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Rerefinement of the crystal structure of trichloridosulfonium(IV) hexachloridouranate(V), $(SCl_3)[UCl_6]$

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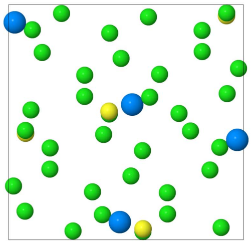
Single crystals of trichloridosulfonium(IV) hexachloridouranate(V) were obtained from the reaction of uranium(IV) chloride with an excess of disulfur dichloride and studied by single-crystal X-ray diffraction. In comparison with the structure model reported previously [Sawodny *et al.* (1983). *Z. Anorg. Allg. Chem.* **499**, 81–88.], the lattice parameters and fractional atomic coordinates were determined to a much higher precision, leading overall to an improved structure model. The ionic compound contains trigonal–pyramidal $(SCl_3)^+$ cations and slightly distorted octahedral $[UCl_6]^-$ anions. The structure was refined as an inversion twin with a twin ratio of 4.4:1.

3D view



Structure description

We explored the reaction of uranium tetrachloride with disulfur dichloride out of curiosity. Moreover, we investigated whether the latter compound could be a potential solvent for uranium halides. During these studies, high-quality single crystals of $(SCl_3)[UCl_6]$ were obtained.

The lattice parameters determined at 100 K from the current single-crystal X-ray structure determination (Table 3) agree with those reported previously [a = 10.668 (10), b = 10.712 (4) c = 11.333 (6) Å at T = 293 K; Sawodny *et al.*, 1983].

The U^V atom is located on Wyckoff position 4 a and has six chloride ligands in its slightly distorted octahedral coordination sphere (Fig. 1). The U—Cl bond lengths range between 2.4869 (16) and 2.5209 (14) Å and are in good agreement with the previously reported values [U—Cl distances = 2.485 (11)–2.531 (10) Å; Sawodny *et al.*, 1983]. A comparison between the U—Cl bond lengths and Cl—U—Cl angles obtained from the current and the previous refinements is collated in Tables 1 and 2, respectively. Similar

Table 1
Selected interatomic distances d (Å) for $(SCl_3)[UCl_6]$ from the current and the previous refinement.

Bond	d (current study)	d (Sawodny *et al.*, 1983)
$U1—Cl1^{ii}$	2.5263 (15)	2.510 (10)
$U1—Cl2^{iii}$	2.5297 (15)	2.531 (9)
$U1—Cl3$	2.5151 (16)	2.521 (10)
$U1—Cl4$	2.4869 (16)	2.485 (11)
$U1—Cl5^{i}$	2.5045 (16)	2.499 (10)
$U1—Cl6^{ii}$	2.5209 (15)	2.511 (9)
$S1—Cl7$	1.975 (2)	1.955 (14)
$S1—Cl8$	1.975 (2)	1.973 (13)
$S1—Cl9$	1.979 (2)	1.959 (13)

Symmetry codes: (i) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$; (ii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 2$.

U—Cl distances are observed: (i) in the crystal structure of the low-temperature modification of UCl_6 where the coordination sphere for the U atom is also distorted octahedral but with slightly shorter U—Cl bonds of 2.4443 (15)–2.4570 (20) Å (at 100 K; Deubner *et al.*, 2019) due to the presence of a U^{VI} atom, and (ii) in $Cs_2[UCl_6]$ with longer U—Cl bonds of 2.621 Å (at 293 K; Schleid *et al.*, 1987) due to the presence of an U^{IV} atom.

The S^{IV} atom is also located on Wyckoff position 4 *a* and has three chloride atoms in its trigonal–pyramidal coordination sphere (Fig. 1). The S—Cl bond lengths are virtually the same at 100 K. In comparison, Sawodny *et al.* (1983) reported slightly shorter S—Cl bond lengths for $(SCl_3)[UCl_6]$ at 293 K (Table 1). Nevertheless, these atomic distances are also in good agreement with those reported for the ionic compound β-$[SCl_3][SbCl_6]$ [1.979 (5) to 1.992 (7) Å at 169 K; Minkwitz *et al.*, 1992]. The Cl—S—Cl bond angles in $(SCl_3)[UCl_6]$ resulting from the current and the previous refinements differ slightly (Table 2).

The packing of U and S atoms in the crystal structure of $(SCl_3)[UCl_6]$ is shown in Fig. 2. As can be seen, the U and S atoms are arranged according to a distorted NaCl-type of structure. The overall coordination sphere of the S atom can be regarded as [3 + 3], with the three long S—Cl interactions being 3.0721 (2), 3.160 (2) and 3.287 (2) Å. The corresponding coordination polyhedron is a distorted trigonal antiprism, with the S atom displaced from the center.

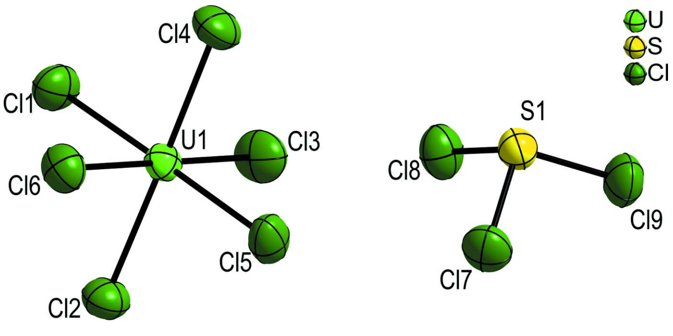


Figure 1
The slightly distorted trigonal–pyramidal $[SCl_3]^+$ cation and octahedral $[UCl_6]^-$ anion of the title compound. Displacement ellipsoids are shown at the 90% probability level.

Table 2
Comparison of selected angles φ (°) for $(SCl_3)[UCl_6]$ from the current and the previous refinement.

Angle	φ (current study)	φ (Sawodny *et al.*, 1983)
$Cl1^{ii}—U1—Cl2^{iii}$	89.86 (5)	89.9 (3)
$Cl3—U1—Cl6^{ii}$	179.02 (6)	179.3 (4)
$Cl3—U1—Cl2^{iii}$	91.20 (5)	91.8 (4)
$Cl3—U1—Cl1^{ii}$	89.76 (6)	90.0 (4)
$Cl4—U1—Cl2^{iii}$	178.87 (6)	179.4 (4)
$Cl4—U1—Cl1^{ii}$	89.44 (5)	89.6 (4)
$Cl4—U1—Cl3$	89.69 (6)	88.2 (4)
$Cl4—U1—Cl5^{i}$	91.56 (6)	91.3 (4)
$Cl4—U1—C6^{ii}$	90.83 (6)	91.2 (4)
$Cl5^{i}—U1—Cl1^{ii}$	178.95 (6)	179.0 (4)
$Cl5^{i}—U1—Cl6^{ii}$	90.89 (5)	90.1 (4)
$Cl5^{i}—U1—Cl2^{iii}$	89.14 (5)	89.2 (4)
$Cl5^{i}—U1—Cl3$	89.92 (6)	89.5 (4)
$Cl6^{ii}—U1—Cl1^{ii}$	89.42 (5)	90.4 (4)
$Cl6^{ii}—U1—Cl2^{iii}$	88.28 (5)	88.7 (3)
$Cl7^{iv}—S1—Cl8$	102.92 (10)	101.7 (7)
$Cl7^{i}—S1—Cl9$	102.93 (10)	103.5 (7)
$Cl8—S1—Cl9$	102.21 (9)	101.8 (6)

Symmetry codes: (i) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$; (ii) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 2$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 2$.

Synthesis and crystallization

$(SCl_3)[UCl_6]$ was synthesized in a borosilicate Schlenk tube from uranium tetrachloride (35 mg, 0.09 mmol) in disulfur dichloride (3 ml) at 358 K over a period of four months. A selected dark-yellow crystal was chosen for single-crystal X-ray diffraction.

We assume that S_2Cl_2 disproportionates under the applied reaction conditions and that elemental chlorine, sulfur monochloride, as well as the sulfur chlorides S_3Cl_2 and S_3Cl_4 are produced in the chemical equilibria described in equations (1)–(3).

$3\ S_2Cl_2 \rightarrow S_3Cl_2 + S_3Cl_4$ [equation (1); Spong, 1933].
$S_3Cl_4 \rightarrow S_2Cl_2 + SCl_2$ [equation (2); Spong, 1933].
$S_3Cl_4 \rightarrow S_3Cl_2 + Cl_2$ [equation (3); Spong, 1933].

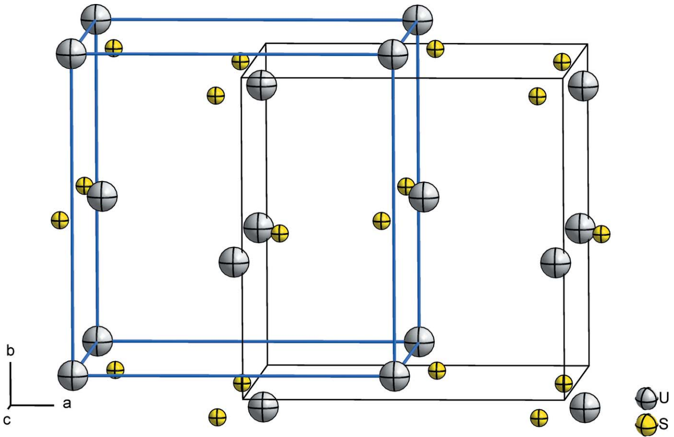


Figure 2
Packing of the U and S atoms in the crystal structure of $(SCl_3)[UCl_6]$, showing a distorted NaCl-type arrangement. The unit cell drawn in black can be shifted to the one highlighted in blue to make the relation more easily visible. The idealized blue unit cell shows the deviation of U atoms from *F*-centering as well as the deviation of the $(SCl_3)^+$ entities (Cl atoms not shown) from the octahedral voids.

Chlorine is dissolved in an excess of S_2Cl_2 and may then act as an oxidant oxidizing uranium(IV) chloride to form UCl_5 [equation (4)]. Other chlorine-sulfur species may also be responsible for the oxidation.

$2\ UCl_4 + Cl_2 \rightarrow 2\ UCl_5$ [equation (4); Cordfunke *et al.*, 1982].

We further assume that the formed SCl_2 [equation (2)] may disproportionate to S_2Cl_2 and SCl_4 [equation (5)].

$3\ SCl_2 \rightarrow S_2Cl_2 + SCl_4$ [equation (5); Lowry *et al.*, 1927].

Finally, the formation of the title compound may be described by the reaction of the Lewis acid UCl_5 with SCl_4 under abstraction of a chloride ion [equation (6)].

$SCl_4 + UCl_5 \rightarrow (SCl_3)[UCl_6]$ [equation (6); Sawodny *et al.*, 1983].

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Atomic coordinates of the previously reported $(SCl_3)[UCl_6]$ structure (Sawodny *et al.*, 1983) were used for refinement. The structure was refined as an inversion twin with a twin ratio of 4.4:1. As a result of the similarity of the *a* and *b* lattice parameters, a fourfold twin was also considered; refinement of this twin model led to insignificant twin fractions. $R_{\rm int}$ for the tetragonal crystal system was above 0.4, ruling out a higher symmetry model.

Table 3
Experimental details.

Crystal data	
Chemical formula	$(SCl_3)[UCl_6]$
M_r	589.14
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	100
a, b, c (Å)	10.534 (2), 10.545 (2), 11.217 (2)
V (Å^3)	1246.0 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	15.07
Crystal size (mm)	0.15 × 0.1 × 0.08
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Numerical (*X-RED32*; Stoe 2016)
$T_{\rm min}$, $T_{\rm max}$	0.036, 0.090
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18340, 3364, 3304
$R_{\rm int}$	0.046
$(\sin \theta/\lambda)_{\rm max}$ (Å^{-1})	0.686
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.019, 0.043, 1.08
No. of reflections	3364
No. of parameters	101
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.53, −1.01
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.186 (6)

Computer programs: *X-AREA* (Stoe, 2016), *SHELXL* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2019) and *publCIF* (Westrip, 2010).

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full crystallographic data

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Trichloridosulfonium(IV) hexachloridouranate(V)

Crystal data

$(SCl_3)[UCl_6]$
$M_r = 589.14$
Orthorhombic, $P2_12_12_1$
$a = 10.534\ (2)$ Å
$b = 10.545\ (2)$ Å
$c = 11.217\ (2)$ Å
$V = 1246.0\ (4)$ Å^3
$Z = 4$
$F(000) = 1044$

$D_x = 3.141$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 23552 reflections
$\theta = 3.6$–$58.9°$
$\mu = 15.07$ mm^{-1}
$T = 100$ K
Block, dark yellow
0.15 × 0.1 × 0.08 mm

Data collection

STOE IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Planar graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation method, ω scans
Absorption correction: numerical (X-Red32; Stoe 2016)

$T_{min} = 0.036$, $T_{max} = 0.090$
18340 measured reflections
3364 independent reflections
3304 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 29.2°$, $\theta_{min} = 2.7°$
$h = -14 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.043$
$S = 1.08$
3364 reflections
101 parameters
0 restraints

Primary atom site location: other
$w = 1/[\sigma^2(F_o^2) + (0.0148P)^2 + 3.5607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -1.01$ e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.186 (6)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
U1	0.97364 (2)	0.42494 (2)	0.98324 (2)	0.01499 (6)
S1	0.42766 (14)	0.54654 (14)	0.91370 (13)	0.0181 (3)
Cl1	0.82355 (14)	0.89033 (16)	0.63247 (14)	0.0239 (3)
Cl2	0.59526 (14)	0.94785 (14)	0.86341 (13)	0.0225 (3)
Cl3	0.93040 (17)	0.62131 (16)	0.86263 (15)	0.0273 (3)
Cl4	0.85717 (15)	0.29644 (17)	0.83292 (15)	0.0258 (3)
Cl5	0.72554 (14)	0.53738 (16)	0.59988 (14)	0.0241 (3)
Cl6	0.97901 (16)	0.72883 (13)	0.39615 (13)	0.0220 (3)
Cl7	0.92843 (16)	0.96521 (16)	0.91059 (14)	0.0250 (3)
Cl8	0.60091 (14)	0.60665 (15)	0.87712 (15)	0.0241 (3)
Cl9	0.32415 (15)	0.69986 (15)	0.88359 (15)	0.0255 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.01381 (8)	0.01650 (8)	0.01466 (9)	−0.00076 (7)	−0.00008 (7)	−0.00013 (7)
S1	0.0170 (6)	0.0191 (7)	0.0180 (6)	0.0009 (5)	−0.0012 (5)	0.0006 (5)
Cl1	0.0180 (6)	0.0306 (8)	0.0232 (7)	0.0019 (5)	0.0051 (5)	0.0038 (6)
Cl2	0.0221 (7)	0.0233 (8)	0.0221 (7)	0.0034 (5)	0.0020 (5)	−0.0045 (5)
Cl3	0.0355 (8)	0.0223 (7)	0.0241 (7)	0.0010 (6)	−0.0012 (7)	0.0060 (6)
Cl4	0.0219 (7)	0.0316 (8)	0.0239 (7)	−0.0038 (6)	−0.0057 (6)	−0.0059 (6)
Cl5	0.0170 (6)	0.0342 (8)	0.0211 (7)	0.0039 (6)	−0.0024 (5)	−0.0018 (6)
Cl6	0.0227 (6)	0.0192 (6)	0.0240 (6)	0.0011 (6)	−0.0028 (6)	−0.0027 (5)
Cl7	0.0273 (7)	0.0295 (8)	0.0182 (7)	−0.0015 (6)	−0.0004 (6)	0.0028 (6)
Cl8	0.0179 (6)	0.0283 (8)	0.0262 (7)	−0.0016 (5)	0.0012 (5)	0.0053 (6)
Cl9	0.0240 (7)	0.0243 (7)	0.0280 (8)	0.0073 (6)	−0.0025 (6)	0.0035 (6)

Geometric parameters (Å, º)

U1—Cl4	2.4869 (16)	U1—Cl2$^{\mathrm{iii}}$	2.5297 (15)
U1—Cl5$^{\mathrm{i}}$	2.5045 (16)	S1—Cl7$^{\mathrm{iv}}$	1.975 (2)
U1—Cl3	2.5151 (16)	S1—Cl8	1.975 (2)
U1—Cl6$^{\mathrm{ii}}$	2.5209 (14)	S1—Cl9	1.979 (2)
U1—Cl1$^{\mathrm{ii}}$	2.5263 (15)		
Cl4—U1—Cl5$^{\mathrm{i}}$	91.56 (6)	Cl6$^{\mathrm{ii}}$—U1—Cl1$^{\mathrm{ii}}$	89.42 (5)
Cl4—U1—Cl3	89.69 (6)	Cl4—U1—Cl2$^{\mathrm{iii}}$	178.87 (6)
Cl5$^{\mathrm{i}}$—U1—Cl3	89.92 (6)	Cl5$^{\mathrm{i}}$—U1—Cl2$^{\mathrm{iii}}$	89.14 (5)
Cl4—U1—Cl6$^{\mathrm{ii}}$	90.83 (6)	Cl3—U1—Cl2$^{\mathrm{iii}}$	91.20 (5)
Cl5$^{\mathrm{i}}$—U1—Cl6$^{\mathrm{ii}}$	90.89 (5)	Cl6$^{\mathrm{ii}}$—U1—Cl2$^{\mathrm{iii}}$	88.28 (5)
Cl3—U1—Cl6$^{\mathrm{ii}}$	179.02 (6)	Cl1$^{\mathrm{ii}}$—U1—Cl2$^{\mathrm{iii}}$	89.86 (5)
Cl4—U1—Cl1$^{\mathrm{ii}}$	89.44 (5)	Cl7$^{\mathrm{iv}}$—S1—Cl8	102.92 (10)
Cl5$^{\mathrm{i}}$—U1—Cl1$^{\mathrm{ii}}$	178.95 (6)	Cl7$^{\mathrm{iv}}$—S1—Cl9	102.93 (10)
Cl3—U1—Cl1$^{\mathrm{ii}}$	89.76 (6)	Cl8—S1—Cl9	102.21 (9)

Symmetry codes: (i) $-x+3/2, -y+1, z+1/2$; (ii) $-x+2, y-1/2, -z+3/2$; (iii) $x+1/2, -y+3/2, -z+2$; (iv) $x-1/2, -y+3/2, -z+2$.