ELSEVIER

Thermochimica Acta 348 (2000) 169–174

thermochimica acta

www.elsevier.com/locate/tca

Synthesis, characterization and thermal decomposition of pyridinium uranyl acetate

Ilinka Donova, Slobotka Aleksovska*, Viktor Stefov

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

Received 9 July 1999; received in revised form 21 December 1999; accepted 22 December 1999

Abstract

The synthesis, characterization and thermal decomposition of pyridinium uranyl acetate are presented. The identification of the compound was performed by chemical analysis and by infrared spectroscopy. Thermal decomposition of pyridinium uranyl acetate took place in several steps due to the decomposition of the salt to UO_2, and to partial oxidation to UO_3 and formation of U_3O_8. The intermediate and the final products of thermal analysis were identified by means of thermogravimetric, differential thermal analysis and X-ray powder diffraction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: FTIR spectra; Pyridinium uranyl acetate; Synthesis; TG-DTA analysis; X-ray powder diffraction

1. Introduction

Great interest for the uranium compounds in the world is due to the possibility of their application in nuclear industry on one hand, and in medicine on the other. Also, they have very important environmental aspects. This is why complexes of the uranyl ion, especially uranyl carboxylates, have been found interesting for many investigators.

Thermal decomposition of double uranyl salts with Li^+, Na^+, K^+, Rb^+, Cs^+ and $NH_4{}^+$ have been studied by Dunaeva et al. [1]. Also, investigations on several uranyl carboxylato compounds with some alkyl substituted ammonium ions have been reported. Thus, tricarboxylatouranates of methylammonium and ethylammonium [2] were synthesized and investigated by X-ray diffraction, infrared (IR) spectroscopy and thermal analysis, as well as, tetraalkylammonium tricarboxylatouranates(VI), $R_4N[UO_2(O_2CR)_3]$, (R=Me, Et) [3].

Hydrazinium uranylcarboxylato complexes, $N_2H_5[UO_2A_3]$, (A=Oac, O_2CEt) have been studied by Seisenbaeva et al. [4]. According to their investigation, the thermolysis occurs in a narrow temperature range yielding $UO_{2.21-2.22}$ as a final product. One of these compounds, hydrazinium uranyl acetate, was studied in our laboratory as well [5]. The compound was characterized by spectral, crystallographic and thermal analysis, and some differences in thermal decomposition were found. Namely, the decomposition occurred in three steps. Two of them are due to the decomposition of hydrazinium uranyl acetate to UO_2 via $(NH_4)_2U_2O_7$ and the third one to partial oxidation of UO_2 to UO_3 and formation of U_3O_8.

---

* Corresponding author. Tel.: +389-91-117-055; fax: +389-91-226-865.
E-mail address: bote@iunona.pmf.ukim.edu.mk (S. Aleksovska)

PII: S0040-6031(00)00362-2

The monohydrate of the same compound was obtained by Kuppusamy et al. [6] and studied by electronic, infrared spectroscopy, thermogravimetric (TG) and differential thermal analysis (DTA).

Recently, we have also reported the synthesis, IR spectral analysis and thermal decomposition of hydroxylammonium uranyl acetate [7].

Continuing our work on synthesis and investigation of uranyl acetates with non-metallic cations, the investigation of pyridinium uranyl acetate is presented in this paper. To the best of our knowledge, the results presented here have not been reported yet.

2. Experimental

Pyridinium uranyl acetate was obtained by slow evaporation of the reaction mixture of uranyl acetate and pyridinium acetate in acetic acid (2 mol l^{-1}) solution, taken in molar ratio 1:6. The precipitate was filtered off, washed with water and ethanol and dried on air. Yellow needle-like crystals, stable at room temperature, were obtained.

The compound was identified and studied by elemental analysis, Fourier transform infrared (FTIR) spectroscopy, X-ray powder diffraction and thermal analysis.

The elemental analysis (C, H, N) was performed according to Liebig's method (C and H) on the Coleman Model 33 analyzer and N was determined by the method of Dumas. Uranium was determined gravimetrically.

The FTIR spectra from KBr pellets were recorded on Perkin-Elmer System 2000 in the frequency range 4000–400 cm^{-1}.

The X-ray powder diffraction patterns were obtained on a Jeol-diffractometer, model JDX-7E with a goniometer model DX-GO-F, using Cu Kα radiation with Ni filter.

TG and DTA curves were recorded on a NETZSCH thermoanalyser in flow of dry air, in the temperature range from 20–800°C, at a heating rate of 5°C min^{-1}, with α-Al_2O_3 as a reference substance.

3. Results and discussion

The experimental values from the quantitative chemical analysis (C, H, N and U), and the mass loses during thermal decomposition at certain temperatures, followed by the theoretically calculated values are given in Table 1.

As can be seen, the results correspond to the empirical formula $(C_5H_5NH)[UO_2(CH_3COO)_3]$. In order to confirm these results we recorded and analysed the FTIR spectrum of the synthesized compound as well. The spectral analysis showed a well agreement with the supposed formula of the compound. The IR spectral analysis was performed comparing this spectrum with those of several different uranyl compounds [8–11], acetate compounds [12–18] and uranyl acetate compounds [4,6–8,19–22].

As shown in Fig. 1. the expected vibrational bands of the constituent groups: $C_5H_5NH^+$, UO_2^{2+}, CH_3 and COO^- are evident. At about 3450 cm^{-1} there is a broad band which can be attributed to either NH stretching modes and/or vibrations related to NH stretches. The bands in the 3100–3000 cm^{-1} region can be assigned as CH stretching vibrations of the aromatic ring. The bands due to the antisymmetric and symmetric stretching vibration of CH_3 group appear in the region between 2980–2890 cm^{-1} and are probably overlapped with a complex band which is found in the same region. Similar picture as in our spectrum between 3600 and 2600 cm^{-1} is observed also in the FTIR spectrum of pyridinium chloride [23].

A complex band in the region from 1800–1300 cm^{-1} appears, as well. Here, the bands from

Table 1
Results of the chemical and thermal analysis of pyridinium uranyl acetatate[a]

	w(C) (%)	w(H) (%)	w(N) (%)	w(U) (%)	Δm (%)		
					to 240°C	to 560°C	to 780°C
Experimental	25.25	2.98	2.72	45.00	26.60	50.53	49.60
Theoritical	25.06	2.87	2.67	45.05	26.33	48.78	46.76

[a] w: mass fraction; Δm: mass loss.

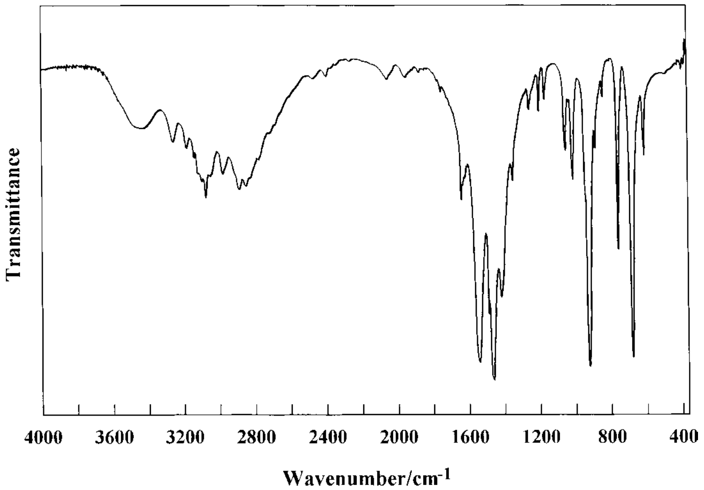

Fig. 1. FTIR spectrum of pyridinium uranyl acetate.

some vibrations of NH, COO$^-$, CH$_3$ groups and the aromatic ring are expected. We assigned the bands due to these vibrations using the previously made assignments of the infrared spectra of some acetate compounds [12–18], uranyl acetate compounds [4,6–8,19–22] and pyridinium chloride [23]. Thus, we assigned the band at 1638 cm^{-1} to deformation NH vibrations, whereas an intensive band at 1540 cm^{-1} due to the COO$^-$ antisymmetric vibrations. Two bands are found at 1460 and 1415 cm^{-1} in the region of symmetric stretching COO$^-$ vibrations. The one at 1460 cm^{-1} can originate or be strengthened by the band from the antisymmetric bending vibrations of CH$_3$ groups. We assigned the band at 1350 cm^{-1} to the symmetric bending vibrations of CH$_3$ groups. One should bear in mind that in this region (1650–1300 cm^{-1}) bands from C=C stretching modes of the aromatic ring appear, as well. They can contribute to the shape and intensity of the bands appearing in the discussed region.

In accordance to the previously published assignments of some uranyl acetate compounds [4,6–8,19–22], the bands at 1052 and 1010 cm^{-1} can be attributed mainly to the rocking CH$_3$. The shoulder around 940 cm^{-1} probably originates from stretching C–C modes whereas intensive band at 920 cm^{-1} and a weak one at 885 cm^{-1} we assigned as antisymmetric and symmetric stretching vibrations of UO$_2$$^{2+}$ ions [8–11].

The appearance of a sharp band at 768 cm^{-1} is probably due to the γ(CH) of the pyridine ring. We assigned the intensive band at 675 cm^{-1}, as well as the weak one at 608 cm^{-1} as symmetric bending and wagging COO$^-$ vibrations, respectively.

In order to obtain more information about the thermal stability of the obtained compound, TG and DT analyses were performed. TG and DTA curves, under dynamic conditions, are shown in Fig. 2.

Thermal decomposition takes place in several stages. In the first one the compound decomposes to uranyl acetate, in the temperature range from 120–240°C. This is followed by an endothermic peak with maximum at 200°C. The experimental value for mass loss, in this stage, is 26.60%, while the calculated one is 26.39%. Taking into account these values, it can be assumed that in the first stage pyridinium acetate releases.

In the next stage, in the temperature range from 240–560°C, uranyl acetate decomposes to uranium(IV) oxide. Thus, the experimental value for mass loss on the TG curve is 23.93%, which is in good agreement with the calculated value (22.39%). This stage is characterized by three endothermic peaks on DTA curve. A sharp peak appears at 340°C, but two small peaks appear at 380 and 530°C, as well. Actually, firstly a nonstoichiometric oxide of uranium is formed. It is well known that uranium forms nonstoichiometric oxides of genaral formula UO$_{2+x}$

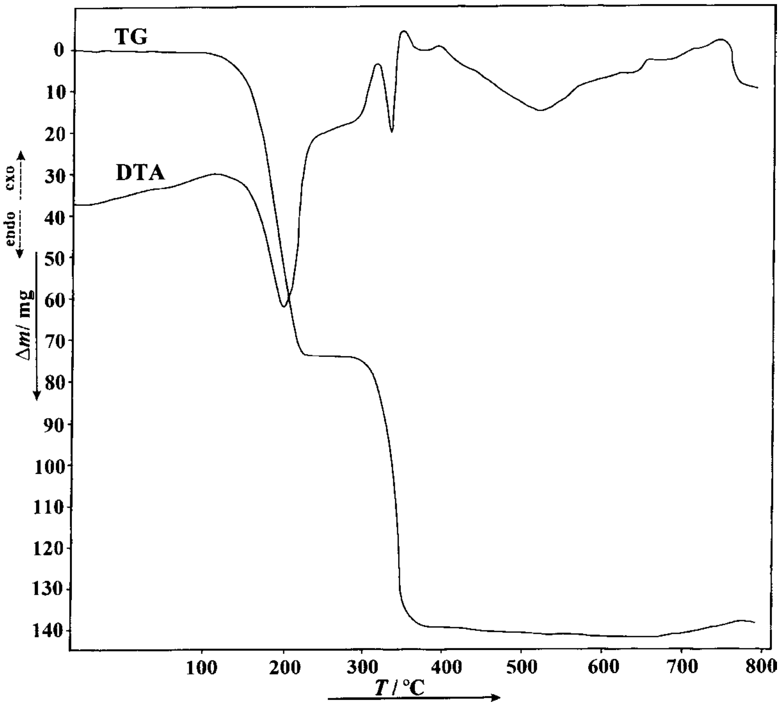

Fig. 2. TG and DTA diagrams of pyridinium uranyl acetate (m=280.00 mg).

(x=0.2–0.22) [2,4]. Thus, the two endothermic peaks at 380 and 530°C, can be due to transformation of some nonstoichiometric oxides to UO_2 that is connected with a very small mass loss.

In the temperature range from 560–640°C, no changes are observed, but from 640–780°C, the slight weight increase on TG curve and also an exothermic peak with maximum at 740°C on DTA curve appear. These changes are probably due to partial oxidation of UO_2 to UO_3. Above 780°C, a reaction in solid state between UO_2 and UO_3 takes place resulting in U_3O_8 as a final product of thermal decomposition. This can be concluded both from the X-ray powder diffraction pattern of the residue of thermal decomposition and from its color which is dark green. The total experimental mass loss up to 780°C is 49.46% and the calculated one is 46.76%.

In general, the thermal decomposition can be expressed by the following reactions:

$$(C_5H_5NH)[UO_2(CH_3COO)_3] \rightarrow UO_2(CH_3COO)_2 \quad (70-240^\circ C)\ \text{endo} \tag{1}$$

$$UO_2(CH_3COO)_2 \rightarrow UO_2 \quad (240-560^\circ C)\ \text{endo} \tag{2}$$

$$UO_2 + \tfrac{1}{2}\,O_2 \rightarrow UO_3 \quad (640-780^\circ C)\ \text{exo} \tag{3}$$

$$UO_2 + 2\,UO_3 \rightarrow U_3O_8 \quad (\text{above}\ 780^\circ C) \tag{4}$$

In order to obtain more data about the intermediate products during the thermal decomposition, we undertook isothermal measurements at 200, 400 and 600°C. Also, X-ray powder diffraction patterns were recorded of pyridinium uranyl acetate and of the residues of thermal decomposition (Figs. 3 and 4).

The initial compound is crystalline (Fig. 3a), and the intermediates (Fig. 3b and Fig. 4), as well. The d-values and the relative intensities of pyridinium uranyl acetate are given in Table 2. However, we could not recognize any compound at 200°C. The powder diffraction patterns of the residues at 400 and 600°C, both show the formation of U_3O_8 (U_3O_8 File No. 2–276: 4.15x; 3.43x; 2.64$_9$; 1.77$_6$; 3.36$_5$; 2.61$_4$; 2.07$_4$; 1.95$_4$) [24]. The main reason for U_3O_8 formation at lower temperatures (400°C) is probably due to the isothermal heating for 1 h in presence of air.

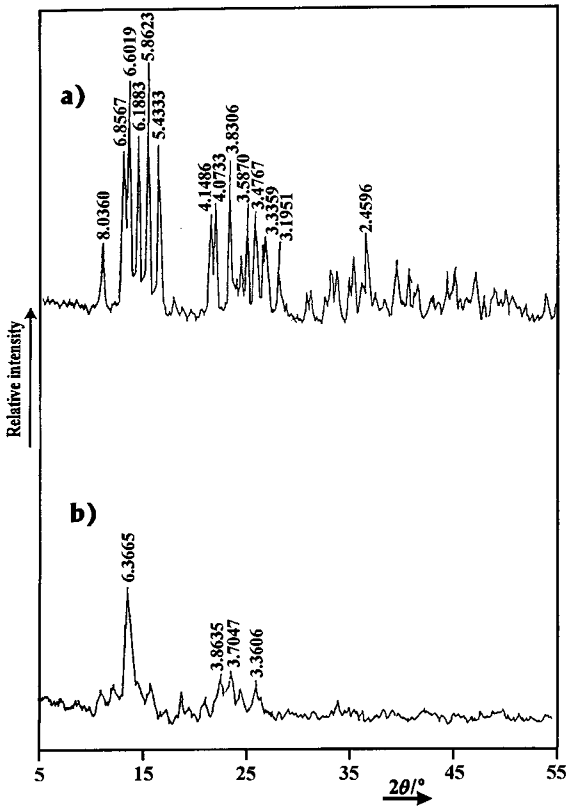

Fig. 3. X-ray powder diffraction patterns of: (a) pyridinium uranyl acetate; (b) residue at 200°C.

Table 2
The *d*-values and relative intensities of pyridinium uranyl acetate

d (Å)	*I*/*I*$_0$
8.0360	0.4062
6.8567	0.6719
6.6019	0.9219
6.1883	0.7500
5.8623	1.000
5.4333	0.6875
4.1486	0.5156
4.0733	0.5312
3.8306	0.6719
3.5870	0.5156
3.4767	0.4687
3.3359	0.4062
3.1951	0.3594
2.4596	0.4062

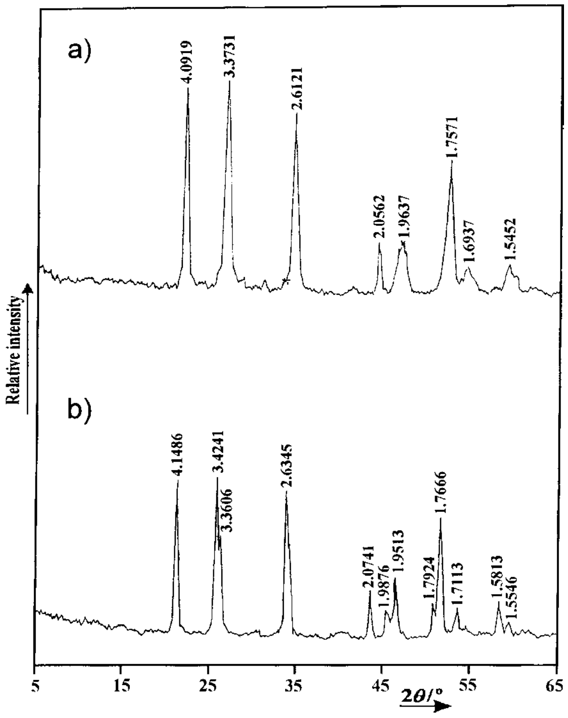

Fig. 4. X-ray powder diffraction patterns of residues obtained following isothermal treatment at: (a) 400°C; (b) 600°C.

Acknowledgements

The investigation of which the partial results are presently reported has been financially supported by the Ministry of Science of the Republic of Macedonia and this support is gratefully and sincerely appreciated.

References

[1] K.M. Dunaeva, N.A. Santalova, Koord. Khim. 11 (1985) 1432.
[2] G.A. Seisenbaeva, N.A. Santalova, K.M. Dunaeva, Koord. Khim. 14 (1988) 1214.
[3] N.A. Santalova, G.A. Seisenbaeva, A.N. Kor'eva, K.M. Dunaeva, Vestn. Mosk. Univ. Ser.2: Khim. 31 (1990) 597.
[4] G.A. Seisenbaeva, K.M. Dunaeva, N.A. Santalova, Zh. Neorg. Khim. 36 (1991) 1235.
[5] I. Donova, Bull. Chem. Technol. Macedonia 15 (1996) 113.
[6] K. Kuppusamy, B.N. Sivasankar, S. Govindarajan, Thermochim. Acta 274 (1996) 139.
[7] I. Donova, V. Stefov, Croat. Chem. Acta, submitted for publication.

[8] G.L. Caldow, A.B. Van Cleave, R.L. Eager, Can. J. Chem. 38 (1960) 772.
[9] D.M. Adams, Metal-Ligand and Related Vibrations, Edward Arnold, London, 1967, pp. 244–245, 261.
[10] J.I. Bullock, J. Chem. Soc. (A), (1969) 781.
[11] H. Gerding, G. Prins, W. Gabes, Rev. Chim. Miner. 12 (1975) 303.
[12] K. Nakamura, J. Chem. Soc. Japan (Pur. Chem.) 79 (1958) 1411.
[13] A.I. Grigorev, Zh. Neorg. Khim. 8 (1963) 802.
[14] J.D. Donaldson, J.F. Knifton, S.D. Ross, Spectrochim. Acta 21 (1965) 275.
[15] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1970, pp. 222–224.
[16] A.M. Heyns, J. Mol. Struct. 11 (1972) 93.
[17] B. Šoptrajanov, M. Ristova, Vest. Slov. Kem. Drus. 39 (1992) 231.
[18] L. Šoptrajanova, B. Šoptrajanov, Spectrosc. Lett. 25 (1992) 1131.
[19] B. Mentzen, G. Giorgio, J. Inorg. Nucl. Chem. 32 (1970) 1509.
[20] K. Stojanoski, M.Sc. Thesis, Faculty of Science, Skopje, 1979.
[21] G.N. Mazo, N.A. Santalova, K.M. Dunaeva, Koord. Khim. 6 (1980) 753.
[22] G.N. Mazo, N.A. Santalova, E.V. Andreeva, K.M. Dunaeva, Koord. Khim. 7 (1981) 236.
[23] K.G.R. Pachler, F. Matlok, H.U. Gremlich, Merck FT-IR Atlas, VCH, Weinheim, 1988, 215.pp.
[24] Joint Commitee on Powder Diffraction Standard, International Center for Diffraction Data, Diffraction File, Swanthmore, PA, USA, File No. 2–276, 1972.