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K_2UCl_5, Rb_2UCl_5, UCl_3 AND A COMPARISON WITH ANALOGOUS RARE EARTH CHLORIDES*

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Summary

K_2UCl_5 and Rb_2UCl_5 crystallize isotypically with K_2PrCl_5 (orthorhombic structure; space group, *Pnma*; $Z = 4$). Monocapped trigonal prisms $[UCl_7]$ are connected via two common edges to chains $[UCl_5]^{2-}$ in the [010] direction. The lattice constants and molar volumes suggest that the uranium chlorides should be compared with the analogous cerium compounds. The crystal structure of UCl_3 was refined from single-crystal data.

1. Introduction

As the rare earth trichlorides $RECl_3$ (RE ≡ La–Gd) [1] have the UCl_3-type structure [2–4], the KCl–UCl_3 and RbCl–UCl_3 systems are expected to behave in a similar manner to the analogous alkali metal chloride–rare earth metal trichloride (ACl–$RECl_3$) systems. According to phase diagram determinations [5] and X-ray structural investigations [6] only the formula types ARE_2Cl_7, $A_3RE_2Cl_9$, A_2RECl_5 and A_3RECl_6 have been observed, although not in every system.

Compounds of the A_2RECl_5 type were obtained with A ≡ K and RE ≡ La–Dy, A ≡ Rb and RE ≡ La–Eu [7], and with the heavier rare earths with A ≡ Rb and RE ≡ Er–Lu, A ≡ Cs and RE ≡ Dy–Lu [8]. Both the KCl–UCl_3 and RbCl–UCl_3 systems contain compounds of the A_2UCl_5 type [9, 10]. X-ray powder data have apparently been recorded only once for K_2UCl_5 and Rb_2UCl_5 [10] and were indexed using an orthorhombic unit cell (Tl_2AlF_5 type). The magnetic and spectroscopic behaviour of these compounds has also been investigated [11].

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2. Experimental details

UCl_3 was prepared as follows. Uranium metal filings (Zinsser, Frankfurt am Main) reacted with hydrogen at 250 °C to yield UH_3 which was dehydrogenated at 330 °C in a stream of dry argon. The finely divided powder reacted with HCl gas at 250 °C to give a mixture of UCl_3 and UCl_4. Chemical transport with iodine (525–400 °C) gave single crystals of both UCl_3 (deep red) and UCl_4 (green).

K_2UCl_5 and Rb_2UCl_5 were prepared as follows. 2:1 molar mixtures of KCl or RbCl and UCl_3 were heated together in Pyrex tubes under dry argon at 400 °C for 2 days. Purple–violet hygroscopic powders were obtained.

Guinier patterns were obtained using a Simon camera [12] (model FR 553; Enraf–Nonius, Delft) and Cu $K\alpha_1$ radiation. They were measured and the lattice constants were computed [13] for K_2UCl_5 and Rb_2UCl_5. Low temperature quartz (a = 491.323 pm, c = 540.485 pm [14]) was used for calibration.

Single crystals of UCl_3 were mounted under dry argon in glass capillaries and their quality was checked using Weissenberg photographs. The best crystal was transferred to a four-circle diffractometer (Philips, PW 1100) for data collection (Mo Kα radiation; ω scan; scan speed, 0.04° s^{-1}; scan width, 1.2°). The data were treated in the usual way: an R factor of 9.1% was finally obtained for 139 $|F_o|$ with $|F_o| > 2.5\sigma|F_o|$ [15].

3. Results and discussion

Our film readings of Guinier patterns of K_2UCl_5 and Rb_2UCl_5 are essentially identical with published powder data [10] (see Table 1 for the example of K_2UCl_5). However, the assumption that both chlorides crystallize in the Tl_2AlF_5 type [16] is not only unlikely but, furthermore, cannot interpret the powder patterns.

By analogy with our results for K_2RECl_5 (RE ≡ La–Dy) and Rb_2RECl_5 (RE ≡ La–Eu) compounds [7], the powder patterns of K_2UCl_5 and Rb_2UCl_5 can be indexed using the following orthorhombic unit cells: K_2UCl_5, a = 1271.9(2) pm, b = 880.16(9) pm, c = 799.53(9) pm; Rb_2UCl_5, a = 1313.6(4) pm, b = 898.8(3) pm, c = 820.3(3) pm. Therefore both chlorides crystallize isotypically with K_2PrCl_5 whose crystal structure has recently been refined from single-crystal data [7] (space group, *Pnma*; Z = 4). The observed relative intensities are in good agreement with those calculated for this model (see Table 1).

U^{3+} has seven nearest neighbours in both K_2UCl_5 and Rb_2UCl_5, and the coordination polyhedron can be described as a monocapped trigonal prism. The distances were calculated using the atomic coordinates of K_2PrCl_5 and are included in Fig. 1 where the connection of the prisms $[UCl_7]$ to the chains $[UCl_5]$ via two opposite common edges according to $^1_\infty[UCl^t_{3/1}Cl^e_{4/2}]$ is shown (where t denotes terminal and e denotes edge sharing). The U^{3+}–U^{3+} distance through the common edge is 457 pm and this connection is presumably responsible for the reported antiferromagnetism [11] of both compounds. This assumption is confirmed by our preliminary results.

TABLE 1

The first 25 lines of the Guinier pattern of K_2UCl_5 and a comparison with *d* values from ref. 10.

hkl	$4\theta_o$ (deg)	I_o [a]	I_c	$\sin^2\theta_o$	$\sin^2\theta_c$	d_o [b] (pm)	*d* [10] (pm)
101	26.03	vs	1000	0.01248	0.01295	679.8	678
200	27.77	m	569	0.01461	0.01467	637.2	632
011	29.92	w	289	0.01694	0.01694	591.8	
020	40.33	w	214	0.03065	0.03063	440.0	
211	40.88	w	242	0.03147	0.03161	434.2	433
002	44.43	vw	132	0.03712	0.03712	399.8	403
301	47.44	w	364	0.04223	0.04229	374.8	374
121	48.16	m	577	0.04352	0.04358	369.2	368
220	49.15	w	348	0.04529	0.04530	361.9	361
112	50.85	w	236	0.04842	0.04845	350.0	350
202	52.56	vw	74	0.05168	0.05179	338.8	338
221	54.00	vw	39	0.05449	0.05458	330.0	
400	56.04	vw	118	0.05861	0.05868	318.2	318
401	60.42	vw	127	0.06791	0.06796	295.6	296
302	61.44	vw	61	0.07015	0.07013	290.8	290
122	61.98	vw	159	0.07136	0.07143	288.3	288
411	63.83	vw	174	0.07558	0.07562	280.2	280
312	64.79	w	203	0.07781	0.07779	276.1	
222	66.70	w	358	0.08234	0.08243	268.4	268
103	68.69	vw	31	0.08716	0.08720	260.9	
420	69.54	w	356	0.08927	0.08931	257.8	257.5
013	70.30	vw	170	0.09118	0.09119	255.1	
231	70.97	vw	113	0.09286	0.09288	252.8	
501	74.08	vw	42	0.10089	0.10096	242.5	
213	75.93	m	392	0.10581	0.10586	236.8	236.6

[a] vs, very strong; m, medium; w, weak; vw, very weak.

[b] Calculated from $\sin^2\theta_o$.

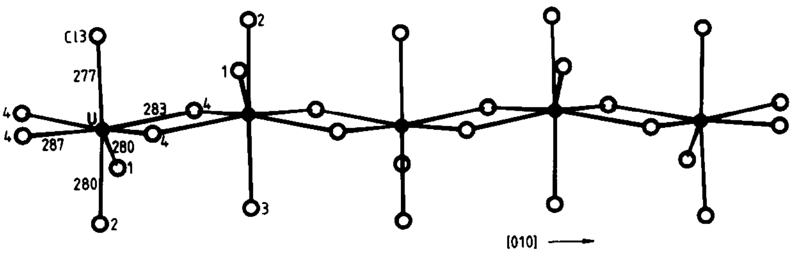

Fig. 1. The $[UCl_5]^{2-}$ chain ($^1_\infty[UCl^t_{3/1}Cl^e_{4/2}]^{2-}$) in K_2UCl_5. The distances are in picometres.

A comparison of the Madelung parts of the lattice energy (MAPLE) [17] of K_2UCl_5 and the sum of the respective values of the binary components KCl (twice) and UCl_3 supports the results derived from the powder data (Table 2). The results of the refinement of the crystal structure of UCl_3 were used to calculate its MAPLE and the values are compared with previous results in Table 3.

TABLE 2
The Madelung parts of the lattice energy of K_2UCl_5

	Lattice energy (kcal mol^{-1})	
	Binary	*Ternary*
K^+	92.2 (2×)	103.9 (2×)
U^{3+}	740.3	720.8
Cl^-	92.2[a]	91.4
Cl^-	92.2	99.3
Cl^-	103.7[b]	94.4
Cl^-	103.7 (2×)	108.9 (2×)
Σ	1420.2	1431.5 (Δ = 0.8%)

[a] From KCl.
[b] From UCl_3; this association is arbitrary.

TABLE 3
A comparison of the results of the structure analyses of UCl_3 ($P6_3/m$; $Z = 2$; uranium in 2c; chlorine in 6h)

	Ref. 2	*Ref. 4*[a]	*This work*
a (pm)	744.3	744.0	744.5
c (pm)	431.2	432.1	431.4
x(Cl)	0.375	0.3858(4)	0.3871(12)
y(Cl)	0.292	0.3009(4)	0.3001(13)
d(U–Cl) (pm)	296 (9×)	293.8 (3×) 293.1 (6×)	291.8 (6×) 294.1 (3×)

[a] Neutron diffraction profile analysis.

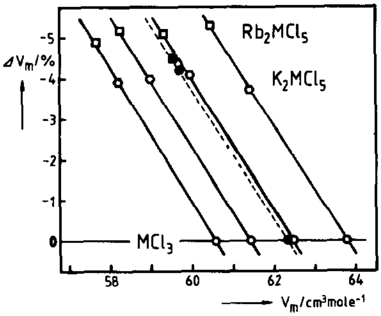

Fig. 2. The molar volumes of MCl_3 (M ≡ La–Nd, U) and the molar volumes derived from the ternary chlorides K_2MCl_5 and Rb_2MCl_5 by subtraction of twice the molar volumes of KCl and RbCl respectively. The molar volumes V_m are plotted against their reduction ΔV_m in the ternary chlorides expressed as a percentage.

The lattice constants and molar volumes suggest that K_2UCl_5 and Rb_2UCl_5 should be compared with the analogous cerium chlorides whose lattice constants are [7] as follows: K_2CeCl_5, $a = 1271.7(3)$ pm, $b = 881.5(2)$ pm, $c = 799.5(2)$ pm; Rb_2CeCl_5, $a = 1312.2(3)$ pm, $b = 898.5(2)$ pm, $c = 819.5(2)$ pm. Figure 2 gives a comparison of the molar volumes of the binary trichlorides MCl_3 ($M \equiv$ La–Nd, U) with the corresponding values obtained using the equation

$$V_m(MCl_3) = V_m(A_2MCl_5) - 2V_m(ACl)$$

The molar volumes V_m are reduced by about 4% (K_2MCl_5) and 5% (Rb_2MCl_5) respectively when compared with V_m of the binary chlorides. This reduction is plotted in Fig. 2 against the respective molar volumes.

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