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Synthesis and Crystallographic Properties of Single Crystals of Alkali Uranium(V) Fluoride Complexes[1a]

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Single crystals of fluoride complexes containing pentavalent uranium and an alkali (or ammonium) fluoride have been prepared, utilizing anhydrous hydrofluoric acid as a solvent. Finely divided UF_5 is mixed with the desired fluoride, MF (M = Li, Na, K, Rb, Cs, or NH_4), and treated with anhydrous liquid HF. The resulting blue solutions yield euhedral crystals of MUF_6 compounds which are suitable for single-crystal X-ray analysis and optical crystallographic measurements. Dimorphism is found with $NaUF_6$; it crystallizes in a face-centered cubic form, isostructural with $NaTaF_6$, and in a new form which is isostructural with rhombohedral $LiUF_6$. Cell dimensions for rhombohedral $NaUF_6$ are: $a_0 = 6.101 \pm 0.005$ Å., $\alpha = 54° 37'$. Rhombohedral $LiUF_6$, $NaUF_6$, and $CsUF_6$ are blue, optically uniaxial, and have characteristic group absorption spectra at 1.36 μ; KUF_6, NH_4UF_6, and $RbUF_6$ are pale yellow-green, optically biaxial, exhibit pseudo-hexagonal X-ray symmetry, and belong to a different spectral class, absorbing at 1.42 μ.

Introduction

Recently we reported the preparation of, and X-ray data for, fifteen compounds formed between alkali fluorides and uranium pentafluoride.[2] They were produced by heating anhydrous mixtures of UF_5 and MF (M = Li, Na, K, Rb, Cs, and NH_4) in integral stoichiometric ratios, MF/UF_5 = 1, 2, and 3. This technique yielded microcrystalline products which were satisfactory for examination by X-ray powder techniques and for measurements of absorption spectra using mulls of the fluorides in Fluorolube. For other purposes, such as single-crystal X-ray studies and optical crystallographic measurements, larger crystals are needed. When it was found[3] that UF_5 was soluble in 48% aqueous HF, possibilities of growing crystals from this medium were explored. With the two heavier alkali fluorides, crystals of $RbUF_6$ and $CsUF_6$ could be obtained by allowing a solution of RbF or CsF in 48% HF to diffuse slowly into a solution of UF_5 in 48% HF. However, this technique was not successful with the lighter alkali fluorides, LiF and NaF, which are themselves quite insoluble in 48% HF.

The appreciable solubilities of even the lighter alkali fluorides in anhydrous liquid HF[4] suggested its use as a solvent in which to carry out the synthesis of $MF-UF_5$ complexes. The use of anhydrous HF as a solvent for the preparation of hexafluoro vanadium and ruthenium complexes was mentioned briefly in the excellent structural study of $A^IB^VF_6$ compounds by Kemmitt, Russell, and Sharp.[5] This solvent has the additional advantage that it should eliminate hydrolysis and disproportionation of U(V) which always occurs to some extent when UF_5 is dissolved in 48% aqueous HF. Uranium pentafluoride alone is not appreciably soluble in liquid HF.[3] However, we observed that the characteristic blue color of the UF_6^- ion appeared in anhydrous liquid HF when alkali fluorides and UF_5 were both present. Slow evaporation of the solvent HF then yielded large crystals well suited both for measurements of optical properties and for single-crystal X-ray analysis. Details of the method of preparation and some of the results of optical and X-ray measurements are given in the following sections.

Experimental

Materials.—UF_5 was prepared by treatment of UF_4 with gaseous UF_6 in a nickel reactor under anhydrous conditions. Special UF_4 of high surface area (prepared by dehydration of $UF_4 \cdot 2.5H_2O$) reacted smoothly with UF_6 at 80–100° to yield β-UF_5. Increase in the temperature to 200° yielded α-UF_5. Both forms of UF_5 had the theoretical weight composition and gave X-ray powder patterns agreeing with published values.[6] The fluorides NH_4F, LiF, NaF, and KF were A.R. grade; UF_4, RbF, and CsF were of >99.7% purity. Anhydrous UF_6 and HF were distilled from cylinders.

Technique.—Reactions were carried out in translucent Kel-F test tubes[7] of about 20 ml. volume which were attached to a copper vacuum line using brass flare fittings. Because of the moisture sensitivity of UF_5, the reaction vessel was loaded in an inert atmosphere box. Weighed amounts of uranium pentafluoride and the desired alkali or ammonium fluoride were used. A plug of Teflon wool was placed in the upper end of the tube to allow for filtration. The vessel was then attached to a vacuum line through a monel valve and evacuated (<25 μ); 10–15 ml. of HF from a supply cylinder was condensed into the reaction vessel by cooling it with liquid nitrogen. The vessel was then closed off from the vacuum system, brought to room temperature, and thoroughly stirred with a Teflon-coated magnetic stirring bar. The HF solution was cooled to about 0° (to avoid boiling of the HF) and then decanted through the Teflon wool into a second, cooled Kel-F tube. This filtrate was allowed to warm to room temperature or, in some cases, heated slightly. As HF evaporated, it was vented to the atmosphere *via* Teflon tubing and through a trap containing Fluorolube to preclude exposure to air and moisture.

After a crop of crystals formed (usually within 12 hr.) they were removed from the mother liquor and patted dry, using filter paper. Some crystals were kept in tightly closed plastic vials and others were covered with Fluorolube. In contrast to the moisture sensitivity shown by the finely divided $MF \cdot UF_5$

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[1] (a) This work was sponsored by the U. S. Atomic Energy Commission; (b) to whom reprint requests may be addressed.

[2] R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *Inorg. Chem.*, **3**, 126 (1964).

[3] L. B. Asprey and R. A. Penneman, *ibid.*, **3**, 727 (1964).

[4] A. W. Jache and G. H. Cady, *J. Phys. Chem.*, **56**, 1106 (1952).

[5] R. D. W. Kemmitt, D. R. Russell, and D. W. A. Sharp, *J. Chem. Soc.*, 4408 (1963).

[6] W. H. Zachariasen, *Acta Cryst.*, **2**, 296 (1949).

[7] Obtained from the Argonne National Laboratory, Argonne, Ill.

complexes when prepared by heating the dry powders,[2] these larger crystals were stable for weeks, gradually becoming altered on the exterior. They showed no decomposition on manipulation in dry refractive index oils or during containment in Lindemann glass capillaries for single-crystal X-ray analysis.

The absorption spectra of the U(V) compounds were measured using Fluorolube mulls which were contained between calcium fluoride optical flats in a Cary Model 14MR spectrophotometer. X-Ray powder patterns were obtained using Lindemann glass capillaries, a Debye–Scherrer 114.6-mm. powder camera, and Ilford-G film. Single crystal studies were carried out with Buerger and Weissenberg cameras. Optical studies were made using a Zeiss polarizing microscope.

Compound Preparation. LiUF$_6$.—Only in the case of LiF–UF$_5$–HF mixtures was the solubility of the complex fluoride sufficiently small so that no visibly blue solution was obtained. Combination of 7 mmoles of UF$_5$ together with an equimolar amount of LiF and about 15 ml. of anhydrous HF resulted in the formation of finely divided LiUF$_6$ as an HF-insoluble precipitate. When a starting ratio LiF/UF$_5$ = 2 was employed, LiUF$_6$ was still the only solid phase observed.

Combinations of LiF and UF$_5$ in molar ratios up to 10:1 were tried, attempting without success to increase the solubility of LiUF$_6$. Finally 7 mmoles of UF$_5$ and an equimolar amount of LiF were extracted with 15-ml. portions of anhydrous liquid HF. Each portion was stirred for 48 hr. and then decanted. From 30 ml. of faintly colored supernatant solution we obtained a small quantity of blue crystals of LiUF$_6$, approximately 0.50 × 0.25 mm. in size.

NaUF$_6$.—Gradual removal of solvent HF from solutions obtained by adding NaF and UF$_5$ in 1:1 and 2:1 mole ratios (7–15-mmole scale) to about 15 ml. of anhydrous HF yielded blue rhombohedral crystals of NaUF$_6$, isostructural with LiUF$_6$ and LiTaF$_6$.[2,5] [The rhombohedral phase was also obtained by grinding in a mortar stoichiometric amounts (1:1) of NaF and HUF$_6\cdot$2.5H$_2$O covered with Fluorolube. However, grinding NaF with UF$_5$ did not give NaUF$_6$.] More rapid removal of HF resulted in precipitation first of the isotropic, face-centered cubic form of NaUF$_6$. This phase is isostructural[6] with NaTaF$_6$; we had prepared it previously by heating equimolar mixtures of NaF and UF$_5$ at 350°.[2] Large (5 mm.) crystals of the fcc phase formed first and, subsequently, crystals of the rhombohedral phase were obtained on slower evaporation.

KUF$_6$.—Evaporation of HF from the blue solution resulting from the combination of 32 mmoles of KF and 16 mmoles of UF$_5$ with about 12 ml. of anhydrous HF yielded clear, yellow-green crystals of KUF$_6$ up to 1 cm. in length. When much higher KF:UF$_5$ ratios, *e.g.*, 10:1, were employed, the excess KF decreased markedly the solubility of the primary phase, KUF$_6$.

RbUF$_6$.—Clear, yellow-green RbUF$_6$ crystals up to 1 cm. in length were obtained by removing HF from a blue solution produced by mixing 9.8 mmoles of UF$_5$ and 17.8 mmoles of RbF (RbF:UF$_5$ = 1.8) with about 18 ml. of anhydrous HF. The same product was obtained from a solution containing 1.1 RbF:UF$_5$.

CsUF$_6$.—The blue solution resulting from the mixing of UF$_5$ with CsF (CsF:UF$_5$ = 6) and about 12 ml. of anhydrous HF yielded clear, blue, prismatic crystals of CsUF$_6$ up to several millimeters in length.

NH$_4$UF$_6$.—Clear, prismatic, yellow-green single crystals of NH$_4$UF$_6$ were obtained from a blue solution prepared by combining about 10 ml. of anhydrous HF with 6 mmoles of UF$_5$ and 12 mmoles of NH$_4$F.

Optical and X-Ray Measurements

Except in the case of the new rhombohedral form of NaUF$_6$, the rest of the MUF$_6$ compounds gave the same X-ray powder patterns as reported by us previously.[2] The partial powder pattern of rhombohedral NaUF$_6$ is presented in Table I. (Optical examination of NH$_4$UF$_6$, KUF$_6$, and RbUF$_6$ with a petrographic microscope showed that these compounds were biaxial. Single-crystal X-ray studies of these materials are in progress and will be reported in conjunction with studies on KPaF$_6$, RbPaF$_6$, and NH$_4$PaF$_6$ which have similar structures.[8])

TABLE I

PARTIAL X-RAY POWDER DIFFRACTION PATTERN OF NaUF$_6$
LiSbF$_6$ type, hexagonal indexing, space group R$\bar{3}$

hkl	d_{obsd}, Å.	d_{calcd}, Å.	I_{obsd}[a]	I_{calcd}[a]
003	5.155	5.175	5	3
101	4.623	4.626	8	8
012	4.095	4.111	10	10
104	3.024	3.029	6	3
110	2.797	2.798	3	2
015	2.607	2.614	4	2
113	2.462	2.461	6	3
021	2.396	2.394	1	1
202	2.313	2.313	2	1
024	2.054	2.056	4	2
107	2.013	2.017	2	1
116	1.895	1.899	7	3
211	1.813	1.819	1	1
018	1.801	1.802	1	1
122	1.783	1.783	2	2
214	1.655	1.656	1	1
027	1.636	1.636	1	1
300	1.616	1.615	1	1
125	1.578	1.578	2	1
303	1.542	1.542	1	1
208	1.514	1.515	2	1
10·10	1.478	1.479	1	1
119	1.468	1.468	1	1
217	1.412	1.412	1	1

[a] I_{obsd} and I_{calcd} on relative magnitude with 10 maximum.

X-Ray Data for Rhombohedral NaUF$_6$.—Space group R$\bar{3}$; LiSbF$_6$ structure type (hexagonal dimensions: $a_0 = 5.596 \pm 0.005$ Å., $c_0 = 15.526 \pm 0.005$ Å.); $a_0 = 6.101$ Å., $\alpha = 54° 37'$; cell volume = 140.4 Å.^{3}; $Z = 1$, $\rho_{\text{calcd}} = 4.43$ g./cm.^{3}

Optical Crystallographic Data.—Optical properties of the six compounds are given in Table II.

Discussion

The use of anhydrous HF as a solvent for reactions yielding complex alkali (or ammonium) heavy-metal fluorides has been demonstrated to be both convenient and, on occcasion, a unique method of obtaining compounds in the form of single crystals. We have used this method primarily to prepare pentavalent uranium fluorides, MUF$_6$. Other crystalline pentavalent fluoride complexes could be made by this method; we also obtained CsTaF$_6$ by this technique, and several hexafluorovanadates were previously prepared from anhydrous HF.[5] It would undoubtedly be satisfactory for the preparation of other fluoride complexes, such as the alkali protactinium fluorides, a study which is in progress. The high solubilities of AgF, SrF$_2$, BaF$_2$, TlF, and PbF$_2$ in anhydrous HF indicate that this solvent may be a useful medium for reactions involving these fluorides as well.

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(8) L. B. Asprey and R. A. Penneman, *Science*, **145**, 924 (1964).

TABLE II

OPTICAL PROPERTIES OF CRYSTALLINE MUF_6 COMPOUNDS
(M = Li, Na, K, Rb, Cs, NH_4)

(1) $LiUF_6$
  Pale blue rhombs, rhombohedral cleavage, polysynthetic twinning evident, 45° extinction usual
  Uniaxial, negative
  $n_0 = 1.486$, $n_\epsilon = 1.478$; birefringence = 0.008
(2) $NaUF_6$
  (a) Cubic phase
    Pale blue cubes
    Refractive index, $n = 1.385 \pm 0.005$
  (b) Rhombohedral phase
    Pale blue rhombs, rhombohedral cleavage, polysynthetic twinning evident, striations frequently appear parallel to the rhomb edges, 45° extinction usual
    Uniaxial, negative
    $n_0 = 1.408$, $n_\epsilon \leqq 1.400$; birefringence $\cong 0.008$
(3) KUF_6
  Light yellow-green chunky prisms or pseudo-hexagonal plates; parallel extinction
  Biaxial, positive
  $n_x = 1.480$, $n_y \cong 1.483$, $n_z = 1.524$
  $2V \cong 25°$ (average of 30° calculated and 20° visual estimate)
  Low dispersion
  Small value of $n_y - n_x$ contributes to pseudo-hexagonal character of these biaxial fluoride complexes
(4) $RbUF_6$
  Pale yellow-green laths or thick plates; parallel extinction. Internal striations and/or twinning parallel to needle axis
  Biaxial, positive
  $n_x = 1.481$, $n_y \cong 1.483$, $n_z = 1.518$
  $2V \cong 25°$
(5) $CsUF_6$
  Pale blue rhombs, rhombohedral cleavage, 45° extinction in thin rhombic plates. Polysynthetic twinning and striations parallel to rhomb edges evident
  Uniaxial, positive
  $n_0 = 1.468$, $n_\epsilon = 1.511$; birefringence = 0.043
(6) NH_4UF_6
  Yellow-green chunky prisms; parallel extinction but no striation or twinning was observed. Pseudo-hexagonal symmetry appeared, but not as evident as for KUF_6 and $RbUF_6$
  Biaxial, positive
  $n_x = 1.488$, $n_y \cong 1.490$, $n_z = 1.520$
  $2V \cong 60°$ (visual estimate)
  $2V \cong 30°$ (calculated from approximate n_y)

Polymorphism, which is quite common among the fluoride complexes of U(IV),[9] has been found in the fluoride complexes of U(V) since $NaUF_6$ occurs in two forms. The rhombohedral form is isostructural with $LiUF_6$ and has the dimensions $a_0 = 6.101$ Å., $\alpha = 54° 37'$ (hexagonal dimensions $a_0 = 5.596$ and $c_0 = 15.526$ Å.). The face-centered cubic phase was previously prepared at temperatures of 350°. The X-ray properties of the isotropic $NaUF_6$ crystals prepared in this study from anhydrous HF were identical with those previously reported.[2]

The stoichiometric molecular volume for cubic $NaUF_6$ is 159.5 Å.^{3}, and the calculated density is 3.91 g./cm.^{3}. The lower symmetry rhombohedral polymorph was prepared by slow evaporation from solution at or below room temperature. In this case a molecular volume of 140.4 Å.^{3} (density 4.43 g./cm.^{3}) was obtained. This is not an unusual polymorphism and the apparently more ordered (and denser) rhombohedral phase is isostructural with a number of $A^IB^VF_6$ compounds displaying the $LiSbF_6$ structure.[5] Interestingly, cubic $NaUF_6$ shows the $NaSbF_6$ structure type reported for a number of other NaB^VF_6 compounds in the compilation by Kemmitt, Russell, and Sharp.[5]

The absorption spectra of KUF_6, $RbUF_6$, and NH_4UF_6 exhibit a narrow and strong absorption peak at 1.42 μ.[2,10] These compounds have pseudo-hexagonal X-ray symmetry but are optically biaxial and, hence, are of orthorhombic or lower symmetry. Single-crystal X-ray studies of these materials are being reported in conjunction with studies on $KPaF_6$, $RbPaF_6$, and NH_4PaF_6.[11]

The three compounds $LiUF_6$ (rhomb), $NaUF_6$ (fcc), and $CsUF_6$ (rhomb) show three closely-spaced absorption peaks with the most prominent occurring at 1.36 μ.[3,12] The spectrum of the new form of $NaUF_6$ (rhomb) has these three characteristic absorptions, but also shows one additional peak at 1.45 μ. There are some differences in the visible absorption of these compounds but the near-infrared absorption is distinctive. With the powders prepared earlier, color was not particularly indicative of what X-ray structure to anticipate. However, upon visual inspection of the large crystals of the MUF_6 compounds, it was obvious that two types of crystalline products occur, confirming spectral and X-ray observations made on microcrystalline materials. The rhombohedral compounds $LiUF_6$, $NaUF_6$, and $CsUF_6$ are a clear blue, changing to nearly white as the particle size was reduced by grinding. The pseudo-hexagonal compounds KUF_6, NH_4UF_6, and $RbUF_6$ were deposited in the form of pale yellow-green crystals from intense blue HF solutions.

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