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# SYNTHESIS, CHARACTERIZATION AND THERMAL DECOMPOSITION OF HYDROXYLAMMONIUM URANYL ACETATE

*I. Donova, V. Stefov and S. Aleksovska*[*]

Institute of Chemistry, Faculty of Science, 'Sts. Cyril and Methodius' University, P. O. Box 162,
91001 Skopje, Macedonia

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## Abstract

The synthesis of hydroxylammonium uranyl acetate is described. The identity of the synthesized compound was confirmed by chemical and infrared analysis. The intermediates and final products of the thermal decomposition were identified by means of thermogravimetric analysis, differential thermal analysis and X-ray diffraction. The thermal decomposition of hydroxylammonium uranyl acetate involves several steps. Two of them are due to decomposition of this compound to $UO_2$ via $UO_2(CH_3COO)_2$, and the third to the partial oxidation of $UO_2$ to $UO_3$ and the formation of $U_2O_8$ in the solid state at higher temperature.

**Keywords:** carboxylates, FTIR spectrum, hydroxylammonium uranyl acetate, synthesis, thermal decomposition

## Introduction

Complexes of the uranyl ion ($UO_2^{2+}$) have attracted considerable interest. Special attention is paid to uranyl carboxylates; the techniques most commonly used for their characterization are infrared (IR) spectroscopy, X-ray diffraction, thermogravimetric analysis (TG) and differential thermal analysis (DTA) [1–5]. A number of studies have been concerned with the uranyl acetates $M[UO_2(CH_3COO)_3]$ where $M$=$Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$ and $NH_4^+$ [6, 7]. In the case of ammonium uranyl acetate, $NH_4(CH_3COO)$ decomposes before $UO_2(CH_3COO)_2$, while in alkali metal uranyl acetates, $UO_2(CH_3COO)_2$ decomposes before $MCH_3COO$. In studies of the triacetatouranates of protonated monosubstituted amines, prepared by the reaction of $UO_2(CH_3COO)_2$ with $RNH_2$ ($R$=Me or Et) in aqueous acetic acid solution, it was found that the thermal decompositions of these compounds occur in two steps, with the successive formation of $UO_2(CH_3COO)_2$ and $UO_{2+x}$ [8]. Tetraalkylammonium tricarboxylato-

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[*] Author for correspondence: Phone: 389-91-117-055, Fax: 389-91-226-861,
E-mail: bote@iunona.pmf.uki.edu.mk

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uranates, $R_4N[UO_2(RCOO)_3]$ (*R*=Me or Et), prepared by the reaction $UO_2(RCOO)_2$ with $R_4N^+$ in the presence of RCOOH [9], and also the corresponding hydrazinium uranyl tricarboxylates, $N_2H_5[UO_2(RCOO)_3]$ (*R*=Me or Et), prepared by the reaction of acidic aqueous $UO_2(RCOO)_2$ solution with $N_2H_4{\cdot}H_2O$ [10, 11], were also studied by means of spectral, crystallographic and thermal analysis. It was shown that the thermal decomposition of hydrazinium uranyl acetate occurs in three steps. Two of them are due to its decomposition to $UO_2$ via $(NH_4)_2U_2O_7$, while the third involves the partial oxidation of $UO_2$ to $UO_3$ and the formation of $U_3O_8$ as a final product [12]. We recently reported on the synthesis and thermal decomposition of pyridinium uranyl acetate [13], the thermal decompositions of which is very similar to that of hydrazinium uranyl acetate.

In a continuation of our work on double uranyl acetate salts with non-metallic cations, in the present paper we describe the preparation of hydroxylammonium uranyl acetate and its characterization by IR spectroscopy, X-ray powder diffraction and TG-DTA.

## Experimental

Hydroxylammonium uranyl acetate was synthesized by evaporation of a reaction mixture of uranyl acetate dihydrate and hydroxylammonium chloride in a molar ratio of $UO_2^{2+}$:$[NH_3OH]^+$=1:9 in 2 mol $dm^{-3}$ acetic acid. This ratio, among several others investigated (from 1:1 to 1:12), was found to be optimal for obtaining the best single product. The precipitate was filtered off, washed with water and ethanol, and air-dried for 24 h. Yellow crystals, stable at room temperature, were obtained.

Quantitative determination of C and H was carried out according to Liebig's method on a Coleman Model 33 analyser. Nitrogen was determined by the method of Dumas. Uranium was determined gravimetrically.

The Fourier transform infrared (FTIR) spectra from KBr pellets were recorded by using a Perkin Elmer System 2000 in the frequency range 4000–500 $cm^{-1}$ with a resolution of 2 $cm^{-1}$ (32 scans were ordinarily accumulated). TG and DTA curves were obtained by using a Netzsch thermoanalyser in dry air in the temperature range 20–1000°C, at a heating rate of 5°C $min^{-1}$, with $\alpha$-$Al_2O_3$ as reference substance, in a platinum crucible. The X-ray powder diffraction patterns were obtained on a Jeol model JDX-7E diffractometer with a model DX-GO-F goniometer, using a $CuK_\alpha$ radiation with a Ni filter. X-ray powder diffraction patterns were recorded on the residues of samples that had undergone isothermal heating at 200, 400 or 600°C.

## Results and discussion

The new uranyl acetate was examined by elemental analysis, IR spectroscopy, TG and DTA and X-ray powder diffraction.

The results of the chemical analysis and the thermal data relating to the mass losses during thermal decomposition at certain temperatures are given in Table 1.

The results obtained imply the empirical formula: $(NH_3OH)[UO_2(CH_3COO)_3]$, for the synthesized compound. The FTIR spectrum shown in Fig. 1 supports the formation of hydroxylammonium uranyl acetate. The IR spectral analysis was performed by comparing this spectrum with those of several different uranyl compounds [14–17], acetate compounds [18–24], uranyl acetate compounds [9–14, 25–28] and solid hydroxylammonium halides [29]. The infrared frequencies associated with the main functional groups, together with the tentative band assignments, are listed in Table 2.

**Table 1** Chemical and thermal data on $(NH_3OH)[UO_2(CH_3COO)_3]^a$

| Chemical analysis/% | | | | Thermal analysis: mass loss, $\Delta m$/% | | | |
|---|---|---|---|---|---|---|---|
| C | H | N | U | to 260°C | to 420°C | to 530°C | to 900°C |
| 15.5<br>(15.00) | 2.9<br>(2.72) | 3.0<br>(2.91) | 49.4<br>(49.47) | 20.1<br>(19.35) | 43.8<br>(43.87) | 42.9<br>(41.65) | 42.9<br>(41.65) |

[a] Calculated values are given in parentheses

**Table 2** Infrared frequencies (in $cm^{-1}$) and assignments for hydroxylammonium uranyl acetate[a]

| Observed frequency | Proposed assignment[b] |
|---|---|
| 3500–2500 vs | $\nu(OH)$, $\nu(NH_3)$, $\nu(CH_3)^c$ |
| 1625 w | $\delta(NH_3)$ |
| 1543 vs | $\nu_{as}(COO^-)$, $\delta_s(NH_3)$ |
| 1465 vs | $\delta_{as}(CH_3)$ |
| 1410 m | $\nu_s(COO^-)$ |
| 1348 m | $\delta_s(CH_3)$ |
| 1222 sh | $\delta(OH)$ |
| 1203 s | $\rho(NH_3)$ |
| 1055 m | $\rho(CH_3)$ |
| 1012 s | $\rho(CH_3)$ |
| 948 w | $\nu(C\text{–}C)$ |
| 925 vs | $\nu_{as}(UO_2)$, $\nu(N\text{–}O)$ |
| 855 vw | $\nu_s(UO_2)$ |
| 680 vs | $\delta_s(OCO)$, $\gamma(OH)$ |
| 610 m | $\omega(COO^-)$ |

[a] KBr pellets. Abbreviations: s=strong, m=medium, w=weak, v=very, sh=shoulder, s=symmetric, as=antisymmetric, ρ=rocking, ω=wagging; [b] Only major contributions to a given mode are listed
[c] Resonance overlap

In the 3500–2500 $cm^{-1}$ region of the spectrum, there is a complex and broad band, which is probably mainly due to the NH and OH stretching vibrations of the $NH_3OH^+$. The bands due to the antisymmetric and symmetric $CH_3$ stretching vibrations of the $CH_3COO^-$ group, which should appear at around 2950 $cm^{-1}$, overlap with this complex band. In the region between 1800 and 1300 cm$^{-1}$, overlapping bands likewise appear. We assign the intense band at 1543 cm$^{-1}$ to antisymmetric COO$^-$ stretching vibrations and symmetric NH$_3$ deformation modes. In the region where bands from symmetric stretching vibrations of COO$^-$ are expected, two bands are found, at 1465 and 1410 cm$^{-1}$. The former may be due to (or overlap with the band from) the antisymmetric bending vibrations of the CH$_3$ groups. We assign the band at 1348 cm$^{-1}$ to a symmetric CH$_3$ bending vibration. The band at around 1625 cm$^{-1}$ could be from the antisymmetric δ(NH$_3$) mode. The asymmetric band at 1203 cm$^{-1}$ probably originates from NH$_3$ and δ(OH) rocking vibrations.

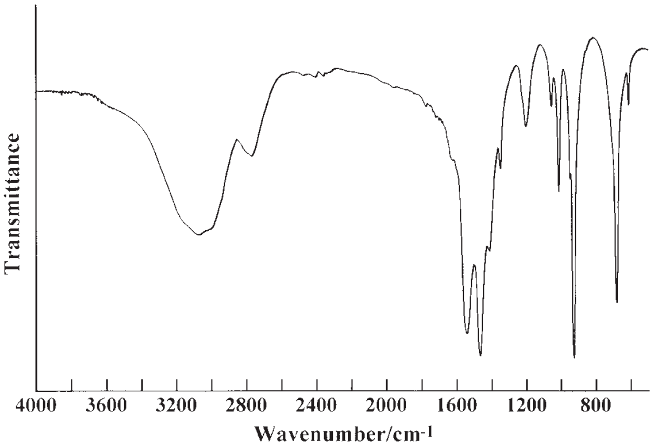

**Fig. 1** FTIR spectrum of hydroxylammonium uranyl acetate

We made an attempt to assign bands in the low-frequency region of the spectrum taking into account their frequencies and intensities, in agreement with the published assignments for some uranyl acetate compounds [9–14, 25–28] and solid hydroxylammonium halides [29]. The bands at 1055 and 1012 cm$^{-1}$ may be due to the CH$_3$ rocking vibration. The sharp band at 948 cm$^{-1}$ probably originates from ν(C–C) modes, and the intense band at 925 cm$^{-1}$ from antisymmetric stretching vibrations of the uranyl ion and N–O stretching modes. As expected, a very weak band appears at around 855 cm$^{-1}$, which can be attributed to the symmetric stretching vibration of the uranyl ion. Another intense band at 680 cm$^{-1}$, and a weak one at 611 cm$^{-1}$, were assigned to symmetric COO$^-$ bending and wagging vibrations, respectively. The intense band at 680 cm$^{-1}$ can also be strengthened by out-of-plane OH bending modes.

We would like to emphasize here that, in the region of absorption of the acetate and uranyl groups, the spectral pattern of the studied compound is practically the same as that of Na[UO$_2$(CH$_3$COO)$_3$] [26]. This spectral picture implies similar structural characteristics of these two uranyl acetate compounds.

The analysis of the TG and DTA curves (Fig. 2) shows that the thermal decomposition begins at around 200°C and proceeds in several steps.

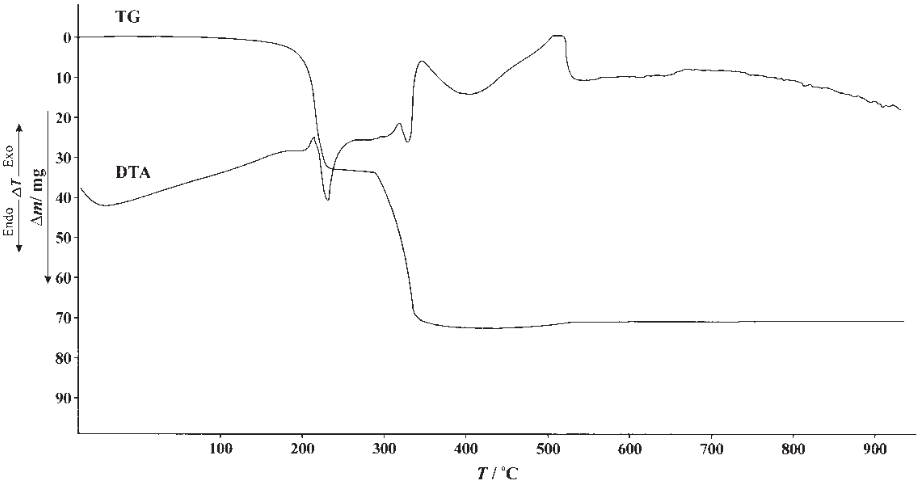

**Fig. 2** TG and DTA curves of hydroxylammonium uranyl acetate ($m$=171.00 mg)

The first step is the decomposition of $(NH_3OH)[UO_2(CH_3COO)_3]$ to $UO_2(CH_3COO)_2$, corresponding to the endothermic DTA peak at about 230°C. The inflection point reflecting a 20.1% mass loss at about 260°C in the TG curve is in good agreement with the theoretical value (19.35%) for one unit of $(NH_3OH)(CH_3COO)$. However, it was impossible to isolate this phase.

In the temperature range from 260 to 420°C, two endothermic peaks (one at 340 and another, rather broad one at about 400°C) were observed. In this step, the compound probably decomposes to uranium oxides mainly $UO_2$.

The experimental mass loss up to 420°C (43.8%) is in good agreement with the theoretical value (43.87%) calculated for $UO_2$ as the final product of thermal decomposition. From 420 to 470°C, no changes were observed. The slight mass increase between 470 and 530°C in the TG curve is probably due to the partial oxidation of $UO_2$ to $UO_3$. The reaction $UO_2+1/2O_2=UO_3$ coincides with a slight exothermic peak at about 510°C in the DTA curve.

Our thermal decomposition results (experimental residue 42.9, theoretical value 41.65%) and literature data [2, 3] indicate that $U_3O_8$ is obtained as the final decomposition product. $U_3O_8$ exists from 530 to 900°C, and changes are not observed in the TG curve.

The possible reactions of thermal decomposition (under dynamic conditions) can be expressed as:

I $(NH_3OH)[UO_2(CH_3COO)_3] \xrightarrow{\text{to } 260\,°\text{C}} UO_2(CH_3COO)_2$ endo

II $UO_2(CH_3COO)_2 \xrightarrow{\text{to } 420\,°\text{C}} UO_2$ endo

III $UO_2+1/2O_2 \xrightarrow{\text{from } 470 \text{ to } 530\,°\text{C}} UO_3$ exo

IV $UO_2+2UO_3 \xrightarrow{\text{above } 530\,°\text{C}} U_3O_8$ solid-state reaction

The initial hydroxylammonium uranyl acetate and the products obtained by isothermal treatment at 200, 400 and 600°C were additionally examined by X-ray diffraction. The diffractograms are depicted in Fig. 3.

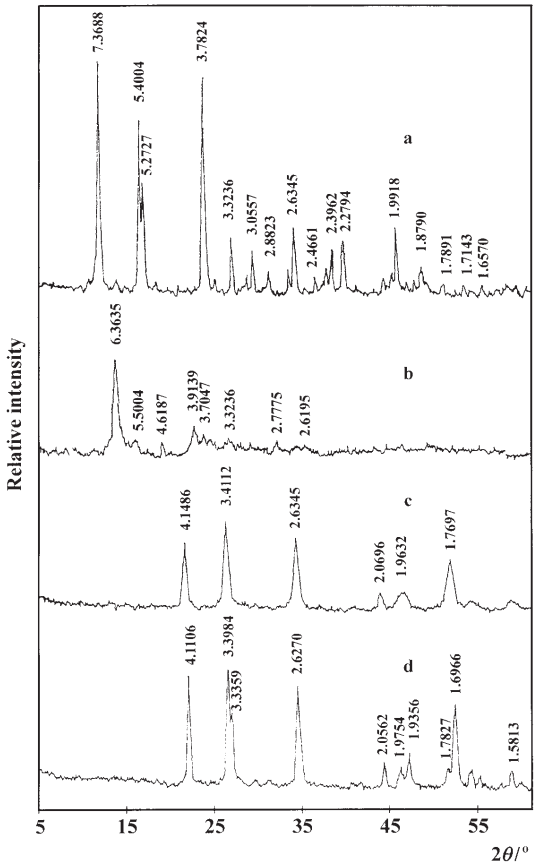

**Fig. 3** X-ray powder diffraction patterns of a – hydroxylammonium uranyl acetate; and residues obtained following isothermal treatment at b – 200; c – 400 and d – 600°C

From the X-ray powder diffraction patterns of the initial compound (Fig. 3a), it can be concluded that it is crystalline. The *d* values are given in Table 3. When heated at 200°C for 1 h, it is transformed practically completely to $UO_2(CH_3COO)_2$ (Fig. 3b) [4]. The diffractograms of the residues obtained after isothermal heating at 400 and at 600°C (Figs 3c and 3d) show mainly the formation of higher uranium oxides. The *d* values of these two phases are closest to the corresponding values for $UO_3$ [($3.44_x$; $2.65_9$; $1.78_9$; $4.17_8$; $1.98_6$; $1.43_6$; $1.32_6$; $1.29_6$) and for $U_3O_8$ ($4.15_x$; $3.43_x$; $2.64_9$; $1.77_6$; $3.36_5$; $2.61_4$; $2.07_4$; $1.95_4$)] [30].

**Table 3** *d*-values and relative intensities for hydroxylammonium uranyl acetate

| *d*-Values/Å | $I/I_0$ |
|---|---|
| 7.3688 | 1.00 |
| 5.3040 | 0.80 |
| 5.2111 | 0.459 |
| 3.5870 | 0.951 |
| 3.2995 | 0.278 |
| 3.0354 | 0.229 |
| 2.8732 | 0.180 |
| 2.5804 | 0.197 |
| 2.6345 | 0.360 |
| 2.3901 | 0.197 |
| 2.3599 | 0.262 |
| 2.2739 | 0.270 |
| 2.0085 | 0.197 |
| 1.9795 | 0.360 |
| 1.8717 | 0.213 |
| 1.5132 | 0.180 |

In conclusion, a new uranyl carboxylate corresponding to the formula $(NH_3OH)[UO_2(CH_3COO)_3]$ has been synthesized. The compound is crystalline and stable at room temperature. Its thermal decomposition proceeds in several steps, beginning with the decomposition of $(NH_3OH)[UO_2(CH_3COO)_3]$ to $UO_2$ at about 420°C, via $UO_2(CH_3COO)_2$ as intermediate, under dynamic conditions. The partial oxidation of $UO_2$ to $UO_3$ takes place between 470 and 530°C and a solid-state reaction of $UO_2$ above 530°C leads to $U_3O_8$ as final product.

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