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Abstract

Full Text

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X-RAY STUDY OF URANATES OF THE ALKALI ELEMENTS

The literature contains information on the structures of the monouranates of magnesium ($\bar{1}$), calcium ($\bar{2}$), strontium ($\bar{2}$), barium ($\bar{3}$), and β - $\text{UO}_2(\text{OH})_2$ ($\bar{4}$). In the structures of the monouranates of magnesium, barium, and β - $\text{UO}_2(\text{OH})_2$, somewhat distorted UO_6 octahedra form either pseudotetragonal layers (barium uranate, β - $\text{UO}_2(\text{OH})_2$) or chains (magnesium uranate) of composition $(\text{UO}_2)\text{O}_2$. Hexagonal layers of composition $(\text{UO}_2)\text{O}_2$ are present in the structures of the monouranates of calcium and strontium. In this case the uranium atoms are surrounded by oxygen atoms at the vertices of a somewhat distorted cube. In the structures of the monouranates of lithium, sodium, and potassium, hexagonal or pseudo-hexagonal layers, analogous to those present in calcium monouranate ($\bar{5}$), were also found; however, more detailed information on the structures of the monouranates of the alkali elements has not been published. No experimental data whatever are available on the structures of diuranates.

We obtained single crystals of the normal uranates of lithium (α -modification), sodium (β -modification), and of the diuranates of sodium, potassium, and rubidium. The indicated compounds were studied by the Laue, rotation, and powder methods. α - Na_2UO_4 , K_2UO_4 , Rb_2UO_4 , and Cs_2UO_4 , single crystals of which could not be obtained, were studied by the powder method. In all cases the intensities of reflections were determined visually on a ten-point scale from Debyeograms. All data are given in angstroms.

Table 1

Some X-ray data for mono- and diuranates of the alkali elements

Compound	Space group	a	b	c	Z	ρ -ray	ρ ycn
α - Li_2UO_4	$Fmmm$	6.06	5.13	10.52	4	6.43	6.13*
α - Na_2UO_4	$Cmmm$	9.74	5.72	3.49	2	5.94	—

Compound	Space group	<i>a</i>	<i>b</i>	<i>c</i>	<i>Z</i>	ρ -ray	ρ ycn
β -Na ₂ UO ₄	<i>Fmmm</i>	5.97	5.795	11.68	4	5.73	5.51*
K ₂ UO ₄	<i>I</i>	4.335	—	13.10	2	5.15	4.66*
Rb ₂ UO ₄	<i>I</i>	4.345	—	13.83	2	6.02	5.42
Cs ₂ UO ₄	<i>I</i>	4.38	—	14.79	2	6.65	6.04
Na ₂ U ₂ O ₇	<i>R 3 m</i>	3.93	—	17.76	1/2**	6.17	—
K ₂ U ₂ O ₇	<i>R 3 m</i>	3.98	—	19.67	1/2**	6.15	6.12
Rb ₂ U ₂ O ₇	<i>R 3 m</i>	4.00	—	20.77	1/2**	6.57	—

* In the literature (⁷) for Li₂UO₄, Na₂UO₄, and K₂UO₄, the data given are (respectively) 6.61; 5.06; 4.98. The last two figures are underestimated; the first, apparently, is overestimated.

** For the rhombohedral cell.

Table 1 gives the values of the lattice parameters of the uranates studied, their space groups, and the density values calculated from the X-ray data and determined pycnometrically.

To determine the structures of the indicated uranates we used the trial method, with the use of geometrical and crystal-chemical con-

reflections. Calculation of the intensities confirms the structures described below.

In the structures of α -Li₂UO₄, β -Na₂UO₄, K₂UO₄, Rb₂UO₄, and Cs₂UO₄, tetragonal or pseudotetragonal layers (UO₂)O₂ were found, analogous to those present in the structures of BaUO₄ and β -UO₂(OH)₂ (^{3,4}). The alkali-element atoms are located between the layers.

Normal uranates of potassium, rubidium, and cesium are isostructural with K₂NiF₄ (⁶):

2U in (*a*); 4Me^I in (*e*); 4O_I in (*e*); 4O_{II} in (*c*) (here and below O_I is oxygen belonging to the uranyl grouping). The values of the parameters Z_{Me^I} (Me—alkali element) and Z_{O_I} , as well as the interatomic distances U—O, Me^I—O and the shortest O—O distances, are given in Table 2.

Table 2

Some data on the structures of α -Li₂UO₄, β -Na₂UO₄, K₂UO₄, Rb₂UO₄, and Cs₂UO₄

Compound	Z_{O_I}	Z_{Me^I}	U—2O _I	U—4O _{II}	Me ^I —O _I	Me ^I —4O _{II}	Me ^I —4O _I	O—O ¹
α -Li ₂ UO ₄	0.18	0.39 ²	1.89	1.98	2.14	2.32	2.65–3.1	2.56
α -Li ₂ UO ₄	0.18	— ³	1.89	1.98	—	2.63 ⁴	2.12	2.56
β -Na ₂ UO ₄	0.165	0.38	1.93	2.12	2.52	2.52	2.96–3.04	2.88
K ₂ UO ₄	0.145	0.36	1.90	2.17	2.82	2.84	3.07	2.86
Rb ₂ UO ₄	0.138	0.354	1.91	2.17	2.99	2.97	3.07	2.87
Cs ₂ UO ₄	0.129	0.344	1.91	2.19	3.18	3.18	3.16	2.89

¹ Shortest distance. ² Li in 8(*i*). ³ Li in 8(*f*). ⁴ Li—2O_{II}.

The structure of β -Na₂UO₄ is an orthorhombically distorted structure of the K₂NiF₄ type: 4U in (*a*); 8Na in (*i*); 8O_I in (*i*); 8O_{II} in (*e*). The values of the parameters Z_{Na} , Z_{O_I} and of the interatomic distances are given in the same Table 2. In lithium uranate, a somewhat different arrangement of the alkali-element atoms than in β -Na₂UO₄ is also possible, namely, 8Li in (*f*). The arrangement of the other atoms in β -Na₂UO₄ and α -Li₂UO₄ coincides. Table 2 gives data for both variants of the arrangement of the lithium atoms.

In the structure of α -Na₂UO₄ there are infinite chains of UO₆ octahedra joined by common edges. 2U in (*a*); 4Na in (*f*); 4O_I in (*i*) with $y = 0.195$; 4O_{II} in (*h*) with $x = 0.245$; U—2O_I = 1.90; U—4O_{II} = 2.24; Na—2O_{II} = 2.44; Na—4O_I = 2.32; the shortest O—O distance is 2.73.

The structures of lithium, sodium, and potassium monouranates described above differ from the structures of these compounds studied by Zachariassen (⁵).

The structures of the diuranates of sodium, potassium, and rubidium are defective structures of the CaUO₄ type: U in (*a*); Me^I in (*b*); 2O_I and 1½O_{II} in (*c*). The parameters X_{O_I} and $X_{O_{II}}$, together with the values of the interatomic distances, are given in Table 3. In these structures, hexagonal layers of composition UO_{3.5} were found.

Table 3

Some data on the structures of the diuranates of sodium, potassium, and rubidium

Compound	X_{O_I}	$X_{O_{II}}$	U—2O _I	U—6O _{II}	Me ^I —6O _I	Me ^I —2O _{II}
Na ₂ U ₂ O ₇	0.108	0.357	1.92	2.35	2.50	2.54
K ₂ U ₂ O ₇	0.098	0.357	1.93	2.38	2.67	2.81
Rb ₂ U ₂ O ₇	0.093	0.355	1.93	2.39	2.78	3.01

Oxygen atoms can be partially replaced by fluorine with the formation of a fluorouranate, for example, NaUO_3F , likewise isostructural with CaUO_4 . On calcination in air, NaUO_3F gradually transforms into sodium diuranate. The samples remain single-phase throughout, so that, probably, a continuous region of solid solutions exists between the fluorouranate and sodium diuranate.

By reduction of sodium and potassium diuranates at 450–500° we obtained sodium and potassium uranates (V) of composition Me_3^{UO} , which were studied by the powder method. Both compounds belong to the perovskite structural type. For NaUO_3 , $a \sin \beta = b = c \sin \beta = 4.129 \pm 0.002$; $\beta = 88^\circ 36' \pm 6'$; $\rho_{\text{rent}} = 7.38$; for KUO_3 , $a = 4.290 \pm 0.001$; $\rho_{\text{rent}} = 6.85$. Using KUO_3 as an example, it has been shown that uranates (V) have a narrow homogeneity range (the lattice constant does not change either in the presence of an excess of potassium (upon reduction of K_2UO_4) or in the case of its deficiency—the latter samples, along with KUO_3 , always contained uranium dioxide). Uranates (V) dissolve readily in nitric acid and slowly in acetic acid. Thus, uranates (V) are not analogues of “tungsten bronzes.” Upon reduction of Li_2UO_4 and Na_2UO_4 , uranates (V) are not formed, in agreement with the data of Rüdorff and Leutner (7). As a result of reduction, Rb_2UO_4 forms Rb_2UO_3 with cubic pseudocell parameter $d = 4.316$. Cs_2UO_4 on reduction does not give uranates (V) or (IV).

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