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FACILE SYNTHESIS OF UCl_4 AND $ThCl_4$, METALLOTHERMIC REDUCTIONS OF UCl_4 WITH ALKALI METALS AND CRYSTAL STRUCTURE REFINEMENTS OF UCl_3, UCl_4 AND Cs_2UCl_6

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Summary

Uranium and thorium tetrachloride (UCl_4 and $ThCl_4$) were obtained via the ammonium chloride route from UH_3 and thorium metal respectively, with the ternary chlorides $(NH_4)_2UCl_6$ and $(NH_4)_2ThCl_6$ acting as intermediates. The crystal structure of UCl_4 was refined ($R = 0.031$, $R_w = 0.026$). Cs_2UCl_6 and Cs_2ThCl_6 were synthesized, their lattice constants refined from powder data, and the crystal structure of Cs_2UCl_6 refined from single-crystal data ($R = 0.066$, $R_w = 0.052$). Some indication for stacking disorder in the [00.1] direction was found. Metallothermic reductions of UCl_4 with lithium and sodium led to UCl_3 whose crystal structure was also refined ($R = 0.029$, $R_w = 0.023$). Potassium reduced UCl_4 to K_2UCl_5. No further reduction could be detected.

1. Introduction

Within the wealth of uranium chlorides, UCl_x ($x = 3$ - 6), UCl_4 is probably the most feasible starting material for many subsequent syntheses. Consequently, reports on the preparation of UCl_4 are numerous [1 - 3]. However, with uranium metal and its hydride UH_3, readily available therefrom, a facile synthesis may be added. This is the low temperature reaction of UH_3 with ammonium chloride yielding $(NH_4)_2UCl_6$ which may subsequently be decomposed thermally to UCl_4. Thorium metal reacts analogously to $ThCl_4$.

These products, UCl_4 and $ThCl_4$, were used for the synthesis of Cs_2UCl_6 and Cs_2ThCl_6 and also in metallothermic reductions with alkali metals (lithium, sodium and potassium) yielding UCl_3 and K_2UCl_5 respectively. Single crystals of UCl_4, Cs_2UCl_6 and UCl_3 were obtained during this study and structural refinements are reported below.

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2. Experimental details

2.1. UCl_4 and $ThCl_4$

Uranium and thorium metal were available as bulk metal and powder respectively. To enhance the reactivity of the uranium metal, UH_3 was produced in a hydrogen stream at 250 °C. The ammonium chloride route to anhydrous rare earth chlorides and americium trichloride has been described elsewhere in detail [4 - 7] and was applied analogously. UH_3 or thorium were mixed together with six times the molar amount of NH_4Cl in a dry box and filled into Pyrex tubes with necks which were then pulled off to capillary tips. The tubes were heated to 300 °C (for details see ref. 6 ('dry' route)). In either case, after a reaction time of about 30 h, the ternary chlorides $(NH_4)_2MCl_6$ ($M \equiv U, Th$) had formed quantitatively. Their subsequent decomposition in a vacuum (approximately 10^{-3} Torr) at 350 °C led to UCl_4 and $ThCl_4$, which were pure on the basis of Guinier X-ray patterns.

Single crystals of UCl_4 were grown from the melt (sealed quartz tube, 750 °C) by slow cooling (10 °C day^{-1}). A dark green irregularly shaped columnar specimen of the approximate size 0.03 mm × 0.04 mm × 0.1 mm was used for data collection (see Table 1).

2.2. Cs_2UCl_6 and Cs_2ThCl_6

To the tetrachlorides thus obtained, two millimolar amounts of CsCl were added and the admixtures were heated together in sealed quartz tubes to 750 °C for seven days. Light green irregular single crystals (for example 0.4 mm × 0.15 mm × 0.09 mm) of Cs_2UCl_6 were obtained from the melt by slow cooling (at 10 °C day^{-1}).

2.3. Metallothermic reductions of UCl_4

Reactions of UCl_4 with alkali metals were carried out in helium arc-sealed tantalum containers, jacketed in silica tubing under vacuum, usually at 700 °C for seven days. Lithium or sodium as reductants resulted in the formation of two-phase mixtures consisting of alkali chloride and uranium trichloride UCl_3, in the former case as single-crystalline dark red columns of typical size 0.1 mm × 0.1 mm × 0.3 mm. Synproportionation reactions of UCl_4 and uranium metal ($3UCl_4 + U$; at 800 °C for seven days, in a tantalum tube) also frequently yielded single crystals of UCl_3.

K_2UCl_5 was the principal product of the reduction of UCl_4 with potassium. It was identical with the product previously obtained from KCl and UCl_3 [13]. Further reduction of UCl_3 with potassium (to a divalent state, for example), although attempted, was not achieved.

2.4. Identification of the products

The products were mainly identified by X-ray crystallographic methods either with single crystals (UCl_3, UCl_4, Cs_2UCl_6) or by powder techniques (Guinier–Simon [8, 9]).

TABLE 1

UCl_4: crystallographic data and their determination

Lattice constants (pm) *and molar volume* V_m ($cm^3\ mol^{-1}$)

a = 830.18(4)[a], c = 748.13(6)[a], V_m = 77.631(8)[a]

a = 831.3[b], c = 749.2[b], V_m = 77.95[b]

Crystal system and space group

Tetragonal $I4_1/amd$ (no. 141, origin at $\bar{4}m2$), $Z = 4$

Data collection

Four-circle diffractometer Philips PW 1100, Mo Kα radiation, graphite monochromator, λ = 71.07 pm, ω scan, scan speed = 0.10° s^{-1}, scan width = 3.0°, $3° \leqslant \theta \leqslant 30°$, $F(000)$ = 640, μ = 317.98 cm^{-1}

Data corrections

Background, polarization and Lorentz factors; absorption: ϕ scan, $\Delta\phi$ = 10°, θ = 7.855° (*hkl*, 031), absorption coefficients ranging from 0.797 (*hkl*, $-5\ 8\ -5$) to 0.991 ($-3\ 4\ 3$)

Data statistics

1619 data collected, 217 unique reflections (R_{int} = 0.044), 202 reflections with $|F_o| \geqslant 1.5\ \sigma|F_o|$

Structure determination and refinement

Program system SHEL-X 76 [10], scattering factors from Cromer *et al.* [11, 12], Patterson (U) and difference Fourier syntheses (Cl), full-matrix least-squares refinement, $R = 0.031$, $R_w = 0.026$ ($w = 2.258\ (\sigma^2|F_o| + 2.33 \times 10^{-4}\ F_o^2)^{-1}$

Atomic coordinates

		x/a	y/b	z/c
U	4a	0.0	0.0	0.0
Cl	16h	0.0	0.3113(3)	0.9255(3)

Temperature factors[c]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	50(2)	$\equiv U_{11}$	123(3)	0	0	0
Cl	394(15)	81(10)	143(11)	18(9)	0	0

[a] Guinier–Simon data [8, 9].

[b] Four circle diffractometer data.

[c] $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^* + \ldots)\}$, U_{ij} (pm^2)

3. Results and discussion

The tetrachlorides of uranium and thorium, UCl_4 and $ThCl_4$, were synthesized by a method analogous to that for many other metals [5]. The first step of their preparation was the oxidation of the metals to the tetravalent state together with complexation yielding $(NH_4)_2UCl_6$ and $(NH_4)_2ThCl_6$. Uranium hydride was used because it can be easily pulverized and mixed with ammonium chloride. As a powder sample of thorium metal was available there seemed to be no need to hydrogenate it. The subsequent second step was the thermal decomposition of $(NH_4)_2MCl_6$ ($M \equiv U$, Th) to the tetrachlorides, MCl_4. Therefore, their synthesis can be summarized in the two following equations

TABLE 2

A comparison of crystallographic data for UCl_4 and $ThCl_4$

	UCl_4			*$ThCl_4$*	
	[14] *(XRP)*[a]	*[15]* *(ND)*[b]	*This work* *(XR)*[c]	*[16]* *(XR)*[c]	*This work* *(XRP)*[a]
a (pm)	829.6(9)	826.3(3)	830.18(4)	848.6	849.04(4)
c (pm)	748.7(9)	745.7(3)	748.13(6)	746.5	748.74(6)
c/a	0.9025	0.9025	0.9012	0.8797	0.8819
y (Cl)	0.281	0.3125(5)	0.3113(3)	0.3133(8)[e]	—
z (Cl)	0.917	0.9261(5)	0.9255(3)	0.9242(8)[e]	—
d (U–Cl)[d] (pm)	241	263.8(4)	264.4(2)	271.8(8)	—
	309	286.9(3)	288.9(1)	290.3(7)	—

[a] XRP: X-ray powder diffraction data.
[b] ND: neutron diffraction data.
[c] XR: X-ray single-crystal work.
[d] Four times each.
[e] Transformed for the non-centrosymmetric setting (origin at $\bar{4}m2$).

$$M + 6NH_4Cl = (NH_4)_2MCl_6 + 4NH_3 + 2H_2$$

$$(NH_4)_2MCl_6 = MCl_4 + 2NH_4Cl$$

The tetrachlorides were obtained as finely divided, almost colorless ($ThCl_4$) and apple-green (UCl_4) powders that dissolved readily in water. No major impurities were detected, since Guinier patterns were free of any extra lines. Lattice constants derived therefrom are compared with literature data in Table 2.

The crystal structure of UCl_4 had previously been determined only from X-ray [14] and neutron diffraction [15] powder data. As single crystals of UCl_4 could be grown rather easily from the melt by slow cooling, a structural refinement was undertaken from single-crystal X-ray diffraction data. The results are summarized in Table 1. A comparison with previous results is shown in Table 2. No major deviations from the neutron diffraction data were detected, although our X-ray results were more precise.

The powder samples of UCl_4 and $ThCl_4$ prepared as described above were subsequently used for two types of syntheses. Firstly, Cs_2UCl_6 and Cs_2ThCl_6 were prepared by heating together stoichiometric amounts of CsCl and tetrachloride and, secondly, metallothermic reductions with alkali metals (lithium, sodium and potassium) were carried out.

Lattice constants of Cs_2UCl_6 and Cs_2ThCl_6 are compared with literature data and those of other actinide chlorides, Cs_2MCl_6 in Table 3. Single crystals of Cs_2UCl_6 were grown from the melt by slow cooling and a structural refinement was undertaken (for details see Table 4). The refinement ended with

TABLE 3

Lattice constants, *c*/*a* ratios and molar volumes for the ternary chlorides Cs_2MCl_6 (M ≡ actinides)

	a (pm)	*c* (pm)	*c*/*a*	V_m ($cm^3\ mol^{-1}$)	*Reference*
Cs_2ThCl_6	762.9(7)	605.0(3)	0.7930	183.67	[17]
	762.16(4)	605.84(4)	0.7949	183.55(2)	This work
Cs_2PaCl_6	754.6(2)	605.6(2)	0.8025	179.87	[18]
Cs_2UCl_6	750.7(3)	605.0(3)	0.8059	177.84	[17]
	750.37(3)	605.40(4)	0.8068	177.79(2)	This work
Cs_2NpCl_6	746.0	603.0	0.8083	175.0	[19]
Cs_2PuCl_6	744.5(10)	604.2(10)	0.8116	174.7	[20]
	745.79(4)	604.27(5)	0.8102	175.31	[21]
Cs_2BkCl_6	745.0(3)	1209.8(5)	1.6239	175.12	[22]

rather unsatisfactory R values of 0.066 and 0.052 (R_w). Furthermore, the 'internal' R value calculated from averaging symmetrically equivalent reflections (R_{int} = 0.098) and the large absorption coefficients (down to 0.332) indicated that there was something 'wrong' with this crystal structure. Indeed, the final difference map showed a peak at the same height as caesium but with inverse x and y coordinates ($\frac{2}{3}, \frac{1}{3}$ instead of $\frac{1}{3}, \frac{2}{3}$) attesting to a 60° rotation of ($CsCl_3$) layers perpendicular to [001]. This peak refined to a 1:12 ratio for caesium in the 'irregular' *vs.* the regular position with a reasonable isotropic temperature factor [166(50) pm^2] and the R value dropped to 0.061. As the crystal structure of Cs_2UCl_6 may be described as a hexagonal close-packing of ($CsCl_3$) layers with U^{4+} occupying every other 'octahedral' hole with respect to BcA–BcA, the slight occupation of 'irregular' caesium sites may be interpreted as a stacking disorder due to an occasional (one out of twelve) 60° rotation of A or B layers normal to [001]. A similar stacking 'disorder' (polytypism) dominates the structure of Cs_2BkCl_6 [22] (≡K_2MnF_6) with the stacking sequence AcB–AbC–AcB exhibiting an ordered superstructure with doubling of the c axis constant with respect to Cs_2UCl_6.

The Cs^+–Cl^- distances (366.2 (3×), 375.6 (6×), 376.8 pm (3×)) average to a comfortable 373.6 pm. The U^{4+}–Cl^- distances in the "octahedral" $(UCl_6)^{2-}$ (only slightly compressed to a trigonal antiprism with angles of 87.89° and 92.11°) were all equal (262.1 pm). Compared with the average distance of 276.7 pm in UCl_4, this is a 5.3% reduction owing to the decrease of the coordination number from eight (UCl_4) to six (Cs_2UCl_6). The electrostatic (Madelung) parts of the lattice energies (MAPLE [23]) have been calculated for Cs_2UCl_6 (2066.4 kcal mol^{-1}) and for UCl_4 (1710.4 kcal mol^{-1}). Twice the MAPLE value of CsCl (163.9 kcal mol^{-1}) added to the

TABLE 4

Cs_2UCl_6: crystallographic data and their determination

Lattice constants (pm) *and molar volume* V_m (cm^3 mol^{-1})

$a = 750.37(3)^a$, $c = 605.40(4)^a$, $V_m = 177.79(2)^a$

$a = 750.9^b$, $c = 605.8^b$, $V_m = 178.14^b$

Crystal system and space group

Trigonal $P\bar{3}m\,1$ (no. 164), $Z = 1$

Data collection

Four-circle diffractometer Philips PW 1100, Mo Kα radiation, graphite monochromator, $\lambda = 71.07$ pm, ω scan, scan speed = 0.20° s^{-1}, scan width = 6.0°, $3° \leqslant \theta \leqslant 30°$, $F(000) = 304$, $\mu = 200.73$ cm^{-1}

Data corrections

Background, polarization and Lorentz factors; absorption: ϕ scan, $\Delta\phi = 10°$, $\theta = 7.118°$ (*hkl*, 0 −2 −1), absorption coefficients ranging from 0.332 (*hkl*, 0 1 −1) to 0.9844 (211)

Data statistics

1853 data collected, 357 unique reflections ($R_{int} = 0.098$), 323 reflections with $|F_0| \geqslant 2\sigma|F_0|$

Structure determination and refinement

Program system SHEL-X 76 [10], scattering factors from Cromer *et al.* [11, 12], Patterson (Cs, U) and difference Fourier syntheses (Cl), full-matrix least-squares refinement, $R = 0.066$, $R_w = 0.052$ ($w = 2.397\ \sigma^{-2}|F_0|$)

Atomic coordinates

		x/a	y/b	z/c
Cs	2d	0.3333	0.6667	0.7298(4)
U	1a	0.0	0.0	0.0
Cl	6i	0.1677(3)	−0.1677(3)	0.2406(9)

Temperature factors[c]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs	395(9)	$\equiv U_{11}$	513(17)	0	0	198(4)
U	154(5)	$\equiv U_{11}$	161(9)	0	0	77(2)
Cl	394(19)	$\equiv U_{11}$	466(30)	40(10)	$\equiv -U_{23}$	250(21)

[a] Guinier–Simon data [8, 9].

[b] Four circle diffractometer data.

[c] $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^* + \ldots)\}$, U_{ij} (pm^2).

latter, amounts to 2038.2 kcal mol^{-1} for the 'sum of the binaries', which is 28.2 kcal mol^{-1} (1.4%) smaller than MAPLE for the ternary Cs_2UCl_6. The reason for this might be the above-mentioned reduction of the U^{4+}–Cl^- distances for eightfold *vs.* sixfold coordination.

Metallothermic reductions of lanthanide halides with alkali metals resulted in the formation of binary or ternary halides of the divalent lanthanides [24], *e.g.* $NdCl_2$ or KNd_2Cl_5 [25], in the formation of ternary

TABLE 5

UCl_3: crystallographic data and their determination

Lattice constants (pm) *and molar volume* V_m ($cm^3\ mol^{-1}$)

$a = 744.39(3)^a$, $c = 432.43(3)^a$, $V_m = 62.487(6)^a$

$a = 744.9^b$, $c = 432.7^b$, $V_m = 62.61^b$

Crystal system and space group

Hexagonal $P6_3/m$ (no. 176), $Z = 2$

Data collection

Four-circle diffractometer Philips PW 1100, Mo Kα radiation, graphite monochromator, $\lambda = 71.07$ pm, ω scan, scan speed = $0.08°\ s^{-1}$, scan width = 2.4°, $3° \leqslant \theta \leqslant 30°$, $F(000) = 286$, $\mu = 389.77\ cm^{-1}$

Data corrections

Background, polarization and Lorentz factors; absorption: ϕ scan, $\Delta\phi = 10°$, $\theta = 5.680°$ (*hkl*, —111), absorption coefficients ranging from 0.404 (*hkl*, 015) to 0.990 (—215)

Data statistics

1279 data collected, 226 unique reflections ($R_{int} = 0.062$), 203 reflections with $|F_0| \geqslant 1.5\sigma|F_0|$

Structure determination and refinement

Program system SHEL-X 76 [10], scattering factors from Cromer *et al.* [11, 12], Patterson (U) and difference Fourier syntheses (Cl), full-matrix least-squares refinement, $R = 0.029$, $R_w = 0.023$ ($w = 3.681\ \sigma^2|F_o| + 4.6 \times 10^{-5}F_o^2)^{-1}$)

Atomic coordinates

		x/a	y/b	z/c
U	2c	0.3333	0.6667	0.25
Cl	6h	0.3866(4)	0.3016(4)	0.25

Temperature factors^c

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
U	52(2)	$\equiv U_{11}$	105(3)	0	0	26(1)
Cl	97(9)	114(9)	171(10)	0	0	63(8)

[a] Guinier–Simon data [8, 9].

[b] Four circle diffractometer data.

[c] $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^* + \ldots)\}$, U_{ij} (pm^2)

halides of the trivalent lanthanides, *e.g.* $LiGdCl_4$ [26] when there is no stable divalent state, or in the formation of more reduced lanthanide compounds such as Li_zGdClH_x [27]. Reduction of UCl_4 with lithium or sodium both resulted in the formation of UCl_3, as single crystals in the case of lithium reduction. One may conclude from this observation that there are no ternary chlorides in the systems LiCl–UCl_3 and NaCl–UCl_3 which is obviously in agreement with previous reports [1]. K_2UCl_5 (together with UCl_3) resulted from the reduction of UCl_4 with potassium; it was previously obtained by 'direct' synthesis from KCl and UCl_3. Further reduction of UCl_3 with potassium to divalent uranium appeared to be impossible; its absence was not surprising in the light of a calculated —4.7 V reduction potential [$E°(U^{3+}/$

TABLE 6

A comparison of crystallographic data for UCl_3

	[*20*]	[*15*]	[*13*]	*This work*
a (pm)	744.3	744.0	744.5	744.39(3)
c (pm)	431.2	432.1	431.4	432.43(3)
c/a	0.5793	0.5808	0.5794	0.5809
x(Cl)	0.375	0.3858(4)	0.3871(12)	0.3866(4)
y(Cl)	0.292	0.3009(4)	0.3001(13)	0.3016(4)
d(U–Cl) (pm)	296(9×)	293.1(2)(6×) 293.8(3)(3×)	291.8(6×) 294.1(3×)	293.0(2)(6×) 293.6(2)(3×)

U^{2+}] [28]. Again, K_2UCl_5 was the main product of the reaction of UCl_3 with potassium together with some reduction to uranium metal.

Single crystals of UCl_3 yielded via the lithium reduction of UCl_4 were used for a structural refinement. A much better data set than in our previous refinement [13] resulting in much lower R values (see Table 5), was obtained so that the crystallographic data are now more reliable. The new results also match better with the results from the neutron diffraction powder refinement [15]. A comparison is given in Table 6. Most importantly, the nine U^{3+}–Cl^- distances of the tricapped trigonal prism (UCl_9) are equal within 3σ.

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