.

Table 3. Reported atomic distances in UI_3.

Distance /Å	4.2 K[42]	100 K (this work)	293 K[42]	293 K[45]
U–I1 (2×)	3.189(10)	3.1447(7)	3.147(10)	3.165(12)
U–I1 (1×)		4.6765(13)		
U–I2 (4×)	3.254(7)	3.2449(6)	3.265(7)	3.244(8)
U–I2 (2×)	3.417(8)	3.4048(8)	3.454(7)	3.456(11)
I2–I2	3.689(10)	3.6792(10)	3.713(9)	3.679(18)
U–U	4.324(6)	4.3208(9)	4.334(6)	4.328(5)

The $^{2}_{\infty}[UI1_{2/2}I2_{6/3}]$ slabs are stacked such that the I1 atoms are situated above the rectangular face of a UI_6 prism in the neighboring slab. With 4.6765(13) Å however, the distance is too long to be regarded as a bond.

The shortest I–I contacts between two layers correspond with 4.2043(9) Å to the sum of the van der Waals radii of I atoms (4.2 Å).[46]

Conclusions

Pure and crystalline uranium(III) halides, UX_3 (X = Cl, Br, I) were prepared by reduction of the respective uranium(IV) halides with elemental silicon inside borosilicate glass ampoules. Excessive UX_4 was removed in situ from the products via a chemical vapor transport reaction with the formed silicon halide. Using steel ampoules and a higher temperature, UF_3 was synthesized in a similar manner, yet without the benefit of an in situ purification.

The crystal structure of UI_3 was determined using single-crystal X-ray diffraction for the first time and more precise structural data was gathered. The $PuBr_3$ structure type was confirmed for this compound.

Experimental Section

All work was carried out excluding humidity and air in an atmosphere of dried and purified argon (5.0, Westfalen AG) using high-vacuum glass lines or a glovebox (MBraun). UF_4 was synthesized by reduction of UF_6 with sulfur in anhydrous HF. UCl_4, UBr_4, and UI_4 were synthesized by metathesis of UO_2 and the respective aluminum halide and purified by in situ chemical vapor transport.[30] Silicon (Alfa Aesar –100 mesh 99.9 %) was used as supplied. All glass vessels were made of borosilicate glass and flame-dried under vacuum before use.

UF_3 was synthesized in steel ampoules. An 8 cm piece of 3/8th inch steel tube (316L / 1.4435) was crimped in a vise on one side and TIG-welded. The other side was tapered to 8° on the inside, to facilitate crimping the ampoule tightly with a vise in a glovebox after inserting the starting materials. The steel ampoules were heated in a vacuum inside a fused silica tube.

For the synthesis of UCl_3, UBr_3, and UI_3, we used ampoules similar to those used for the synthesis of the uranium(IV) halides.[30] The size should be such that a consistent temperature is achieved over the whole length during the reaction and that after the reaction a temperature gradient can be applied for the chemical vapor transport. Ampoules of about 100 mm length, 19 mm outer diameter, and 1.3 mm wall thickness suited our tubular furnaces. These ampoules were equipped with a NS14 ground joint for flame drying and sealing. A constriction in the middle of the ampoule was used for facilitated breakup of the ampoule and prevented mixing of byproduct in the sink with product in the source. The ampoules were filled with a long funnel in a glovebox, to prevent soiling the sink as well as the sealing constraint with nonvolatile substances.

Preparation of UF_3: A steel ampoule was charged with finely ground UF_4 (100 mg, 0.318 mmol) and powdered Si (2.24 mg, 0.080 mmol), crimped and welded in an argon atmosphere (ca. 900 mbar). The mixture was heated to 700 °C for 7 d. The yield was quantitative with respect to silicon.

Preparation of UCl_3: An ampoule was charged with finely ground UCl_4 (1000 mg, 2.633 mmol, 20 mg excess) and Si (18.12 mg, 0.645 mmol) and flame sealed under vacuum (1×10^{-3} mbar). The starting materials were reacted at 450 °C for 20 d before the transport reaction was conducted with a source temperature of 350 °C and a sink temperature of 250 °C, to remove the excess of UCl_4. The yield was quantitative with respect to silicon.

Preparation of UBr_3: An ampoule was charged with finely ground UBr_4 (1000 mg, 1.793 mmol, 20 mg excess) and Si (12.34 mg, 0.440 mmol) and flame sealed under vacuum (1×10^{-3} mbar). The starting materials were reacted at 400 °C for 14 d before the transport reaction was conducted with a source temperature of 350 °C and a sink temperature of 230 °C, to remove the excess of UBr_4. The yield was quantitative with respect to silicon.

Preparation of UI_3: An ampoule was charged with finely ground UI_4 (1000 mg, 1.341 mmol, 20 mg excess) and Si (9.23 mg, 0.329 mmol) and flame sealed under vacuum (1×10^{-3} mbar). The starting materials were reacted at 450 °C for 7 d before the transport reaction was conducted with a source temperature of 450 °C and a sink temperature of 300 °C. The yield was quantitative with respect to silicon.

Powder X-ray Diffraction: Powder X-ray diffraction was conducted with a STOE StadiMP powder diffractometer using Cu-$K_{\alpha1}$ radiation, a Ge monochromator, and a Mythen1K detector. Samples were powdered in agate mortars in a glovebox and filled into borosilicate-glass capillaries, which were flame-dried in vacuo before use.

Phase analysis was carried out with WinXPOW,[47] using the ICDD database.[48] Le Bail fitting was done with JANA 2006.[49]

Single Crystal X-ray Diffraction: Single crystals were selected under exclusion of air in cooled perfluorinated polyether (Galden, Solvay Solexis) and mounted using the MiTeGen MicroLoop system. X-ray diffraction data were collected using the graphite monochromated Mo-K_α radiation of a Stoe IPDS2T diffractometer. The diffraction data were reduced with the X-Area software package, scaled with the Laue Analyzer[50] and corrected for absorption numerically using X-Red and X-Shape.[51–53] The structure was solved using Direct Methods (SHELXS-97) and refined against F^2 (SHELXL-2016/6) using the ShelXle software package.[54–56] Atoms were refined anisotropically. Reciprocal layers were calculated with the program BuildSpace[57] and plotted with ViewSpace[58] implemented in the Xarea software package. Crystallographic data and structure refinement results are summarized in Table 4.

Table 4. Crystallographic data and refinement results for UI_3.

	UI_3
Color and appearance	black laths
Space group	*Cmcm* (no. 63)
Crystal system	orthorhombic;
a /Å	4.3208(9)
b /Å	13.923(3)
c /Å	9.923(2)
V /Å^3	596.9(2)
Z	4
λ /Å	0.71073
T /K	100(2)
μ(Mo-K_α) /mm^{-1}	42.544
R_{int}; R_σ	0.112; 0.048
$R(F)$ [$I \geq 2\sigma$ (I); all]	0.039; 0.039
$wR(F^2)$ [$I \geq 2\sigma$ (I); all]	0.090; 0.090
S (all data)	1.188
Data; parameter; restraints	662; 16; 0
$\Delta\rho_{max}$; $\Delta\rho_{min}$ /e·Å^{-3}	5.405; –5.954

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository number CSD-433740.

IR Spectroscopy: IR spectra were recorded with a Bruker alpha FT-IR spectrometer using the Diamond ATR unit with a resolution of 4 cm^{-1} inside a glovebox. Spectra were processed with the OPUS software package.[59]

Supporting Information (see footnote on the first page of this article): The supporting information contains the powder diffraction pattern of a mixture of uranium triiodide and diamond powder as well as the IR spectra of the uranium(III) halides. Furthermore, a projection of the (h0l) plane of uranium(III) iodide is depicted which shows the mentioned systematic absence violations.

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Keywords: Halides; Uranium; Solid state; Synthesis; Transport reaction

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