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Synthesis of metal fluorouranate(IV) compounds in aqueous solution

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Abstract

Metal fluorouranate(IV) compounds have been prepared previously under the initial conditions of the vapor or molten state. We have been able to synthesize a number of metal fluorouranate(IV) compounds in aqueous solution at room temperature. The reduction of UO_2^{2+} to U^{IV} with the appropriate metal dithionite takes place in a solution of the metal fluoride. The metal ion may be Na^+, Rb^+, K^+, Zn^{2+} or NH_4^+. In this work, the prepared compounds, Na_2UF_6, K_2UF_6, $K_7U_6F_{31}$, $RbUF_5$, $Rb_7U_6F_{31}$, ZnU_2F_{10} and $(NH_4)_7U_6F_{31}$, have been confirmed by X-ray powder diffraction.

Keywords: Synthesis; Metal fluorouranate(IV) compounds; X-ray diffraction

1. Introduction

Synthesis of a variety of compounds all of which have the formula $M_xU_yF_z$, where $x=z-4y$ for monopositive metal ions and $x=(z-4y)/2$ for dipositive metal ions have been reported by a number of investigators [1,2]. These compounds were synthesized by two general procedures: (a) by heating the reactants to the molten state and allowing them to cool at varying rates forming different stoichiometries; or (b) maintaining them at an elevated temperature in the vapor state and allowing them to cool and crystallize into the desired compounds. In the vapor state, the mole ratio of the reactants was changed to obtain the various stoichiometries. The usefulness of these sparingly soluble compounds has been shown in the recovery of uranium from wastewater settling ponds [3].

Reported here is a procedure for the synthesis of Na_2UF_6, K_2UF_6, $K_7U_6F_{31}$, $RbUF_5$, $Rb_7U_6F_{31}$, ZnU_2F_{10} and $(NH_4)_7U_6F_{31}$ in aqueous solution at room temperature.

The uranyl ion, UO_2^{2+}, must be reduced to U^{IV} in the presence of an excess of the desired metal fluoride. The reducing agent preferred in this case is the dithionite ion, $S_2O_4^{2-}$. It reacts rapidly with the uranyl ion to produce the desired product uncontaminated. Sodium dithionite is commercially available but other alkali metal dithionites must be synthesized as needed. In aqueous solution, the dithionite ion is not stable for long periods of time. For this reason it was freshly made daily as needed, but not allowed to stand more than 30 min before use. It can be crystallized by cooling and pumping the water from the solution until the remaining solid metal dithionite is dry. The solid can be kept moisture-free for long periods.

2. Experimental details

A standard uranyl nitrate solution was prepared by dissolving an appropriate weight of recrystallized $UO_2(NO_3)_2\cdot 6H_2O$, 99% Baker Chemical, in deionized water. An aliquot of this solution was heated to evaporate the water and then placed in a furnace to convert the uranium gravimetrically to U_3O_8. From this, it was determined that the standard solution was 1.57 M with respect to $UO_2(NO_3)_2$. The sulfur dioxide purchased from Air Products was 99.9% pure. All the reagents were used without further purification except for the uranyl nitrate. The purity of the other reagents is listed in Table 1.

The preparation of the required reducing agent, $S_2O_4^{2-}$, was a modification of an existing preparation of the sodium salt [4]. The example provided here is for the preparation of potassium dithionite. Preparations of other dithionites were similar and only the hydroxides were changed. Granular zinc metal (0.50 g, 7.65 mmol) was placed in 50 ml of deionized, distilled water, and the mixture cooled in an ice bath. It was then stirred while gaseous SO_2 was slowly bubbled into the mixture. As the zinc reacted, the product formed an amber

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Table 1

Metal	Reagent purity (%)		Chemical company
	Hydroxide	Fluoride	
Na^+	95	99.8	Baker Scientific
K^+	85	99.6	Mallinckrodt
NH_4^+	28 (solution)	99.99	Baker Scientific
Rb^+	99	99.8	Aldrich
Zn^{2+}	–	98 (hydrated)	Aldrich
Zn (as the metal, 100.0%)			Baker Scientific

colored solution which, upon standing, turned colorless with the evolution of some gas. After about 20 min, when all the zinc had dissolved, the colorless solution was treated with a 50 wt.% aqueous solution of KOH until no further $Zn(OH)_2$ precipitated. This formed a solution of $K_2S_2O_4$. Care must be taken not to add an excess of KOH as this will form the soluble tetrahydroxozincate(II) ion which could contaminate the final product with a zinc compound. The mixture was filtered and the precipitated $Zn(OH)_2$ separated from the filtrate containing $K_2S_2O_4$.

An aliquot of 8.0 ml of a 1.57 M solution of $UO_2(NO_3)_2$ (12.56 mmol) was diluted to 100 ml with deionized water. An excess of KF (three times the calculated stoichiometry) was dissolved in the uranyl ion solution. The solution of $K_2S_2O_4$ was then slowly added with stirring. The color of the solution immediately changed from yellow (uranyl ion), through a fleeting brown color, to a finely divided, lime-green slurry. The particles settled out of solution slowly. In this preparation, the slurry was allowed to stand overnight to complete the precipitation. The sample was then filtered, washed with deionized water and allowed to air-dry. The intent was to allow all of the reducing agent to react but not to reduce all of the uranyl ion.

3. Results and discussion

The preparation of the potassium form of the reducing agent proceeds according to the following reactions.

$$Zn + 2SO_2 \longrightarrow ZnS_2O_4$$

$$ZnS_2O_4 + 2KOH \longrightarrow K_2S_2O_4 + Zn(OH)_2\downarrow$$

The reduction of the UO_2^{2+} to U^{IV} and formation of $K_7U_6F_{31}$ can be expressed by the reaction

$$31KF(aq) + 6UO_2(NO_3)_2(aq) + 6K_2S_2O_4(aq) \longrightarrow K_7U_6F_{31}(s) + 12KNO_3(aq) + 12K_2SO_3(aq)$$

Other metals follow similar reactions but the stoichiometry depends upon which species of $M_xU_yF_z$ is synthesized. In each case, the limiting reagent is the uranyl ion.

The compounds formed were identified by their X-ray powder diffraction patterns. In some cases, there was more than one structure for an individual compound. The powder diffraction pattern of the Na compound matches the β_3-Na_2UF_6 structure. In the case of the K_2UF_6, the α-K_2UF_6 structure was synthesized. The solution method for synthesis appears to lead to only one structure being formed for each compound. All these metal uranium(IV) fluorides are sparingly soluble compounds.

Possible contaminates include the SO_3^{2-} and SO_4^{2-} ions. Elemental microanalysis of sulfur provided a range of sulfur in these compounds between 0% to 0.7% with an average of 0.1%. The only exception was 3.2% S in $K_7U_6F_{31}$.

The amber color observed in the preparation of the dithionite is probably due to the radical-ion, $\cdot SO_2^-$ [5]. This color faded within 30 min upon standing, but the presence or absence of this color appeared not to affect compound preparation. The aqueous synthesis of these compounds is limited by the solubility of the metal fluoride, since most metal fluorides are sparingly soluble. Preparation of $M_xU_yF_z$ via the solution method even though straightforward does not provide the variety of stoichiometries as do other methods.

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