

SYNTHESIS AND NON-ISOTHERMAL DEGRADATIONS OF THE BRIDGED DIACETATO–DIAMIDO–DIAMINE–URANYL COMPLEX

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The new bridged diacetato–diamido–diamine–uranyl complex $\{2[(\text{UO}_2)(\text{H}_2\text{N})(\text{H}_3\text{N})(\text{OOCCH}_3)]\}$ was prepared and characterized by elemental analysis, IR measurement as well as TG and DTA analysis. The kinetic parameters; activation energy (E_a), pre-exponential factor (A) and the order of decomposition (n) were calculated from TG curves using Coats–Redfern and Flynn–Wall–Ozawa methods. The mechanism of decomposition has been established from TG and DTA data. The data obtained agree quite well with the expected structure and show that the complex finally decomposes to form UO_3 . A general mechanism describing the formation of bridged complex $\{2[(\text{UO}_2)(\text{H}_2\text{N})(\text{H}_3\text{N})(\text{OOCCH}_3)]\}$ is proposed.

Keywords: bridged diacetato, DTA analysis, IR spectra, synthesis, TG analysis, uranyl complex

Introduction

The reactions of urea with many transition metal ions have been extensively investigated and characterized by many workers [1–5]. Most of these complexes, urea may coordinate either via the oxygen or the nitrogen atom, depending on the type of metal ions; the nature of such coordination can be easily decided from the shift in both the frequencies of $\nu_{\text{C=O}}$ and $\nu_{\text{N-H}}$ of the coordinated urea compared with those of free urea. Lanthanide and actinide metal salts at high temperature are rare in the literature, and the available publications reported that the reaction products depend on the type of metal ions and the metal salt used in the reaction [6–10].

In the last decades, the investigations directed to the thermal degradation of metal complexes proved to be major interest, due to the possibility of their use for the controlled preparation of metal and metal oxide powders [11–13].

The present article, describes the preparation, characterization and thermal behavior of the coordination compound bridged diacetato–diamido–diamine–uranyl $\{2[(\text{UO}_2)(\text{H}_2\text{N})(\text{NH}_3)(\text{OOCCH}_3)]\}$ complex prepared at high temperature.

Experimental

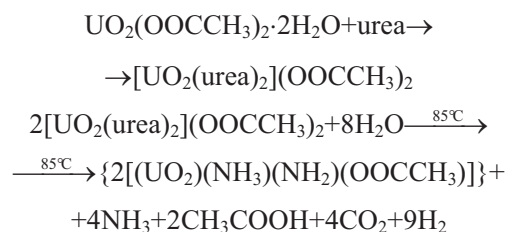
The bridged diacetato–diamido–diamine–uranyl complex $\{2[(\text{UO}_2)(\text{H}_2\text{N})(\text{NH}_3)(\text{OOCCH}_3)]\}$ was prepared by mixing equal volumes of aqueous solutions of 0.1 M of $\text{UO}_2(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ and 0.6 M of urea.

The mixture was heated to ca 85°C for about 12 h. The precipitated pale yellow complex was filtered and then washed several times with hot water. The obtained complex $\{2[(\text{UO}_2)(\text{H}_2\text{N})(\text{NH}_3)(\text{OOCCH}_3)]\}$ was identified through elemental analysis, IR spectra and thermal properties (TG–DTA).

The IR spectra and thermal analysis (TG and DTA) were obtained as given before [14].

Results and discussion

The formation of the solid bridged diacetato–diamido–diamine–uranyl complex $\{2[(\text{UO}_2)(\text{NH}_3)(\text{NH}_2)(\text{OOCCH}_3)]\}$ during the reaction of urea with $\text{UO}_2(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$ in aqueous solution indicates that UO_2^{2+} ions decompose the coordinated urea at high temperatures. From the elemental analysis C; 6.60 (6.63), H; 1.95 (2.21) and N; 7.71 (7.73) and infrared spectra, we suggest the formation of the complex may take place as given in the following reactions;

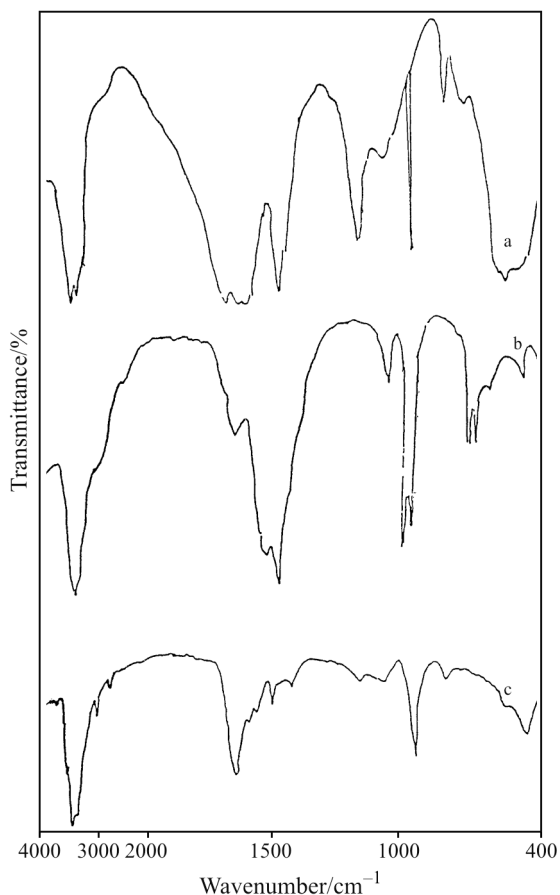


The infrared spectra Fig. 1, of the complex clearly indicated the absence of the bands due to NH_2 of coordinated urea, while bands due to $\nu_{\text{N-H}}$ are observed at

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Table 1 The kinetic parameters of decomposition of $\{2[(\text{UO}_2)(\text{H}_2\text{N})(\text{NH}_3)(\text{OOCCH}_3)]\}$ complex

Order of decomposition, n	T_{range} of decomposition/ $^{\circ}\text{C}$	Equation due to	$E_a/\text{kJ mol}^{-1}$ (average)	$\log A/\text{s}^{-1}$	$-\Delta S^{\ddagger}/\text{kJ mol}^{-1} \text{K}^{-1}$
1	50–280	Coats–Redfern	16.88	3.35	80.75
		Flynn–Wall–Ozawa	14.96	4.20	72.65
1	280–600	Coats–Redfern	22.67	3.78	77.87
		Flynn–Wall–Ozawa	20.89	4.74	68.60

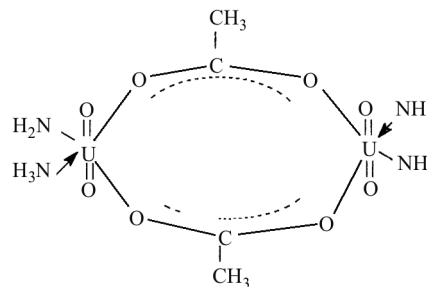
**Fig. 1** IR spectra of a – urea, b – $[\text{UO}_2(\text{urea})_2](\text{OOCCH}_3)_2$ and c – $2[(\text{UO}_2)(\text{NH}_2)(\text{NH}_3)(\text{OOCCH}_3)]$ complex

3495 and 2900 cm^{-1} , these values fall in the range of frequency typical free ammonia and amido group respectively, the bands of coordinated acetate ions are observed at 1580 and 1480 cm^{-1} . These values fall in the range of frequency typical for bridging acetate ligands [15]. The two bands at 2955 and 2850 cm^{-1} correspond to asymmetric and symmetric stretching vibrations of C–H bonds in the methyl groups.

The band at 1400 cm^{-1} is due to CH_3 in plane deformation, while that at 900 cm^{-1} is due to its out of plane bending. The three bands at 950 , 520 and 480 cm^{-1} can be assigned to the U–N (coordinated free ammonia), U–N (amido group) and U–O stretching modes. The U=O stretching vibration is observed at 785 cm^{-1} .

The most probable structure according to the chemical analysis and the infrared spectrum is shown in Fig. 2.

Thermogravimetry and DTA were carried out for the bridged diacetato–diamido–diamine–uranyl $\{2[(\text{UO}_2)(\text{NH}_2)(\text{NH}_3)(\text{OOCCH}_3)]\}$ complex in air at different heating rates. Figure 3 shows the TG curves and Table 1 gives the maximum temperature values T_m for the decomposition, together with the corresponding activation energy (E_a), pre-exponential factor (A), order of reaction (n), and the activation entropy (ΔS^{\ddagger}) as calculated from TG curves in the temperature range 50 – 600°C in air using Flynn–Wall–Ozawa [16, 17] and Coats–Redfern method [18] of analysis Figs 4a and b. The kinetic analysis of the dynamic TG data according to various solid state reaction models shows that the decomposition of the complex under investigation is best described by random nucleation and that the best fit of data was obtained using Avrami equation model [19]. These data support the proposed complex structure and indicate that the decomposition of the complex occurs in two degradation steps. The first stage of decomposition occurs at 50 – 280°C and is accompanied by mass losses of 8.86, 8.80 and 8.50% (9.11% calculated), at heating rates $\beta=5.5$, 7.5 and $10^{\circ}\text{C min}^{-1}$, respectively, and activation energies of 14.3, 17.4 and 18.9 kJ mol^{-1} . This exothermic step corresponds to the loss of two molecules of ammonia followed by the two amino groups. The second decomposition step occurs at 280 – 600°C with a mass loss of 11.67, 11.53 and 11.49% (11.87% calculated) at heating rates, $\beta=5.5$, 7.5, $10^{\circ}\text{C min}^{-1}$, respectively and an activation energy of 17.35, 22.17 and $27.84 \text{ kJ min}^{-1}$. This exothermic step is associated with the loss of the two $(2\text{CH}_3\text{CO}^-)$ acetyl groups. The infra-

**Fig. 2** Structure of bridged diacetato–diamido–diamine–uranyl complex

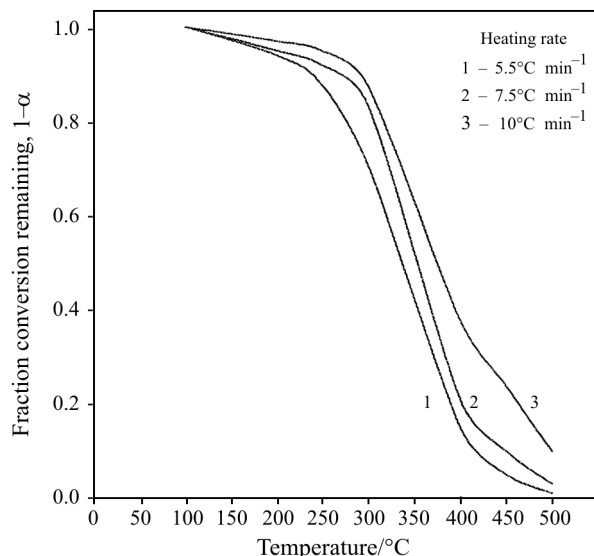


Fig. 3 Dynamic measurement of $\{2[(\text{UO}_2)(\text{H}_2\text{N})(\text{NH}_3)(\text{OOCCH}_3)]\}$ complex

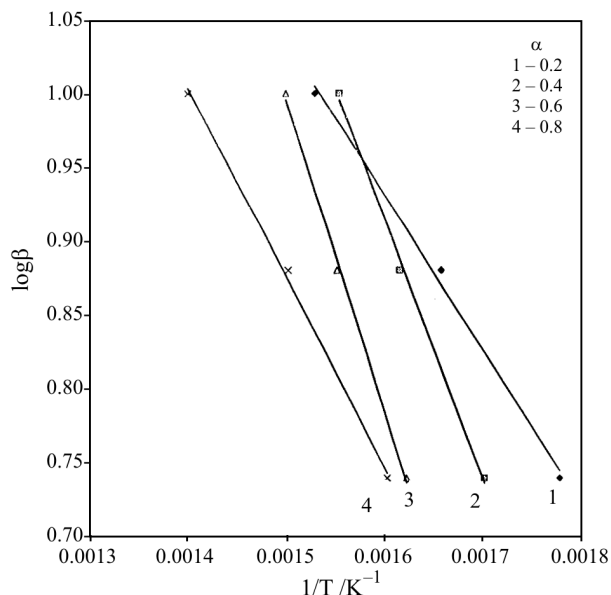


Fig. 4b Flynn–Wall–Ozawa method of analysis

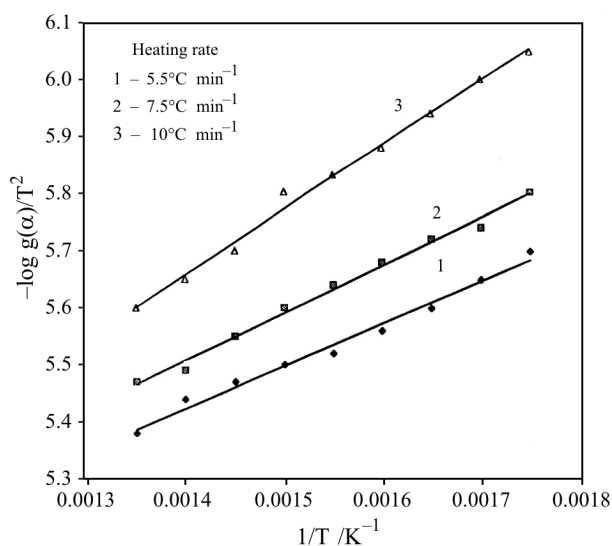
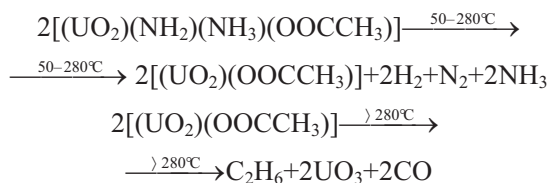


Fig. 4a Coats–Redfern method of analysis

red spectrum of the final product of the thermal analysis indicated the absence of any bands corresponding to amino or bridged-acetato groups supporting thus the previous suggestion.

According to the above discussion, the mechanism of the thermal decomposition of bridged diacetato–diamido–diamine–uranyl complex $\{2[(\text{UO}_2)(\text{NH}_2)(\text{NH}_3)(\text{OOCCH}_3)]\}$ may be represented as follow;



Conclusions

- The main decomposition steps of new UO_2^{2+} bridged diacetato complex have been evidenced.
- The non-isothermal analysis of the complex in initial and final stages of thermal decomposition, associated with the results of elemental analysis and IR spectra enabled the establishment of its decomposition mechanism.
- The kinetic parameters; activation energy (E_a), pre-exponential factor (A), activation entropy (ΔS^\ddagger) and order of the decomposition (n) were calculated.

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