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A simple synthesis of *bis*(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$

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Abstract. A new and direct route to *bis*(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, based upon the reaction of $UO_3 \cdot 4H_2O$ with acetylacetone ($C_5H_8O_2$), is described.

Keywords. *Bis*(acetylacetonato)dioxouranium(VI) dihydrate; mass spectrometry.

1. Introduction

Bis(acetylacetonato)dioxouranium(VI) dihydrate has been one of the most important compounds of uranium especially because of its moderate volatility, solubility in a variety of organic solvents, and stability. The compound is a very good synthon for accessing organouranium products and is expected to be of great synthetic value in the preparation of inorganic materials. Synthesis of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ is a prerequisite and the widely used method of its preparation (Schlesinger *et al* 1953) requires a large amount of sodium hydroxide to maintain the appropriate pH of the reaction medium to enable coordination of the ligand with UO_2^{2+}. Similarly, the methods of syntheses of the monohydrate, $UO_2(C_5H_7O_2)_2 \cdot H_2O$ (Blume *et al* 1956; Comyns *et al* 1958), also use appreciably high amounts of alkali. Owing to the use of such amounts of alkali, the end product is often contaminated with the alkali itself as well as by the alkali diuranate that originates from the alkali-assisted decomposition of the metal acetylacetonate. In an attempt to modify the procedure, a new method was introduced in 1986 (Bhattacharjee *et al* 1986). The method has some advantages but involves extra preparation and purification steps for obtaining the starting material. In this method ammonium diuranate, $(NH_4)_2U_2O_7$, was first prepared by treating an aqueous solution of $UO_2(NO_3)_2 \cdot 6H_2O$ with concentrated aqueous ammonia. The diuranate then needed repeated washing with water to render it free from the alkali. Particularly tedious and time consuming was the purification (making alkali-free) step. In order to overcome all the difficulties, a straightforward synthesis was sought. Here we describe a simple synthesis of the title compound. A combination of chemical analyses of the constituents, verification of uranium content of the product by atomic absorption spectrometry, and mass spectrometry has been used to judge the purity of the product.

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2. Experimental

Elemental analyses were performed by the Microanalysis Laboratory of our University. Uranium was estimated with a Perkin-Elmer 2380 AA spectrometer. IR spectra (Bhattacharjee *et al* 1990), pH values (Bhattacharjee *et al* 1990) and mass spectra (Bhattacharjee *et al* 1986) were recorded as earlier.

2.1 *Synthesis*

In a typical synthesis, 1·0 g (2·79 mmol) of $UO_3 \cdot 4H_2O$ was reacted with 4 cm^3 (39·95 mmol) distilled acetylacetone with continuous stirring on a steam-bath ($\approx$ 10 min) until a clear orange-yellow solution resulted. The pH value at this stage was found to be 5–5·5. The solution on being cooled to room temperature ($\approx$ 22°C) afforded orange-yellow crystals of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$. The compound was separated by filtration and dried by pressing between folds of filter paper. The yield was 1·3 g (92%); (Found: U, 47·08; C, 23·63; H, 3·74. Calcd: U, 47·20; C, 23·82; H, 3·61%).

3. Results and discussion

We describe a direct 'one-pot' rapid synthesis of the title compound based on the acid–base concept. The oxide UO_3 being basic in nature readily reacted with weakly acidic acetylacetone ($C_5H_8O_2$) to provide $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ in nearly quantitative yield.

$$UO_3 + C_5H_8O_2 \rightarrow UO_2(C_5H_7O_2)_2 + H_2O$$

The colour, solubility properties, and the results of chemical analysis and IR measurements conform to the formula of the compound as $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ and agree very well with those reported in the literature (Schlesinger *et al* 1953; Bhattacharjee *et al* 1986). Further support of the identity was obtained from mass spectral studies. The salient characteristic features of the spectrum (recorded at an ion-source temperature of 100°C) were the molecular ion signal at *m/z* (55%) $[UO_2(C_5H_7O_2)_2]^+$, the most dominant (100%) signal at *m/z* 369 $[UO_2(C_5H_7O_2)]^+$, and a medium intensity (45%) signal at *m/z* 270 $[UO_2]^+$. These and the other features were similar to those reported (Bhattacharjee *et al* 1986). The clear advantages of the method are that it is simple and rapid and does not require any buffer or alkali, thus eliminating chances of contamination of the end product. In addition, the new method does not need any extra preparation and purification thereby rendering this procedure superior to the existing ones. The importance of having $UO_2(acac)_2$ in pure form lies in its probable application in isotope enrichment of uranium, since this requires a pure compound of the metal. Besides this, the purity of the product is expected to render it a better starting material for the synthesis of other compounds of uranium, in particular, organo-uranium derivatives. The procedure can be regarded as a general one applicable to many acetylacetonato-metals. For instance, hydrous oxides or hydroxides of iron(III), cobalt(II), nickel(II), copper(II), and zinc(II) reacted with acetylacetone to provide $Fe(C_5H_7O_2)_3$, $Co(C_5H_7O_2)_2 \cdot 2H_2O$, $Ni(C_5H_7O_2)_2 \cdot 2H_2O$, $Cu(C_5H_7O_2)_2 \cdot 2H_2O$, and $Zn(C_5H_7O_2)_2 \cdot 2H_2O$, respectively, in very high yields.

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