

First reported synthesis of ammonium hexafluorodioxouranate(VI), $(\text{NH}_4)_4[\text{UO}_2\text{F}_6]$

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Abstract

Bis(acetylacetonato)dioxouranium(VI) dihydrate, $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, reacts with NH_4F in the presence of an excess of acetylacetone and a trace of water to produce $(\text{NH}_4)_4[\text{UO}_2\text{F}_6]$ in high yield. The results of chemical analyses, molar conductance, IR and laser Raman spectroscopic studies have been used for characterisation of the compound.

Introduction

The syntheses of many oxofluoro complexes of hexavalent uranium are well documented [1, 2], but that of $[\text{UO}_2\text{F}_6]^{4-}$ seems, to the best of our knowledge, missing from the literature, although some physicochemical studies involving the complex appear to have been conducted [3, 4]. Hence, a synthetic procedure for hexafluorodioxouranate(VI) seems warranted. Accordingly, the present investigation has been addressed to the reaction of $\text{UO}_2(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ with NH_4F in the presence of acetylacetone and a trace of water enabling the synthesis of $(\text{NH}_4)_4[\text{UO}_2\text{F}_6]$.

Experimental

Reagent grade chemicals were used for the synthesis. Acetylacetone was distilled before use. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer and laser Raman (LR) on a SPEX Ramalog 1403 spectrophotometer using the 4880 Å laser line from a Spectra-Physics model 165 Argon laser. The pH was measured using a Systronics type 335 digital pH meter and also with BDH indicator paper. Molar conductances were measured with a Systronics type 304 digital direct-reading conductivity meter. Bis(acetylacetonato)dioxouranium(VI) dihydrate, $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, was prepared by a method developed in this laboratory [5].

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A mixture consisting of 1.0 g (1.98 mmol) of $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ and 0.3 g (8.1 mmol) of NH_4F was allowed to react in the presence of 20.0 cm³ (199.75 mmol) of distilled acetylacetone and a trace of water (1 cm³). The atomic ratio of U:F was maintained as 1:4. The solution was stirred continuously in a 100 cm³ polyethylene beaker and heated over a steam bath for c. 6 h until a yellow solid formed. The pH of the mother liquor was found to be c. 4. The yellow solid thus formed was separated by filtration, washed several times with ethanol, and finally dried *in vacuo* over conc. H_2SO_4 . The yield of $(\text{NH}_4)_4[\text{UO}_2\text{F}_6]$ was 0.6 g (66.7%). Analysis: Calc. for $(\text{NH}_4)_4[\text{UO}_2\text{F}_6]$: U, 52.17; F, 24.99; N, 12.28; H, 3.54%. Found: U, 51.87; F, 24.81; N, 12.25; H, 3.66%. Molar conductance: 495 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR (cm⁻¹): 356 [$\nu(\text{U-F})$]; 913 [$\nu_{\text{as}}(\text{U=O})$, ν_3]; 1418 [$\nu(\text{N-H})$, ν_4]; 3025 [$\nu(\text{N-H})$, ν_1]; 3160 [$\nu(\text{N-H})$, ν_3]. LR (cm⁻¹): 340 [$\nu(\text{U-F})$]; 853 [$\delta(\text{O-U-O})$, ν_1]; 951 [$\nu_{\text{as}}(\text{U=O})$, ν_3]; 1379 [$\nu(\text{N-H})$, ν_4].

Elemental analyses

Uranium was estimated gravimetrically as uranyl oxinate [6a]. Fluoride was precipitated as PbClF and chloride estimated by Volhard's method from which the fluoride content was calculated [6b]. Nitrogen and hydrogen were determined by the Micro Analytical Laboratory, Department of Chemistry, NEHU, Shillong 793 003.

Results and discussion

Since the acetylacetonate ion ($\text{C}_5\text{H}_7\text{O}_2^-$) generally binds to a metal centre through its oxygen atoms, it was anticipated that in an acidic environment the ligand would be detached from $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ to produce acetylacetone ($\text{C}_5\text{H}_8\text{O}_2$) and UO_2^{2+} *in situ*. The uranyl ion would then interact with the nucleophile F^- to afford fluoro compounds of the metal. Alternatively, the reaction might proceed via the formation of intermediate fluoro-(acetylacetonato)dioxouranate(VI) complex ions to finally produce oxo-(fluoro)uranates(VI). With this strategy, $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ and NH_4F (molar ratio 1:4) were allowed to react in an acetylacetone medium containing a very small amount of water (*vide* Experimental section) to afford a yellow microcrystalline compound. The product analysed for N, U and F^- in an atomic ratio of 4:1:6. The compound appeared to be stable both in the solid state as well as in solution, with its molar conductance being 495 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. The conductance measured as a function of time over a period of several days did not reveal any significant change, supporting the evidence of the stability of the material in water. Based upon the results obtained, the compound has been formulated as $(\text{NH}_4)_4[\text{UO}_2\text{F}_6]$.

Yellow $(\text{NH}_4)_4[\text{UO}_2\text{F}_6]$ is non-hygroscopic, but on long exposure to moist air, slow etching of a glass slide was observed. The structural assessment of the compound has been based upon the results of IR and laser Raman

(LR) spectroscopic investigations. Thus, the IR spectrum displayed a strong band at 913 cm^{-1} owing to $\nu(\text{U}=\text{O})$ [*trans*-linked $\text{O}=\text{U}=\text{O}$] [7] and another strong band at 356 cm^{-1} attributed to the $\nu(\text{U}-\text{F})$ mode of coordinated fluoride. In addition, IR features attributed to the NH_4^+ ion were observed at $3160(\text{m})$, $3025(\text{s})$ and $1418(\text{s})\text{ cm}^{-1}$. These correlate very well with those observed for the ammonium ion [8] of fluorometallate systems and have been assigned to the ν_3 , ν_1 and ν_4 modes of NH_4^+ . Because of the large polarisability changes involved in U–O and U–F bonds, the complex was amenable to LR spectroscopic studies. Thus, LR signals were observed at 951 , 853 and 340 cm^{-1} due to $\nu(\text{U}=\text{O})(\nu_3)$, $\delta(\text{O}-\text{U}-\text{O})(\nu_1)$ [*trans*-linked $\text{O}=\text{U}=\text{O}$] [7] and $\nu(\text{U}-\text{F})$, respectively. The range covered in the present LR experiment was $200\text{--}1500\text{ cm}^{-1}$ which enabled detection of a further strong signal occurring at 1379 cm^{-1} whose origin is attributed to the ν_4 mode of the N–H vibration of the NH_4^+ ion. The results of the IR and LR spectroscopic studies are thus in full agreement with the formula $(\text{NH}_4)_4[\text{UO}_2\text{F}_6]$ for the compound.

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