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Thermochimica Acta 389 (2002) 71–77

thermochimica acta

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Synthesis, identification, structural and thermal stability investigations on bipyridinium uranyl acetate

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Received 8 June 2001; received in revised form 12 November 2001; accepted 12 November 2001

Abstract

Bipyridinium uranyl acetate (2,2′-bipyridinium triacetatodioxouranate(VI)) was synthesised by slow evaporation, at room temperature, of a reaction mixture of uranyl acetate and bipyridine in molar ratio 1:6 in 2 mol l^{-1} acetic acid. The yellow crystals were examined by elemental analysis, X-ray powder diffraction, FT-IR spectroscopy, thermogravimetric–differential thermal analysis (TG–DTA). According to the elemental, TG analysis and spectroscopy investigations, it could be concluded that the general formula of the compound is $(NC_5H_4\text{-}C_5H_4NH)UO_2(CH_3COO)_3$. Thermal decomposition of the compound takes place in several steps. In the first step, the compound releases acetic acid (in molar ratio 1:1) and consequently undergoes structural changes (Anderson rearrangement). This results with bipyridine complex formation, confirmed by elemental analysis and infrared (IR) spectroscopy. In the second step, the complex decomposes to UO_2, which is partially oxidised to UO_3. The intermediate and the final products of thermal analysis were identified by means of TG–DTA and X-ray powder diffraction. The final product of thermal decomposition is U_3O_8.

Keywords: Bipyridinium uranyl acetate; Identification; FT-IR spectra; TG–DTA; X-ray powder diffraction

1. Introduction

One of the most important of the actinide elements is uranium. Therefore, much information is available about its chemistry, especially its coordination chemistry. Uranium exhibits variable valency, but special attention is paid to its hexavalent uranyl cation (or dioxouranium(VI) cation), UO_2^{2+}, since it forms a number of stable complexes. It is well known that both in solid state and in solution UO_2^{2+} is linear [1]. In the complexes with a number of ligands (negative ions and neutral molecules), the coordination is usually on the equatorial plane, thus the coordination polyhedron being, more or less regular, pentagonal bipyramide or octahedron [2].

A number of structural and thermal stability studies have been performed on uranyl carboxylates with metallic and non-metallic cations. Thermal decomposition of double uranyl salts with Li^+, Na^+, K^+, Rb^+, Cs^+ and NH_4^+ has been studied by Dunaeva and Santalova [1]. Investigations on several uranyl carboxylates with alkyl substituted ammonium ions have also been reported. Thus, triacetatouranates of methylammonium and ethylammonium were synthesised and investigated by X-ray diffraction, infrared (IR) spectroscopy and thermal analysis [2], 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) were studied by Seisenbaeva et al. [4]. According to their investigation the

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PII: S0040-6031(01)00849-8

thermolysis occurs in a narrow temperature range involving several stages. The first one is the so-called *Anderson rearrangement* [4–6], which is a reaction of substitution of some ligand of the internal coordination sphere of the complex with a ligand from the external sphere (initially cation). Usually, this rearrangement appears when cations in the external sphere are protonated amines, and internal ligands are carboxylate anions. Thus, a proton transfer from the amine cation to the carboxylate anion appears, resulting with coordination of the deprotonated amine in the internal sphere of the complex.

Several hydrazinium uranyl carboxylates hydrates were also obtained by Kuppusamy et al. [7] and studied by electronic, IR spectroscopy and thermogravimetric–differential thermal analysis (TG–DTA). One of these compounds was also studied in our laboratory [8]. The compound was characterised 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 from UO_2 to UO_3 and formation of U_3O_8.

Recently, we have reported the synthesis, IR spectrum and thermal decomposition of pyridinium uranyl acetate [9], and on hydroxylammonium uranyl acetate, as well [10]. Continuing our work on synthesis and investigation of uranyl acetates with non-metallic cations, in this paper, we present the preparation and investigation of bipyridinium uranyl acetate.

2. Experimental

Bipyridinium uranyl acetate was obtained by slow evaporation of the reaction mixture of uranyl acetate and 2,2′-bipyridine in acetic acid (2 mol l^{-1}) solution, taken in molar ratio 1:6. The obtained yellow crystals were filtered off, washed with water and ethanol and dried on air.

The compound was studied and identified by elemental analysis, FT-IR, 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 analyser and N was determined by the method of Dumas. Uranium was determined gravimetrically.

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

The IR spectra were recorded using the IR interferometer Perkin-Elmer System 2000 FT-IR (resolution 4 cm^{-1}, OPD rate 0.2 cm/s, 32 background and 64 sample scans) from pellets in KBr. Mulls in Nujol between KBr plates were also used and identical spectra were obtained. The software package GRAMS 2000 [11] was used for acquisition of spectra, and GRAMS/32 [12] was used for analysis of spectra.

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.

3. Results and discussion

The results of the quantitative chemical analysis (C, H, N and U), and the thermal analysis data for the mass losses during thermal decomposition at certain temperatures are given in Table 1.

These results correspond to the empirical formula $(C_5H_4N\text{-}C_5H_4NH)UO_2(CH_3COO)_3$. In order to confirm the supposed protonation of bipyridine and formation of a salt with bipyridinium cation, IR spectra were recorded.

The FT-IR spectrum shown (see Fig. 1) supports the formation of the supposed salt of uranyl acetate with

Table 1
Results of the chemical and thermal analysis of bipyridinium uranyl acetate ($C_{16}H_{18}N_2O_8U$) (w: mass fraction and Δm: mass loss)

	w(C)(%)	w(H)(%)	w(N)(%)	w(U)(%)	Δm (%)		
					Up to 180 °C	Up to 340 °C	Up to 550 °C
Experimental	31.2	2.9	4.8	40.0	9.3	51.0	53.3
Theoretical	31.8	3.0	4.6	39.4	9.8	50.4	53.6

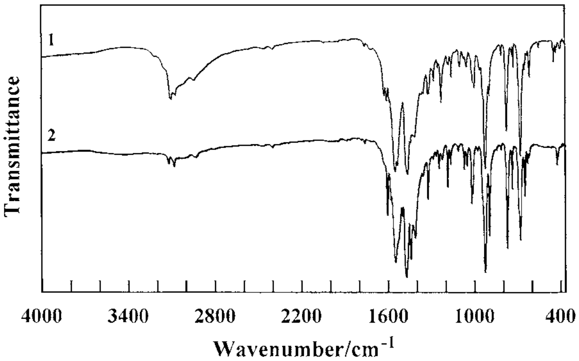

Fig. 1. The FT-IR spectra of bipyridinium uranyl acetate (1) and residue obtained at 150 °C (2).

2,2′-bipyridine. The IR spectral analysis was performed comparing this spectrum with those of several different uranyl compounds [13,14], acetate compounds [15–18], uranyl acetate compounds [4,7–10,19–22], 2,2′-bipyridine [23] and some MO_2 2,2′-bipyridine complexes [24,25].

As can be seen in the spectrum (Fig. 1), a complex band with several shoulders appears from around 3280–2800 cm^{-1}. This band can be attributed to stretching CH vibrations of the pyridinium rings, CH_3 groups together with the NH stretching vibrations. The bands due to the antisymmetric and symmetric stretching vibrations of CH_3 groups appear in the region between 2980–2890 cm^{-1}. Between 3100 and 3000 cm^{-1}, the bands due to CH stretches of the aromatic rings are expected, whereas, the bands from NH stretches appear below 3400 cm^{-1}. In the region of the bending N–H vibrations, two bands are found at 1622 and 1605 cm^{-1}.

The intense bands at around 1548 and 1529 cm^{-1} can be assigned as antisymmetric vibrations of the COO^- ions, whereas, the bands at 1461 and 1415 cm^{-1} to the symmetric COO^- vibrations. The asymmetric band at 1465 cm^{-1} can be attributed either to the antisymmetric bending vibrations of the CH_3 groups or, what is more likely, it is intensified by these vibrations. We attributed the band observed at around 1364 cm^{-1} to the symmetric bending vibrations of CH_3 groups. In the region between 1650 and 1300 cm^{-1} in the IR spectra, bands with variable intensity are also expected from the stretching C=C bonds from aromatic rings. The bands in the region from 1250 to 1000 cm^{-1} were assigned as a result of in plane CH bending and rocking CH_3 vibrations.

In accordance with our previous spectroscopic analyses of various uranyl acetate compounds [4,7–10,19–22], having in mind the frequencies and intensities of the bands, we assigned the band at 938 cm^{-1} as a stretching C–C mode and the two bands at 921 and 842 cm^{-1} as a result of antisymmetric and symmetric vibrations of the UO_2^{2+} ions.

The appearance of a sharp band at 773 cm^{-1} is probably due to the γ(CH) of the pyridine ring. In the spectrum of pyridinium uranyl acetate, the band at 768 cm^{-1} was attributed to this vibration [9], whereas, in the spectrum of 2,2′-bypiridine the corresponding band appears at 753 cm^{-1} [23].

The intense band at 675 cm^{-1} and the less intense and sharp one at 612 cm^{-1} were assigned as a result of symmetric bending and wagging vibrations of COO^- ions. In this region, the appearance of medium to weak band of γ(NH) is also expected.

It is interesting to comment on the two possibilities for coordination of the nitrogen atom from the bipyridine cation with the uranium atom, which are formations of a double salt, or a complex. Here, one should have in mind that in complexes, in which it is a bidentate ligand, the two rings of bipyridine are in a *cis* position. Even though the protonation of one N atom of bipyridine was practically confirmed by the IR study, it is hard to be sure that the other nonprotonated N atom is bonded to U and to assign the weak bands observed around 450 cm^{-1} as due to stretching U–N vibrations.

In order to get more information about the thermal stability of the obtained compound, TG–DTA were performed. TG and DTA curves are shown on Fig. 2.

The thermal decomposition of the compound takes place in several stages. Initially, in the temperature range from 100–170 °C, one unit of acetic acid is removed which is followed by an endothermic maximum at 170 °C. This situation is very similar to the one found in hydrazinium uranyl acetate [4]. The compound probably undergoes Anderson rearrangement that results with formation of a bipyridine complex. Thus, removing one unit of acetic acid, the bipyridinium cation is transformed to bipyridine, and a bypiridine complex is formed. The experimental mass loss in this stage is 9.3% which is in good agreement with the theoretical value calculated for the loss of one unit of acetic acid (9.8%). The first

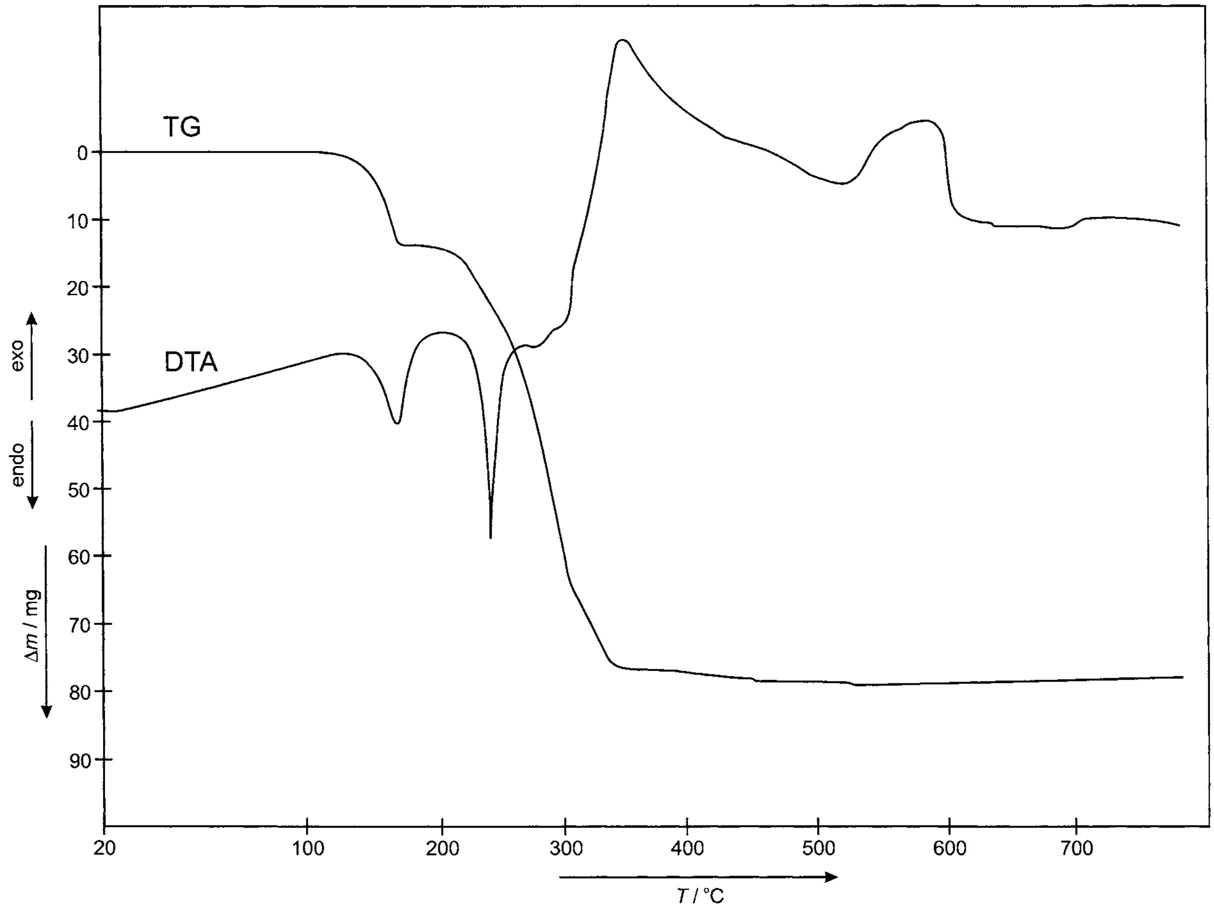

Fig. 2. TG and DTA diagrams of bipyridinium uranyl acetate ($m = 150$ mg).

stage could be expressed with following equation:

$$(C_5H_4N{-}C_5H_4NH)UO_2(CH_3COO)_3 \xrightarrow[-CH_3COOH]{} (C_5H_4N{-}C_5H_4N)UO_2(CH_3COO)_2$$

In order to confirm these structural changes, we undertook isothermal measurement at 150 °C. The elemental analysis (C, H, N) of the residue obtained, supports the assumption that a bipyridine complex is formed during the decomposition (experimental C: 29.91%; H: 2.97%; N: 6.42%; theoretical C: 30%; H: 2.57%; N: 5.14%).

Also, we used IR spectroscopy to confirm the absence of N–H groups in the residue obtained at 150 °C, even though it is difficult to determine the type of coordination of bipyridine either as bidentate bridging or unidentate.

The IR spectrum of the residue dried to constant mass at 150 °C (Fig. 1) implies structural changes in bipyridine uranyl acetate, which causes formation of a new complex without NH groups. Most evident changes in the spectrum occur in the stretching (3400–3000 cm^{-1}) and bending region (1650–1600 cm^{-1}) of the N–H vibrations. Comparing the spectrum of the new complex to the one of bipyridine uranyl acetate, disappearance and shifting of bands in these regions is evident. These observations bring us to the conclusion that in the complex obtained at 150 °C, the NH groups are missing due to Anderson rearrangement. Also, comparison of

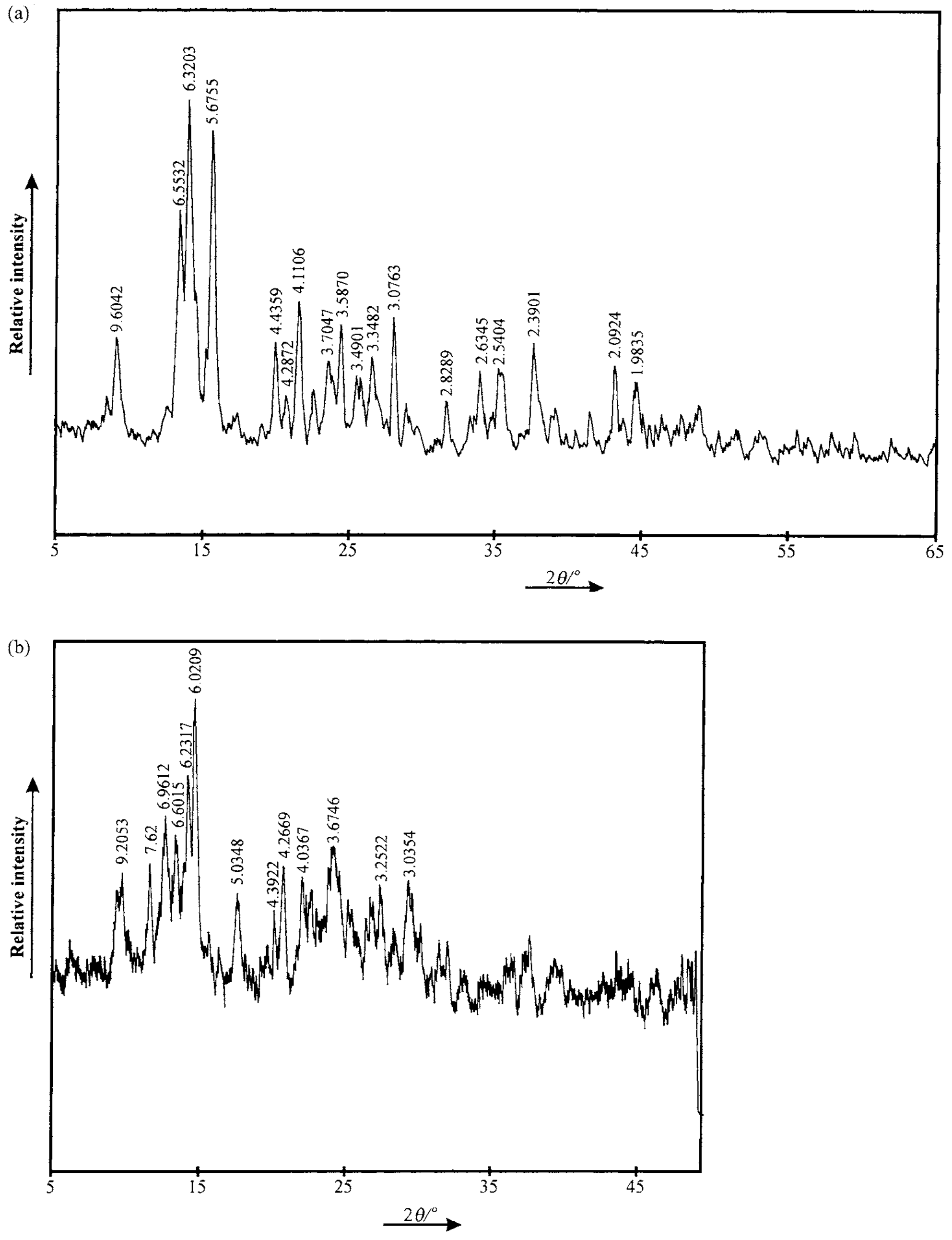

Fig. 3. X-ray powder diffraction patterns of: (a) bipyridinium uranyl acetate; (b) residue at 150 °C.

the X-ray powder diffraction patterns of the initial compound and the residue at 150 °C (Fig. 3a and b) clearly shows formation of new different compound from the initial one.

This complex is stable in a very narrow temperature range (170–190 °C). It decomposes in the second stage of thermal decomposition to UO_2, in the temperature range from 190–340 °C, which is manifested

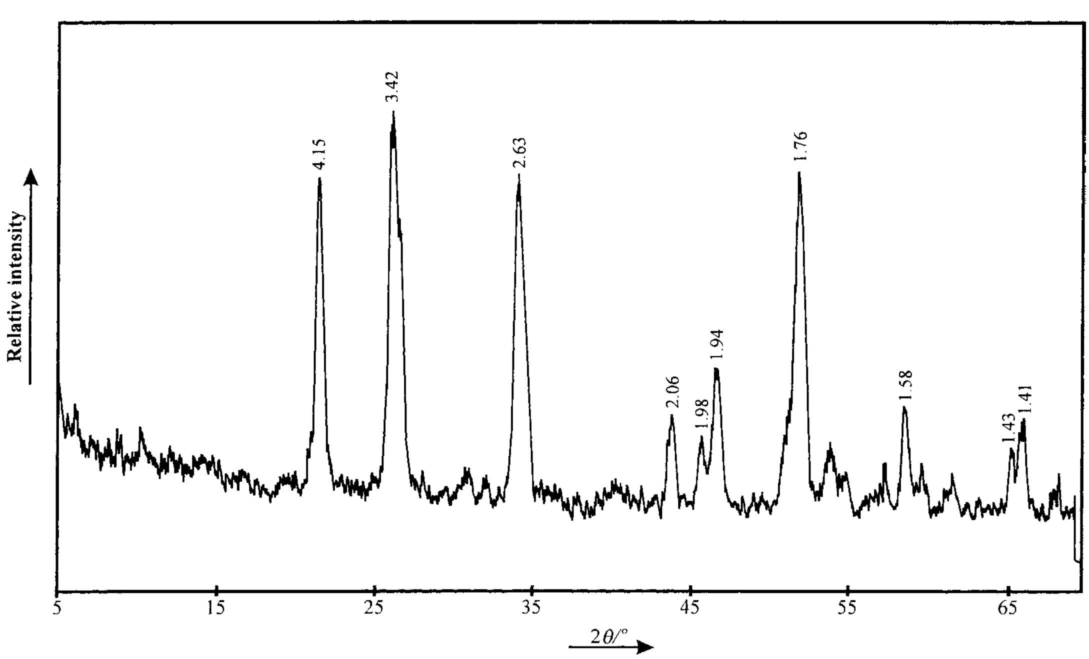

Fig. 4. X-ray powder diffraction patterns of the final residue of thermal decomposition.

by an endothermic peak with maximum at 240 °C. The experimental value for mass loss in this stage is 51%, while the calculated one is 50.4%. This can be expressed by the following equation:

$$(C_5H_4N{-}C_5H_4N)UO_2(CH_3COO)_2 \xrightarrow[\substack{-\text{bipy}\\ -2CH_3COO^-}]{} UO_2$$

In the next stage, in the temperature range from 340–780 °C, two reactions appear. The first one is oxidation from UO_2 to UO_3 producing an exothermic peak on the DTA curve, with maximum at 350 °C. Another exothermic peak on DTA curve occurs at 580 °C, followed by a slight weight increase on the TG curve. This is due to a reaction in a solid state involving UO_2 and UO_3 which results in formation of U_3O_8 (U_3O_8 file No. 2–276: $4.15_{0.x}$; 3.43_x; $2.64_{0.9}$; 1.77_6; 2.07_4; 1.95_4) [26] as a final product of thermal decomposition. This conclusion is supported both by the X-ray powder diffraction pattern of the residue of thermal decomposition (Fig. 4) and also by the colour of the residue which is dark green

$$UO_2 + 0.5O_2 \rightarrow UO_3$$

$$UO_2 + 2UO_3 \rightarrow U_3O_8$$

The total experimental mass loss up to 780 °C is 53.3% and the calculated one is 53.6%.

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

Acknowledgements

The investigation, the results of which are presently reported, has been financially supported by the Ministry of Education and Science of Republic of Macedonia, which is here gratefully acknowledged. The authors are very grateful to professor K.M. Dunaeva from the Moscow State University, Russia, for the helpful discussion.

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