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Surprises in the Solvent-Induced Self-Ionization in the Uranium Tetrahalide $\text{UX}_4$ ($X = \text{Cl}, \text{Br}, \text{I}$)/Ethyl Acetate System

H. Lars Deubner, Tim Graubner, Magnus R. Buchner, Florian Weigend, Sergei I. Ivlev, Antti J. Karttunen, and Florian Kraus*

ABSTRACT: The reaction of the uranium(IV) halides $\text{UCl}_4$, $\text{UBr}_4$, or $\text{UI}_4$ with ethyl acetate (EtOAc) leads to the formation of the complexes $[\text{UX}_3(\text{EtOAc})_4][\text{UX}_5(\text{EtOAc})]$ ($X = \text{Cl, Br}$) or $[\text{UI}_4(\text{EtOAc})_3]$. Thus, both $\text{UCl}_4$ and $\text{UBr}_4$ show self-ionization in ethyl acetate to a distorted pentagonal bipyramidal $[\text{UX}_3(\text{EtOAc})_4]^+$ cation and a distorted octahedral $[\text{UX}_5(\text{EtOAc})]^{-}$ anion. Surprisingly, the chloride and bromide compounds are not isotypic. While $[\text{UCl}_3(\text{EtOAc})_4][\text{UCl}_5(\text{EtOAc})]$ crystallizes in the orthorhombic crystal system, space group $P_{2_1}2_12_1$ at 250 K, the bromide compound crystallizes in the monoclinic crystal system, $P_{2_1}1/2$ at 100 K. Unexpectedly, $\text{UI}_4$ does not show self-ionization but forms $[\text{UI}_4(\text{EtOAc})_3]$ molecules, which crystallize in the monoclinic crystal system, $P_{2_1}/c$, at 100 K. The compounds were characterized by single-crystal X-ray diffraction, IR, Raman, and NMR spectroscopy, as well as molecular quantum chemical calculations using solvent models.

INTRODUCTION

Self-ionization is a long known property of many inorganic compounds and has been proven to occur in the gas, liquid, and solid phases. Water is certainly the best investigated example of a compound showing self-ionization. Neutral water contains only small concentrations of $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions under ambient conditions, that is, the autoprotolysis constant is quite small. Other compounds that show self-ionization are liquid $\text{NH}_3$, $\text{BrF}_3$, anhydrous $\text{HF}$, and other amphoteric molecules. $\text{Cl}_2\text{O}_6$ and $\text{N}_2\text{O}_5$ show electrically neutral molecular structures in the gas phase, but in the solid-state ionic structures, $[\text{ClO}_4]^-$ and $[\text{NO}_2]^-$ are present. In the solid state of $\text{PCl}_5$, tetrahedral $[\text{PCl}_4]^+$ cations and octahedral $[\text{PCl}_6]^-$ anions occur. Self-ionization can also be induced by ligands, and the compounds $[\text{TiF}_3(15\text{-crown-5})][\text{TiF}_3]$, $[[\text{AuCl}_2\text{py}]_2][\text{AuCl}_4]$, $[\text{AuCl}_4]$, $[\text{AuCl}_4]$, $[\text{AuCl}_4]$-2-$[\text{AuCl}_4]$, $[\text{NbF}_6(\text{Me}_3\text{Si})]$, $[\text{NbF}_6]$, and $[\text{Li}]$-$[\text{SbF}_6][\text{SbF}_6]$ or $[\text{Ta}(\text{N}_3)_2(1,10\text{-phen})][\text{M}(\text{N}_3)_2]$, $[\text{BeI}_2(\text{dmf})]$, $[\text{BeI}_6]$, and $[\text{BePh}(12\text{-crown-4})][\text{BePh}_4]$ serve as examples.

To the best of our knowledge, the first actinide complex resulting from self-ionization was reported in 1973. The authors interpreted the UV–vis spectrum of the compound “$\text{UCl}_4(\text{Me}_3\text{SO})_3$” and deduced its composition as $[\text{UCl}_4(\text{Me}_3\text{SO})_6][\text{UCl}_6]$. This was confirmed by its crystal structure in 1975. Only a couple of other U-containing compounds which show self-ionization were reported. In most of them, an octahedral $[\text{UX}_6]^{-}$ ($X = \text{Cl, Br, I}$) anion is present besides various cations. Examples are $[\text{UCl}_2(\text{Me}_3\text{SO})_6][\text{UCl}_6]$, $[\text{UBr}_2(1\text{-H-indene})(\text{MeCN})_4]-[\text{UBr}_6]$, or the mixed-valent compound $[\text{U}(\text{MeCN})_6][\text{UCl}_6]$-$\text{I}$. A few compounds are known containing an anion of the form $[\text{UX}_L]^{-}$ ($X = \text{Cl, Br, I}$; $L = $ organic ligand). Examples are $[\text{UCl}_2(\text{EtC(O)N(ET)_2})_4]$, $[\text{UCl}_4(\text{EtC(O)N(ET)_2})_3]$, or $[\text{Et}_2\text{OH}][\text{UX}_5(\text{Et}_2\text{O})]$.$\text{Et}_2\text{O}$ ($X = \text{Br, I}$). While the chemistry of $[\text{UO}_2]^{2-}$-containing compounds in ethyl acetate is well examined,

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acetate containing complexes of U(IV) seem to be known. Herein we describe the reaction of the uranium(IV) halides UX₄ (X = Cl, Br, I) with ethyl acetate.

## RESULTS AND DISCUSSION

The reaction of uranium(IV) chloride or bromide leads to the formation of complexes resulting from self-ionization of [UX₃(EtOAc)₄][UX₅(EtOAc)₃] (X = Cl, Br), while the iodide does—surprisingly—not dissociate and is obtained as [UL₂(EtOAc)₃]. Scheme 1 gives an overview of the reaction conditions and products.

### Scheme 1. Overview of the Reactions of the Uranium Halides UX₄ (X = Cl, Br, I) with EtOAc and the Respective Reaction Conditions

The starting materials were dissolved in an excess of EtOAc at room temperature. Then, a vacuum was applied to remove the solvent until crystallization started. These solutions were subsequently stored at 2 °C for a couple of days to allow for the growth of single crystals, which were filtered off. Details are available from the Experimental Section.

### Crystal Structure of the Chloride.

The blueish black compound [UCl₃(EtOAc)₄][UCl₅(EtOAc)₃] crystallizes in the space group P2₁/a, No. 14, with a = 15.1255(4), b = 15.4634(7), c = 17.4324(7) Å, V = 4077.3(3) Å³, and Z = 4 at T = 250 K. Unfortunately, the crystals broke apart upon cooling to 100 K, so the single-crystal X-ray structure determination had to be conducted at 250 K to prevent the shattering of the crystals. See Table 1 for selected crystallographic data and details of the structure determinations.

The uranium atom of the [UCl₅(EtOAc)₃]⁻ cation is coordinated by seven ligands, three chloride atoms, and four ethyl acetate molecules, in the shape of a pentagonal bipyramid. The coordination polyhedron of the anion is a distorted octahedron-like coordination polyhedron, as expected. The pentagonal bipyramidal [UCl₅(EtOAc)₃]⁻ cation is only slightly distorted with U−U−L angles between 69.4(3) and 74.6(2)° (ideal 72°) for the equatorial and between 88.8(2) and 91.51(11)° (ideal 90°) for the axial ligands. All distances and angles are however additionally biased as the compound shows a distinct distortion of the coordinated ethyl acetate molecule in the [UCl₅(EtOAc)₃]⁻ anion. The closest U−U distance is between neighboring cations and anions with ca. 7.59 Å. The cations are surrounded by six anions in the shape of very distorted octahedra and vice versa with the U···U distances in a range from ca. 7.59 to 9.98 Å. However, the distortion is so severe that we could not identify any reasonable packing of cations and/or anions, such as in the NaCl structure type for example.

### Crystal Structure of the Bromide.

The reaction of uranium(IV) bromide with ethyl acetate leads to the formation of dark green [UBr₃(EtOAc)₄][UBr₅(EtOAc)₃]. Although the compound has a similar composition and the same structural constitution as the chloride described above, it is not isotypic. It crystallizes in the monoclinic crystal system, space group P12₁/n1, No. 14, with a = 15.7380(10), b = 17.5732(9), c = 16.2532(11) Å, V = 4111.2(5) Å³, and Z = 4 at T = 100 K (Table 1). The uranium atom of the cation is again coordinated by seven ligands, three bromide atoms, and four ethyl acetate molecules, in the shape of a pentagonal bipyramid. The coordination polyhedron of the anion is a distorted octahedron with a central uranium atom with five bromido ligands and one ethyl acetate molecule coordinating to it. A section of the crystal structure illustrating both ions is shown in Figure 1. The atomic distances between the uranium atom and the bromido ligands range from 2.346(8) to 2.374(9) Å in the cation. For the disordered EtOAc ligands of the anion, the distances are 2.30(2) and 2.36(2) Å. The U−O distances are in agreement with the literature. Selected L−U−L distances in a range from 2.346(8) to 2.374(9) Å in the cation. For the disordered EtOAc ligands of the anion, the distances are 2.30(2) and 2.36(2) Å. The U−O distances are in agreement with the literature.
be ruled out, but a reconstructive phase transition could still be possible. Usually, higher symmetry is present in high-temperature phases, which is not the case here. The crystal structure of the bromide, monoclinic with space group $P2_1/n$ at 100 K, shows a recognizable relation to the NaCl structure type, whereas the crystal structure of the chloride, orthorhombic with space group $P2_12_12_1$ at 250 K, does not.

**Crystal Structure of the Iodide.** The reaction of uranium(IV) iodide in ethyl acetate at room temperature leads to the formation of dark red crystals of $[\text{UI}_4(\text{EtOAc})_3]^-$. The compound does not show self-ionization and crystallizes in the monoclinic crystal system $P2_1/c$, No. 14, with $a = 15.085(3)$, $b = 11.753(2)$, $c = 14.176(3)$ Å, $\beta = 93.93(3)^\circ$, $V = 2507.4(9)$ Å$^3$, and $Z = 4$ at $T = 100$ K. Although the anions $[\text{UI}_4\text{L}^-]$ and $[\text{UI}_6]^{2-}$ are known, a formation of one of these was not observed by us at various temperatures ($-35$ to 70 °C).$^{37,41}$ The uranium atom is surrounded by the shape of a slightly distorted pentagonal bipyramid by four iodine and three oxygen atoms (Figure 2). The atomic distances between the U atom and the iodido ligands range from 2.9938(6) to 3.11525(8) Å and for the coordinating O atoms of the ethyl acetate ligands from 2.316(4) to 2.349(4) Å. These distances are in agreement with the literature.$^{37-59}$ The large iodido ligands next to the small O ligand atoms of the ethyl acetate molecules induce a distortion of the pentagonal bipyramidal

### Table 1. Selected Crystallographic Data and Details of the Structure Determinations of the Uranium(IV) Halide Ethyl Acetate Complexes

| formula      | $[\text{UCl}_3(\text{EtOAc})_4]^-[\text{UCl}_5(\text{EtOAc})_2]$ | $[\text{UBr}_3(\text{EtOAc})_4]^-[\text{UBr}_5(\text{EtOAc})_2]$ | $[\text{UI}_4(\text{EtOAc})_3]^-$ |
|--------------|---------------------------------------------------------------|---------------------------------------------------------------|----------------------------------|
| molar mass/g-mol$^{-1}$ | 1200.18                                                      | 1555.86                                                      | 1009.94                          |
| space group (no.) | $P2_12_12_1$ (19)                                              | $P12_1/c$ (14)                                                | $P2_1/c$ (14)                     |
| $\alpha/\AA$ | 15.1255(4)                                                   | 15.7380(10)                                                  | 15.085(3)                        |
| $\beta/\AA$ | 15.4634(7)                                                   | 15.7532(9)                                                   | 11.753(2)                        |
| $\gamma/\AA$ | 17.4324(7)                                                   | 16.2532(11)                                                  | 14.176(3)                        |
| $V/\AA^3$ | 4077.3(3)                                                    | 113.853(5)                                                   | 93.93(3)                         |
| $Z$ | 4                                                          | 4                                                           | 4                                |
| Pearson symbol | $mP2_12_12_1$ w. H atoms                                      | $mP2_12_12_1$ w. H atoms                                      | $mP188$ w. H atoms               |
| $\rho_{calc}$/g-cm$^{-3}$ | 1.955                                                        | 2.514                                                        | 2.675                            |
| $\mu$/mm$^{-1}$ | 8.496                                                        | 15.682                                                       | 11.417                           |
| color | dark blue                                                   | dark green                                                   | dark red                         |
| crystal morphology | block                                                        | block                                                        | block                            |
| crystal size/mm$^3$ | 0.15 × 0.10 × 0.08                                           | 0.20 × 0.10 × 0.07                                           | 0.10 × 0.08 × 0.06               |
| $T/K$ | 250(2)                                                       | 100(2)                                                       | 100(2)                           |
| $\lambda/\AA$ | 0.71073 (Mo $K_\alpha$)                                       | 0.71073 (Mo $K_\alpha$)                                       | 0.71073 k                        |
| no. of reflections | 42194                                                       | 57562                                                        | 36981                            |
| $\theta$ range/° | 2.634–25.028                                                | 2.606–27.984                                                | 2.577–26.833                     |
| range of Miller indices | $-18 \leq h \leq 15$                                        | $-20 \leq h \leq 20$                                        | $-19 \leq h \leq 19$            |
| absorption correction | numerical                                                   | numerical                                                   | numerical                        |
| $T_{min}$ | 0.2722, 0.3859                                                | 0.0738, 0.3021                                              | 0.1784, 0.5198                   |
| $R_{B}$, $R_{p}$ | 0.0620, 0.0390                                                | 0.0415, 0.0866                                              | 0.0506, 0.1142                   |
| completeness of the data set | 1.000                                                        | 0.973                                                       | 0.992                            |
| no. of unique reflections | 7193                                                         | 9651                                                        | 5333                            |
| no. of parameters | 429                                                          | 371                                                         | 214                              |
| no. of restraints | 446                                                          | 0                                                           | 0                                |
| no. of constrains | 0                                                           | 0                                                           | 0                                |
| $S$ (all data) | 1.002                                                        | 1.036                                                       | 1.013                            |
| $R(F)$ ($I \geq 2\sigma(I)$, all data) | 0.0312, 0.0631                                                | 0.0360, 0.0525                                              | 0.0313, 0.0450                   |
| $wR(F)/R_{w}$ ($I \geq 2\sigma(I)$, all data) | 0.0522, 0.0591                                                | 0.0776, 0.0839                                              | 0.0690, 0.0730                   |
| $\Delta$$\rho_{max}$, $\Delta$$\rho_{min}$/e Å$^{-3}$ | 0.607, −0.650                                                | 1.523, −1.818                                               | 1.587, −0.732                    |
| flack x | 0.393(10)                                                    | .                                                           | .                                |
coordination sphere, with L–U–L (L = coordinating ligand atom) angles between 68.36(14) and 74.84(10)° (ideal 72°) for equatorial and between 87.95(11) and 94.49(10)° (ideal 90°) for axial ligands (Figure 2).

The packing of the molecules of the iodide, that is their U atoms, corresponds to the Mg structure type with the hexagonal close-packed layers parallel to the bc plane. The closest U···U distances are ca. 8.24 Å.

IR and Raman Spectroscopic Investigations. The ATR IR spectra of the three compounds (Figures S1–S3) were recorded at room temperature and are dominated by the vibration bands of the ethyl acetate ligands. The bands of the C–H stretching modes are observed around 2936 and 2983 cm\(^{-1}\) and for the C–O–C stretching modes at 1315 and 1034 cm\(^{-1}\), which is in good agreement with noncoordinating ethyl acetate.\(^{60}\) The C=O stretching modes of the chloride, the bromide, and the iodide reported here are observed at 1610, 1603, and 1601 cm\(^{-1}\), respectively. The bathochromic shift of 131–140 cm\(^{-1}\), compared to the free ester, is attributed to a significant weakening of the C=O bond. This is indicative for a strong interaction of the uranium atoms with the coordinating carbonyl oxygen atoms and is typical for carboxylic acid ester complexes of strongly Lewis acidic metals.\(^{61}\) The uranium halide U–X (X = Cl, Br, I) stretching frequencies do not show intensities in the region accessible to our instrument from 4000 to 400 cm\(^{-1}\).\(^{62}−64\) Also, there is no hint toward characteristic bands of commonly observed impurities such as the uranyl cation UO\(_2^{2+}\) that would give rise to a band in the region from ~911 to 960 cm\(^{-1}\).\(^{65}\)

The Raman spectra of the compounds (Figure S4) were also recorded at room temperature and are comparable to the Raman spectrum of free ethyl acetate.\(^{66}\) An overview of the band assignment is given in Table 2, and other bands could not be assigned unambiguously.

NMR Spectroscopic Investigations. \(^1\)H and \(^{13}\)C NMR spectroscopy was used to investigate which species is present in the solutions of the title compounds. Therefore, crystals of the compounds were dissolved in CD\(_2\)Cl\(_2\). The applicability of NMR spectroscopy for the analysis of uranium(IV) compounds is limited due to its paramagnetism. Due to coupling between nuclear and electron spins, the chemical shift becomes unpredictable, and the signals are broadened, sometimes to an extent that they are not observable.\(^{68}\) The \(^1\)H and \(^{13}\)C NMR spectra of the title compounds show discrete signals for the two methyl groups, the methylene group, and the carbon nucleus of the carbonyl group, respectively. However, all signals are broadened and show significant paramagnetic shifts (Figure 3).

![Figure 2. Left: Section of the crystal structure of [UI\(_4\)(EtOAc)\(_3\)]. The displacement ellipsoids are shown at the 70% probability level at 100 K. Hydrogen atoms are omitted, and carbon atoms are shown as a wire frame for clarity. Right: Polyhedron showing the distortion of the pentagonal bipyramid. Atoms are shown isotropic with arbitrary radii.](image)

![Figure 3. \(^1\)H NMR spectra of (a) [UCl\(_3\)(EtOAc)\(_4\)] [UCl\(_5\)(EtOAc)], (b) [UBr\(_3\)(EtOAc)\(_4\)] [UBr\(_5\)(EtOAc)], and (c) [UI\(_4\)(EtOAc)\(_3\)] in CD\(_2\)Cl\(_2\).](image)

**Table 2. Selected Raman Bands and Assignment of the Three Title Compounds\(^{66,67}\)**

| \([\text{UCl}_3(\text{EtOAc})_4]\) | \([\text{UCl}_5(\text{EtOAc})]\) | \([\text{UBr}_3(\text{EtOAc})_4]\) | \([\text{UBr}_5(\text{EtOAc})]\) | \([\text{UI}_4(\text{EtOAc})_3]\) | EtOAc |
|----------------|----------------|----------------|----------------|----------------|--------|
| 390            | 391            | 389            | 381            | 6(C–C), m       |
| 637            | 641            | 703            | 697            | \(\gamma(\text{CH}_3\text{COO}), \text{w}\) |
| 852            | 858            | 847            | 849            | \(\nu(\text{C–C}), \text{w}\) |
| 1120           | 1125           | 1115           | 1117           | \(\nu(\text{skeletal}), \text{m}\) |
| 1666           | 1659           | 1743           | 1738           | \(\nu(\text{C=O}), \text{m}\) |
| 2881           | 2886           | 2878           | 2879           | \(\nu(\text{CH}), \text{m}\) |
| 2936           | 2932           | 2937           | 2943           | \(\nu(\text{CH}), \text{vs}\) |
| 2978           | 2977           | 2974           | 2974           | \(\nu(\text{CH}), \text{s}\) |
in the bromide and iodide these signals are shifted downfield (Table 3). The coordination shift increases from the iodide via the bromide to the chloride compound, which indicates increasing interaction between the uranium atoms and the ester ligands. This is in line with expectations due to the increasing electronegativity of the halides. This results in lower electron density at the metal center and increasing U ester ligands. This is in line with expectations due to the increasing interaction between the uranium atoms and the ester ligands.

### Quantum Chemical Calculations

To clarify the self-ionization behavior, we studied the thermodynamics of reaction 1 for X = Cl, Br, and I with quantum chemical methods (DFT-PBE0/def2-TZVP, see the Experimental Section for the computational details).

\[
2[\text{UX}_4(\text{EtOAc})_3] \rightarrow [\text{UX}_4(\text{EtOAc})_3][\text{UX}_3(\text{EtOAc})]+\text{EtOAc}
\]

The conductor-like screening model (COSMO) was used to simulate the influence of the EtOAc solvent (relative dielectric constant of 6). We evaluated the reaction energies at 0 K and the reaction Gibbs free energies at 298 K (Table 4). The dissociation reaction 1 shows a positive reaction energy at 0 K for all halides with the iodide showing the least unfavorable one with +80 kJ/mol. Consideration of the Gibbs free energies does not change the picture. Overall, the reactions become thermodynamically more favorable but still show a positive ΔG, when moving from X = Cl to I, which is in contrast to the self-ionization observed within the crystal structures of the chloride and the bromide.

We also tested the effect of an electrostatically ideal solvent with COSMO (dielectric constant of infinity). In this case, the reaction becomes thermodynamically slightly more favorable, but the trend remains contrary to the trend observed experimentally in the solid state: self-ionization is then thermodynamically favored for X = I and unfavored for X = Cl (Table S1 in Supporting Information).

In summary, the [UX₄(EtOAc)₃] species are not expected to dissociate in EtOAc solution based on our DFT calculations. Of course, differently composed molecular species compared to [UX₄(EtOAc)₃] could be present and involved in various equilibria upon crystallization of the compounds. However, we can confirm neither the existence nor the absence of such species from the NMR spectra.

### CONCLUSION

The solid-state compounds [UCl₃(EtOAc)₄][UCl₅(EtOAc)] and [UBr₃(EtOAc)₄][UBr₅(EtOAc)] were obtained by self-ionization reactions of the respective uranium tetrahalide in the presence of the solvent and O-donor ligand ethyl acetate (EtOAc). UI₄ does not show the same reactivity under similar conditions, as a compound with the composition [UX₄(EtOAc)₃] is obtained. The crystal structures of the chloride and bromide salts are not isotypic, despite both featuring isostructural complex ions with U atom coordination spheres of distorted pentagonal bipyramids for the cations and slightly distorted octahedra. As the chloride crystallizes orthorhombic, space group P2₁2₁2₂, and the bromide monoclinic, space group P12₁/n1, no direct group–subgroup relation is present excluding a displacive phase transition of an orthorhombic high-temperature to a monoclinic low-temperature phase. However, a reconstructive phase transition may of course be possible, or there simply is no structural relation between the two compounds. While the crystal structure of the bromide can be related to the NaCl structure type, the distortions within the chloride are so profound that no such relation became obvious. The packing of the molecules of the iodide corresponds to the Mg structure type.

In solution, only one signal set of coordinated ethyl acetate ligands can be observed with NMR spectroscopy. The spectra show that exchange on the NMR time scale occurs between the ethyl acetate ligands in solution. Thus, it remains unclear if self-ionization is also present in solution or if there is an effect of different solubilities and shifted equilibria of various

| X   | quantity | energy/kJ mol⁻¹ |
|-----|----------|----------------|
| Cl  | ΔE       | 105            |
|     | ΔG₂⁹⁸   | 84             |
| Br  | ΔE       | 111            |
|     | ΔG₂⁹⁸   | 64             |
| I   | ΔE       | 80             |
|     | ΔG₂⁹⁸   | 28             |

Values obtained at the DFT-PBE0/def2-TZVP level of theory with COSMO solvent model (relative dielectric constant of EtOAc = 6).
dissolved species due to the inset of crystallization of the compounds. IR and NMR spectra as well as quantum chemical calculations show the expected trend of decreasing bond strength and electronegativity from U–Cl to U–I.

Based on the DFT results, the [UX₄(EtOAc)₃] species are not expected to dissociate in EtOAc solution under the studied conditions. So, the question why the chloride and bromide show autodissociation and the iodide does not remains currently unanswered.

### EXPERIMENTAL SECTION

All work was carried out excluding moisture and air in an atmosphere of dried and purified argon (5.0, Praxair) using high vacuum glass lines and a glovebox (MBraun). Aluminum chloride and bromide (Merck, 98%/Alfa Aesar, 98%) were purified by sublimation in vacuo before use. Elemental iodine was sublimed in vacuo several times, the last time from phosphorus pentoxide. Aluminum powder (Fluka, purum >99%) was dried in vacuo at 250 °C.

Phosphorus pentoxide. Aluminum powder (Fluka, purum... was dried in vacuo at 250 °C for 12 h before the transport reaction was conducted with a source temperature of 350 °C and a sink temperature of 250 °C. An amount of 2714 mg (3.64 mmol, 91%) of needle-like black crystals of U₁₄ was obtained after 5 days.

### Synthesis of Trichloro Tetra(ethyl acetate) Uranium(IV) Pentachloride (Ethyl Acetate) Uranate(IV) [UCl₄(EtOAc)₄][UCl₅(EtOAc)]. An amount of 25 mg (0.07 mmol) of UCl₄ was reacted with an excess of ethyl acetate (ca. 5 mL) in a Schlenk tube at room temperature. After the UCl₄ was dissolved completely, the excess of ethyl acetate was slowly removed under a vacuum to ca. 1 mL until crystallization was observed. Then the Schlenk tube was stored at 2 °C. Dark blueish crystals could be obtained after 7 days of storage. Yield was essentially quantitative.

### Synthesis of Trichloro Tetra(ethyl acetate) Uranium(IV) Pentachloride (Ethyl Acetate) Uranate(IV) [UCl₄(EtOAc)₄][UCl₅(EtOAc)]. An amount of 25 mg (0.04 mmol) of UBr₄ was reacted with an excess of ethyl acetate (ca. 5 mL) in a Schlenk tube at room temperature. After the UBr₄ was dissolved completely, the excess of ethyl acetate was slowly removed under a vacuum to ca. 1 mL until crystallization was observed. Then the Schlenk tube was stored at 2 °C. Dark brown crystals could be obtained after 7 days of storage. Yield was essentially quantitative.

### Synthesis of Trichloro Tetra(ethyl acetate) Uranium(IV) Pentachloride (Ethyl Acetate) Uranate(IV) [UCl₄(EtOAc)₄][UCl₅(EtOAc)]. An amount of 40 mg (0.05 mmol) of U₁₄ was reacted with an excess of ethyl acetate (ca. 5 mL) in a Schlenk tube at room temperature. After the U₁₄ was dissolved completely, the excess of ethyl acetate was slowly removed under a vacuum to ca. 1 mL until crystallization was observed. Then the Schlenk tube was stored at 2 °C. Dark red crystals could be obtained after 5 days of storage. Yield was essentially quantitative.

### Synthesis of Trichloro Tetra(ethyl acetate) Uranium(IV) Pentachloride (Ethyl Acetate) Uranate(IV) [UCl₄(EtOAc)₄][UCl₅(EtOAc)]. An amount of 25 mg (0.07 mmol) of U₁₄ was reacted with an excess of ethyl acetate (ca. 5 mL) in a Schlenk tube at room temperature. After the U₁₄ was dissolved completely, the excess of ethyl acetate was slowly removed under a vacuum to ca. 1 mL until crystallization was observed. Then the Schlenk tube was stored at 2 °C. Dark red crystals could be obtained after 5 days of storage. Yield was essentially quantitative.

### Synthesis of Trichloro Tetra(ethyl acetate) Uranium(IV) Pentachloride (Ethyl Acetate) Uranate(IV) [UCl₄(EtOAc)₄][UCl₅(EtOAc)]. An amount of 40 mg (0.05 mmol) of U₁₄ was reacted with an excess of ethyl acetate (ca. 5 mL) in a Schlenk tube at room temperature. After the U₁₄ was dissolved completely, the excess of ethyl acetate was slowly removed under a vacuum to ca. 1 mL until crystallization was observed. Then the Schlenk tube was stored at 2 °C. Dark red crystals could be obtained after 5 days of storage. Yield was essentially quantitative.

### Synthesis of Trichloro Tetra(ethyl acetate) Uranium(IV) Pentachloride (Ethyl Acetate) Uranate(IV) [UCl₄(EtOAc)₄][UCl₅(EtOAc)]. An amount of 25 mg (0.04 mmol) of UBr₄ was reacted with an excess of ethyl acetate (ca. 5 mL) in a Schlenk tube at room temperature. After the UBr₄ was dissolved completely, the excess of ethyl acetate was slowly removed under a vacuum to ca. 1 mL until crystallization was observed. Then the Schlenk tube was stored at 2 °C. Dark red crystals could be obtained after 5 days of storage. Yield was essentially quantitative.

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CD$_2$Cl$_2$ (5.32 and 54.0 ppm). NMR spectra were processed with the MestReNova software.74

**Single-Crystal X-ray Diffraction.** Single crystals of the compounds described above were selected at room temperature under dried perfluorinated oil and mounted using a MiTeGen loop. Intensity data of a suitable crystal were recorded with an IPDS 2T diffractometer (Stoe & Cie). The diffractometer was operated with Mo-$K_{\alpha}$ radiation (0.71073 Å, graphite monochromator) and equipped with an image plate detector. Evaluation, integration, and reduction of the diffraction data were carried out using the X-Area software suite.75 Numerical absorption corrections were applied with the modules X-Shape and X-Red32 of the X-Area software suite. The structures were solved with dual-space methods (SHELXT-2018/2) and refined against $F^2$ (SHELXL-2018/3).76,77 All atoms were refined with anisotropic displacement parameters, and H atom isotropic and riding models were adequate. Disorder was modeled using DSR.78 Cif files were deposited with the CCDC (https://www.ccdc.cam.ac.uk/), depository numbers: 2124219−2124221 (X = I, Cl, Br).

**Quantum chemical calculations.** All calculations were carried out with the TURBOMOLE79,80 program suite using the PBE081,82 hybrid density functional method (DFT-PBE0). Karlsruhe def2-TZVP83 basis sets were applied for hydrogen, carbon, oxygen, chlorine, and bromine. For uranium and iodine, scalar relativistic effects were taken into account by using 60-electron effective core potentials,84−86 together with respective def-TZVP and def2-TZVP valence basis sets.87 Multipole-accelerated resolution-of-the-identity approximation (MA-RIJ) was used to speed up the DFT calculations,88 and the m4 integration grid was used for the numerical integration of the exchange-correlation part. The conductor-like screening model (COSMO) was applied in all calculations to describe an ethyl acetate solvent field.91 The geometries of the complexes were fully optimized within the constraints of their point group symmetries. Numerical harmonic frequency calculations were performed to check if the optimized structures are true local minima on the potential energy surface. The Cartesian coordinates of the optimized structures are available in the Supporting Information. The thermal contributions to the free enthalpy were obtained within the harmonic oscillator rigid rotor model at room temperature, using the free module. The harmonic frequencies were not scaled when evaluating the thermal contributions.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00175.

Recorded IR, Raman, and NMR spectra as well as the technical details of the quantum chemical calculations (PDF)

CIF file for UBr$_6$-EtOAc (CIF)

CIF file for UC$_6$r-2EtOAc (CIF)

CIF file for U$_6$-EtOAc (CIF)

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**Notes**

The authors declare no competing financial interest.

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