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Syntheses and X-ray Observations of New Uranium Fluoride Complexes K_3UF_9 and Rb_3UF_9

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It has been found that the complexes between alkali metal fluoride and uranium tetrafluoride are easily fluorinated to form hexavalent uranium complex fluorides [1, 2]. In the fluorination of Rb_3UF_7 (*i.e.*, $3RbF \cdot UF_4$), formation of a new type complex Rb_3UF_9 (*i.e.*, $3RbF \cdot UF_6$) was confirmed from the results of weight change, chemical analysis, and spectroscopy [2]. The same type of reaction was also found to proceed in the fluorination of K_3UF_7-($3KF \cdot UF_6$). Here, we report the syntheses of these compounds and some of their properties obtained by spectrophotometric and X-ray diffraction analyses.

Experimental

Absorption spectra were measured by the following grating spectrophotometers made by JASCO; DS-601G (30 ~ 500 cm^{-1}), IRA-2 (400 ~ 4000 cm^{-1}), and UVIDEC-505 and -10 (190 ~ 2500 nm). X-ray powder patterns were taken by Philips PW-1730 diffractometer using Cu Kα (1.5418 Å) radiation monochromatized with pyrolytic graphite. All the fluorinations were made under a flow rate of 10% fluorine gas diluted by nitrogen. Other experimental details were the same as reported previously [1,2].

Results

About 150 mg of K_3UF_7 and Rb_3UF_7 were put on nickel boats and fluorinated at 400 and 500 °C for 3 hours, respectively. Weight increased occurred within the first hour, and then the sample weight became constant. Both products were yellow in colour, and their absorption spectra in the range from 200 to 50000 cm^{-1} were closely the same. In the region from 4000 cm^{-1} to ultra violet, absorption bands appeared only above 23000 cm^{-1}, similarly to the absorption of solid UF_6 [3]. These results show that the uranium in the complexes is oxidized to hexavalent state as previously reported [2]. The weight increase due to taking up of fluorine atoms also corresponded to the formation of hexavalent uranium complex, K_3UF_9 or Rb_3UF_9; examples of the calculation gave the compositions such as $K_3UF_{9.05}$ and $Rb_3UF_{9.16}$. No clear pattern of X-ray diffraction was obtained for the products formed by the fluorination of 3 hours. In order to develop their crystallization, the samples were continued to be heated for more than 200 hours under 10% fluorine gas without flow at the temperatures described above. It was found however, that the colour of the samples was partly changed due to the slow reaction between the surface of nickel boat and the sample powder. To avoid this reaction, then, the samples were heated on a CaF_2 plate set in the boat. It was confirmed that there was no change in colour or in weight of the samples in this case. After these treatments, better crystallization of the samples was supported by X-ray analysis.

The X-ray diffraction data were first collected by a Debye camera with the samples sealed in glass capillaries, and then a diffractometer was used to obtain more quantitative intensity data. A nickel sample holder was specially made, and the following mounting procedure was taken to prevent the hydrolysis of the complex fluorides by moisture. The sample powder was mulled with poly(trifluoromonochloroethylene) oil (Daifloil No. 10, Daikin Kogyo Co.), and was spread in the cup of the sample holder. Then, the holder was covered with a film of tetrafluoroethylene-hexafluoropropene co-polymer (Daikin FEP, Daikin Kogyo Co.), 0.7 mm thick, which was clamped tightly by a metal holdfast. These procedure was made under nitrogen atmosphere. The tightness against moisture was confirmed to be satisfactory from the result that there was no change in the diffraction patterns during several times of slow scans. These patterns were consistent with the camera data. The absorption of X-ray by FEP film could be expressed as being proportional to $(\sin\theta)^{-1}$, which was verified by using UO_2 standard sample. Thus, after the proportionality constant was determined, the correction of the intensities was made for each diffraction peak of the samples. The effect of the diffraction of FEP itself was also corrected by comparing with the diffraction of UO_2 standard. The diffraction data obtained are given in Tables I and II. The observed d values of the complexes, K_3UF_9 and Rb_3UF_9, were quite different from those of K_2UF_8 and Rb_2UF_8 [4], respectively. The present complexes were indexed as orthorhombic with the cell dimensions; $a = 6.974 \pm 0.005$, $b = 7.534 \pm 0.005$, $c = 9.768 \pm 0.005$ for K_3UF_9, and $a = 7.121 \pm 0.005$, $b = 7.612 \pm 0.005$, $c = 9.614 \pm 0.005$ for

TABLE I. X-ray Powder Diffraction Data for K_3UF_9.

hkl	d_{obs}	d_{calc}	I/I_o
111	4.48	4.53	24
020	3.76	3.77	14
112	3.52	3.53	52
021		3.51	
200	3.43	3.49	44
120	3.32	3.31	11
003	3.24	3.26	100
210	3.153	3.163	9.3
121	3.114	3.139	7.1
211	3.033	3.011	16
113	2.762	2.747	29
122	2.741	2.742	24
212	2.669	2.656	6.1
030	2.525	2.511	15
203	2.380	2.380	6.0
104	2.297	2.305	17
131		2.297	
310	2.215	2.221	9.9
114	2.193	2.204	23
132	2.127	2.127	6.3
302	2.097	2.099	12
024	2.054	2.049	7.4
320	1.983	1.978	39
303	1.901	1.891	6.5
140	1.817	1.818	9.1
034	1.745	1.751	4.6
400		1.743	
323	1.649	1.691	5.2
240	1.655	1.657	7.1
402	1.638	1.641	9.1
225	1.554	1.553	3.2
324	1.533	1.537	3.6
403		1.537	
305	1.500	1.496	5.0
151	1.455	1.456	7.5
250	1.384	1.383	2.9
343	1.333	1.335	1.8
306		1.334	
424	1.325	1.327	1.9
127	1.289	1.286	2.0
060	1.256	1.256	3.1
344		1.255	
425	1.229	1.230	3.0
146	1.212	1.213	1.6
504		1.211	
443	1.191	1.191	1.7
406		1.190	
064	1.115	1.117	2.4
157	1.012	1.013	1.3
173		1.011	

TABLE II. X-ray Powder Diffraction Data for Rb_3UF_9.

hkl	d_{obs}	d_{calc}	I/I_o
012	4.05	4.07	13
102	3.91	3.98	26
020	3.83	3.81	20
200	3.54	3.56	87
021		3.54	
112	3.51	3.53	36
120	3.37	3.36	100
210	3.22	3.23	18
003		3.20	
121	3.18	3.17	19
220	2.620	2.600	6.9
130	2.384	2.390	29
213	2.270	2.273	58
310		2.266	
032	2.244	2.244	13
114	2.188	2.182	8.0
302	2.129	2.128	14
124	1.941	1.954	32
214	1.926	1.927	38
005		1.923	
313	1.844	1.850	5.1
115	1.799	1.803	7.8
205	1.688	1.692	5.4
402	1.671	1.669	6.8
125		1.671	
420	1.614	1.612	3.8
403	1.553	1.556	6.1
051	1.507	1.504	6.0
243	1.485	1.487	1.8
340		1.485	
341	1.469	1.467	3.5
315		1.466	
500	1.422	1.424	5.2
152		1.422	
424	1.336	1.339	2.6
060	1.268	1.269	3.9
236		1.266	
061	1.257	1.258	7.8
160	1.251	1.249	6.4
532	1.201	1.202	1.7
008		1.202	
355	1.066	1.066	7.7
506		1.064	
057	1.021	1.020	3.5

Rb_3UF_9, in unit of Å. Since there were no systematic absences in the reflected peaks, the types of the unit cell seem to be primitive.

References

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