

New Methods of Syntheses of Ammonium, Sodium & Potassium Triacetatodioxouranates (VI) & Diacetatodioxouranium (VI) Dihydrate

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The product obtained by treating an aqueous solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with ammonia or NaOH or KOH solution reacts with ACH_3COO ($\text{A} = \text{NH}_4, \text{Na}$ or K) and a small amount of 10% acetic acid in 1:3 mol ratio $\{\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} : \text{ACH}_3\text{COO}\}$ at pH to afford the compounds $\text{A}[\text{UO}_2(\text{CH}_3\text{COO})_3]$ ($\text{A} = \text{NH}_4, \text{Na}$ or K), Na at pH 5 to afford the compounds $\text{A}[\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ has been achieved by the reaction of the product obtained by treating a solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with aqueous ammonia, with an excess of glacial acetic acid in the ratio 1:17.5 $\{\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} : \text{CH}_3\text{COOH}\}$.

Acetatouranate (VI) chemistry is rather complicated owing to the formation of a variety of compounds between acetic acid and UO_2^{2+} ion¹ depending upon the reaction conditions and the proportions of the reactants used. Recently, while studying some aspects of uranium chemistry²⁻⁴ we felt the need of synthesising compounds of the types $\text{A}[\text{UO}_2(\text{CH}_3\text{COO})_3]$ where $\text{A} = \text{NH}_4, \text{Na}$ or K and $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. Both these compounds are known^{1,5,6}, but while the synthesis of the former requires an excess of alkali acetate and alkali nitrate⁵ where the chances of contamination of products by acetate and nitrate cannot be ruled out, the recommended synthesis of the latter requires uranium trioxide, UO_3 , that needs extra preparation steps. We report here the direct syntheses of the title compounds which provide an easy access to these important compounds of uranium.

Reagent grade chemicals were used in the present studies. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. Molar conductances were measured using a Philips PR 9500 conductivity bridge.

Uranium²⁻⁴, carbon, hydrogen, nitrogen, sodium and potassium^{3,7} were determined by methods described earlier.

Synthesis of alkali triacetatodioxouranate (VI)

$\text{A}[\text{UO}_2(\text{CH}_3\text{COO})_3]$ ($\text{A} = \text{NH}_4, \text{Na}$ or K)

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 g, 1.99 mmol) was dissolved in 15cm^3 of water followed by the addition of aq.

ammonia (sp. gr. 0.9), or a 15% solution of sodium hydroxide or potassium hydroxide, with stirring until a yellow precipitate ceased to appear. The yellow precipitate (Y) was filtered off, washed free from alkali and nitrate, and then mixed with alkali acetate, ACH_3COO ($\text{A} = \text{NH}_4, \text{Na}$ or K) (6 mmol) while maintaining the $\text{U} : \text{CH}_3\text{COO}^-$ ratio at 1:3. The mixture was stirred for 2 min followed by dropwise addition of 10% acetic acid solution under stirring until a clear solution was obtained (pH 5). The solution was filtered and then concentrated to nearly half the original volume by warming over a steam-bath. The concentrated solution was cooled to room temperature to afford yellow crystalline alkali triacetatodioxouranates (VI), $\text{A}[\text{UO}_2(\text{CH}_3\text{COO})_3]$ ($\text{A} = \text{NH}_4, \text{Na}$ or K). The compound was separated by filtration, washed twice with ethanol and dried *in vacuo* over conc. H_2SO_4 . The yields of $\text{NH}_4[\text{UO}_2(\text{CH}_3\text{COO})_3]$, $\text{Na}[\text{UO}_2(\text{CH}_3\text{COO})_3]$ and $\text{K}[\text{UO}_2(\text{CH}_3\text{COO})_3]$ were 0.67 g (72%), 0.76 g (81%) and 0.75 g (77%) respectively.

Synthesis of diacetatodioxouranium (VI) dihydride, $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$

The yellow precipitate (Y) was obtained in a manner similar to that described above by treating an aqueous solution of 1.0 g (1.99 mmol) of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with aqueous ammonia. An aqueous suspension of the purified product (Y) was then treated with 2.0cm^3 (35 mmol) of glacial acetic acid to obtain a clear solution. The solution thus obtained was worked up in an analogous way as described under the above synthesis. The yellow crystalline diacetatodioxouranium (VI) dihydrate, $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ thus obtained was separated by filtration, and dried *in vacuo* over conc. H_2SO_4 , yield 0.67 g (80%).

The analytical data of the compounds are summarised in Table 1.

Table 1—Analytical Data of the Uranium Complexes

	Found (Calc.) %			
	A or N	U	C	H
$\text{NH}_4[\text{UO}_2(\text{CH}_3\text{COO})_3]$	3.12 (3.01)	51.47 (51.16)	15.51 (15.49)	2.85 (2.82)
$\text{Na}[\text{UO}_2(\text{CH}_3\text{COO})_3]$	4.94 (4.89)	50.52 (50.63)	15.31 (15.33)	1.89 (1.93)
$\text{K}[\text{UO}_2(\text{CH}_3\text{COO})_3]$	8.53 (8.04)	49.12 (48.95)	14.77 (14.82)	1.89 (1.87)
$\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	—	56.31 (56.12)	11.31 (11.33)	2.45 (2.38)

The reaction of uranyl nitrate hexahydrate with alkali hydroxide produces sparingly soluble alkali diuranate which may serve as a very good source of the metal providing a rather easy access to the synthesis of various compounds of uranium²⁻⁴. It has been now shown that similar products can react with stoichiometric amounts of alkali acetates, $A\text{CH}_3\text{COO}$ ($A = \text{NH}_4, \text{Na}$ or K), and a small amount of dilute acetic acid to yield triacetatodioxouranates (VI) at pH 5. The method does not require the use of any excess alkali acetate or alkali nitrate unlike the earlier methods¹⁻⁵. While the reactions of diuranates with stoichiometric amounts of alkali acetates and a small amount of dilute acetic acid give $A[\text{UO}_2(\text{CH}_3\text{COO})_3]$ compounds, the reaction of ammonium diuranate with glacial acetic acid produces pure diacetatodioxouranium (VI) dihydrate, $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, in a very high yield. The method is a direct one and may be used as a paradigm for the synthesis of other molecular complexes. Indeed, it has been shown very recently⁸ that the reaction of ammonium diuranate with acetylacetone ($\text{C}_5\text{H}_8\text{O}_2$, acacH), in the absence of any buffer, gives bis(acetylacetonato)dioxouranium (VI) dihydrate, $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ ⁸, thereby justifying the scope of the method.

The compounds $A[\text{UO}_2(\text{CH}_3\text{COO})_3]$ ($A = \text{NH}_4, \text{Na}$ or K) and $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ are yellow crystalline solids which are stable for long periods. The molar conductance of $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in methanol at ambient temperature was found to be very low indicating the non-electrolytic nature of the compound which was in agreement with the observation made earlier⁹. Anhydrous

$\text{UO}_2(\text{CH}_3\text{COO})_2$ was obtained by heating the dihydrate to $110-120^\circ\text{C}$.

The characteristic features of the IR spectra of $A[\text{UO}_2(\text{CH}_3\text{COO})_3]$ and $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ are the $\nu_{\text{as}}(\text{OUO})$, $\nu_{\text{s}}(\text{OUO})$, $\nu_{\text{as}}(\text{OCO})$, $\nu_{\text{s}}(\text{OCO})$, and $\delta(\text{OCO})$ bands which have been observed at ~ 930 , ~ 850 , ~ 1540 , ~ 1470 , and $\sim 675 \text{ cm}^{-1}$, respectively^{5,10,11}. These features are the most significant ones and typical of the compounds described in the present report. IR spectra of the compounds are similar to those reported in the literature^{5,10,11} for these types of compounds.

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