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Preparation, structure and thermal behaviour of uranyl nitrate complexes with *N*-alkylcaprolactams

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Abstract

A new series of uranyl complexes with *N*-alkylcaprolactams (alkyl = H, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$ or $C_{12}H_{25}$) has been prepared. All these complexes have hexagonal bipyramid structure. The stereochemical configurations were deduced using spectral and X-ray diffractometry studies. The thermal behaviour of each complex and some of the ligands has been investigated using TG and DSC.

INTRODUCTION

Interest has been growing in extracting agents analogous to amides because of their good extracting ability for uranium, zirconium, niobium, thorium and so on [1–4]. We have recently found that *N*-alkylcaprolactams, as a sort of amide, possess even stronger extracting power for uranium than do straight-chain amides [5]. So far as we know, however, the synthesis of the isolated complexes of these compounds with uranyl has never been reported. As studies of the structure, configuration and thermal stability of a complex are helpful in further exploring the extracting mechanism of the corresponding system, in this paper we have prepared a series of the cited complexes $UO_2(NO_3)_2L_2$ ($L = \underline{CH_2(CH_2)_4CON}R$, $R = H$, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$ or $C_{12}H_{25}$). IR and UV–visible spectrometric measurements have been used to characterize each complex and to interpret the type of coordination which takes place with the metal. Thermogravimetry and differential scanning calorimetry have been carried out on each of the complexes and some of the ligands to study their thermal stability.

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EXPERIMENTAL

Chemicals

All chemicals used were of analytical grade.

Preparation of ligands and complexes

The *N*-alkylcaprolactam ligands were prepared by previously published procedures [6]. The vacuum and temperature used during distillation of the products were varied according to the alkyl function as follows: R = C_2H_5, 107–109°C/12 mmHg; C_4H_9, 135–138°C/17 mmHg; C_6H_{13}, 127–130°C/3 mmHg; C_8H_{17}, 152–156°C/3 mmHg; $C_{10}H_{21}$, 173–176°C/4 mmHg and $C_{12}H_{25}$, 185–190°C/3 mmHg.

The $UO_2(NO_3)_2L_2$ complexes were prepared by reaction of $UO_2(NO_3)_2 \cdot 6H_2O$ with the appropriate ligand. The procedural details were as follows. A solution of $UO_2(NO_3)_2 \cdot 6H_2O$ in 3 mol l^{-1} HNO_3 was mixed with a solution of the ligand in petroleum ether in the molar ratio 1:2, and the mixture of solutions was shaken for several hours. Then the pale-yellow solid that precipitated was filtered off and thoroughly washed with deionized water and three times with petroleum ether, and the product was recrystallized from toluene and then washed with petroleum ether again, filtered off and dried in vacuum.

Apparatus

The carbon, hydrogen and nitrogen analyses were made using a Carlo-Erba model 1106 elemental analyser.

The IR spectra were recorded using KBr discs (for solid samples) or NaCl plus a liquid film (for liquid ligand samples) on an Alpha Centuari IR spectrometer. The UV–visible spectra were recorded using a Shimadzu UV-240 UV–visible spectrophotometer. Measurements of conductivity were made using a DDS-11A conductometer. The molecular structures were determined using an R3m/E single-crystal diffractometer.

Thermal studies were carried out on a Delta series TGA-7 thermogravimetric analyser and a DSC-7 differential scanning calorimeter (Perkin–Elmer Corp.) equipped with a 3700 data station [7, 8]. Both TG–DTG and DSC runs were carried out at a heating rate of 5°C min^{-1} in dynamic conditions using a flow rate of 20 ml min^{-1} of pure nitrogen. The temperature ranges investigated were 50–650°C (TG) and 40–600°C (DSC).

RESULTS AND DISCUSSION

The results of the elemental analysis listed in Table 1 indicate that the complexes formed have the composition $UO_2(NO_3)_2L_2$.

The molar conductivities of the complexes in nitrobenzene and/or aqueous solution are also given in Table 1, which suggest that the studied complexes behave as non-electrolytes in organic medium [9] and as electrolytes in water. The latter finding is in accord with the result for an analogous compound described in the literature [10]; i.e. each molecule of complex is dissociated into three ions: one UO_2^{2+} and two NO_3^-.

The UV–visible spectrum of free uranyl ion (solution of uranyl nitrate in water) showed a peak at 24 096 cm^{-1}. Upon coordination of uranyl ion to *N*-alkylcaprolactam, a shift in the peak to lower frequency (23 640 cm^{-1}) was observed. In addition, the UV–visible spectra of all the complexes showed the disappearance of the strong absorption band at 45 045 cm^{-1} contributed by the free uranyl ion and the appearance of a narrow peak near 30 770 cm^{-1}. These changes in the absorption bands indicate the occurrence of coordination between metal and ligand.

The IR spectra of all seven complexes show a very strong absorption peak at 930 cm^{-1} characterizing UO_2, and absorption peaks near 710, 746, 853, 1028, 1276 and 1522 cm^{-1} which are assigned to the vibrations of coordinated NO_3 [11]. In the complexes, the $\bar{\nu}_{CO}$ peaks near 1640 cm^{-1} are observed to move to lower wavenumbers. This suggests that, in the complexes, bonding is taking place between the uranium metal atom and the carbonyl group of the *N*-alkylcaprolactam. Table 2 shows the shifts for $\bar{\nu}_{CO}$ quite clearly.

The study by single crystal X-ray diffraction reveals that the uranyl ion is coordinated to six oxygen atoms. Two of them are provided by two

TABLE 1

Elemental analysis and conductivity of the complexes

No.	Complex	Elemental analysis							
		Theory (%)			Found (%)			Conductivity ($S\ cm^2\ mol^{-1}$)	
		C	N	H	C	N	H	In water	In nitrobenzene
1	$R=H$	24.00	9.03	3.50	23.23	9.34	3.67	265.56	5.200
2	$R=C_2H_5$	28.41	8.28	4.47	28.15	8.27	4.51	287.17	5.544
3	$R=C_4H_9$	32.79	7.65	5.22	32.09	7.66	5.25	282.19	4.648
4	$R=C_6H_{13}$	36.55	7.10	5.87	35.89	6.98	6.10	–[a]	–[b]
5	$R=C_8H_{17}$	39.81	6.63	6.44	29.84	6.38	6.17	–[a]	4.319
6	$R=C_{10}H_{21}$	42.66	6.22	6.93	42.83	6.10	7.13	–[a]	–[b]
7	$R=C_{12}H_{25}$	45.18	5.86	7.37	45.57	5.79	7.79	–[a]	4.036

[a] The complex has very poor solubility in water. [b] Not measured.

TABLE 2

$\bar{\nu}_{CO}$ of ligands and complexes in IR spectra

No.	Ligand (cm^{-1})	Complex (cm^{-1})	$\Delta\bar{\nu}_{CO}$ (cm^{-1})
1	1659.0	1611.0	48.0
2	1628.0	1586.0	42.0
3	1633.8	1582.0	51.8
4	1641.5	1582.0	59.5
5	1642.5	1583.0	59.5
6	1643.5	1584.0	59.5
7	1649.3	1584.0	65.3

carbonyl groups of the ligand molecules and the other four are from two nitrate groups. All the above mentioned metal–oxygen bonds, together with the two in uranyl itself, form approximately a hexagonal bipyramid skeleton centred on the uranium atom. The detailed results will be reported elsewhere.

TABLE 3

Thermal characterization of ligands and complexes [a]

No.	Ligand: TG–DTG		Complex: DSC		Complex: TG–DTG			
	T (°C)	T_p (°C)	T (°C) (endo) [c]	T_p (°C) (exo) [c]	T (°C)	T_p (°C)	W_r (%)	
							Calc. [d]	Found
1	– [b]	– [b]	117.38	172.88	80.31–559.84	191.24	45.27	44.93
2	50.01–354.80	165.06	111.88	203.19	(I) 110.46–263.41	226.31	58.28	59.05
					(II) 263.41–294.17	272.61	55.13	54.84
					(III) 294.17–619.03	311.80	41.52	40.76
3	60.84–355.43	186.32	175.32	217.27	(I) 117.58–265.52	233.45	53.82	54.15
					(II) 265.52–306.66	276.19	50.91	51.83
					(III) 306.66–618.14	320.72	38.34	37.94
4	121.03–358.06	199.01	60.81	208.66	(I) 145.32–251.06	228.15	50.00	48.96
					(II) 251.06–283.35	271.46	47.29	46.03
					(III) 283.35–626.41	317.21	35.62	34.65
5	141.38–384.66	229.62	44.70	218.01	(I) 135.21–285.32	232.64	46.68	46.05
					(II) 285.32–594.92	316.22	33.25	33.98
6	158.64–389.01	244.12	61.36	248.93	(I) 150.36–583.44	259.14	43.78	42.36
					(II) 283.44–587.85	316.88	31.19	30.64
7	(I) 40.83–204.38	163.81	72.40	281.76	(I) 178.46–315.05	293.09	41.21	40.84
	(II) 204.38–330.46	249.85			(II) 315.05–577.25	355.46	29.36	30.63

[a] All the T_p values indicate the peak values on either DSC or DTG curves.

[b] TG–DTG run was not carried out for ligand with R = H.

[c] Endo, endothermic; exo, exothermic.

[d] W_r is the mass percent of residue at the end of the corresponding stage. Calculated on the basis of the assumptions: release of ligands and nitrates simultaneously for single-step decomposition; release of ligands first, then nitrates for two-step decomposition; release of ligands first, then oxygen followed by nitrogen dioxide for three-step decomposition. In all cases, the final product is U_3O_8.

Thermal analysis

The results from thermogravimetry and differential scanning calorimetry for all the complexes, together with those from thermogravimetry of the ligands (except for ligand 1, with R = H), are presented in Table 3. The temperatures quoted as T_p are the values for all the peaks on either the DSC or DTG curves obtained under the conditions used.

All the chosen ligands studied undergo complete volatilization in a single step with the exception of ligand 7 (with R = $C_{12}H_{25}$), which shows a slight tendency towards a two-step decomposition mode. It is postulated that the long-chain alkyl group in the ligand molecule is likely to break while being heated to lose some fragment initially. Inspection of Table 3 demonstrates that the temperature range and the T_p of decomposition rise with an increase in length of the alkyl group in the ligand (see Fig. 1).

There are two peaks on each DSC curve in the range 40–600°C for all

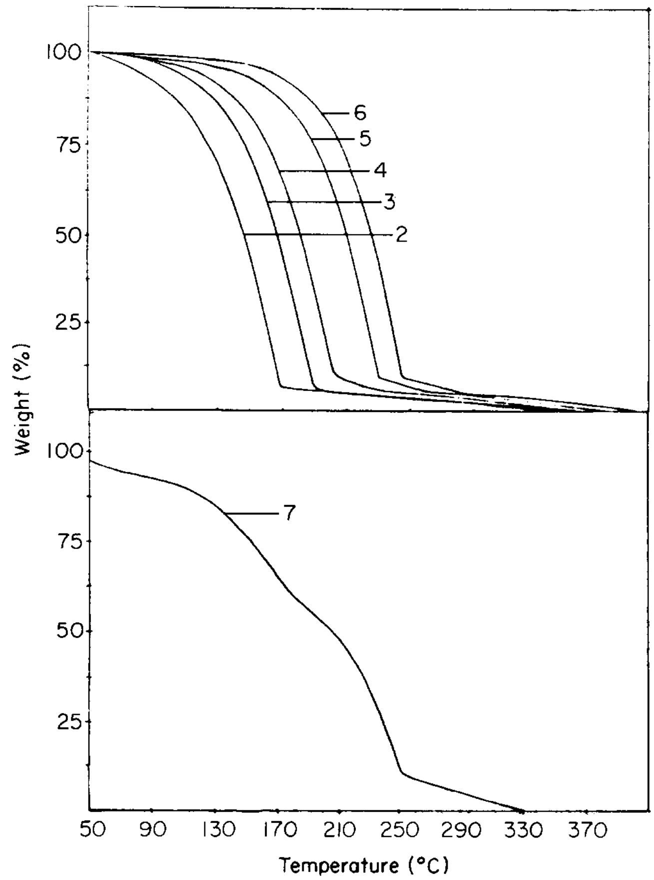

Fig. 1. TG curves for ligand $\underbrace{CH_2(CH_2)_4CON}R$. Curve 2, R = C_2H_5; curve 3, R = C_4H_9; curve 4, R = C_6H_{13}; curve 5, R = C_8H_{17}; curve 6, R = $C_{10}H_{21}$; curve 7, R = $C_{12}H_{25}$.

the complexes. The first one is weakly endothermic. For complexes 4–7, it is located at a temperature far lower than the initial decomposition temperature and thus is not accompanied by any mass loss, which means that thermolysis of these complexes is preceded by solid state phase transition or melting [12]. For complexes 1–3, the first peak falls in the temperature range in which thermolysis just takes place, which suggests that these complexes melt with decomposition. In comparison with the first peak, the second peak on each DSC curve is strongly exothermic and is associated with mass loss. Figure 2 shows the DSC curves for all the complexes.

The TG–DTG curves were obtained for complexes 1–7 over the range 50–650°C. In general, the initial decomposition temperature gradually increased from complex 1 to complex 7. It seems that there are three different patterns of TG–DTG curve for the complexes investigated. Complex 1 has a single-step decomposition mode. Complexes 5–7 follow a two-step decomposition mechanism; the mass losses suggest that in this case the compounds release ligand molecules first, then immediately two

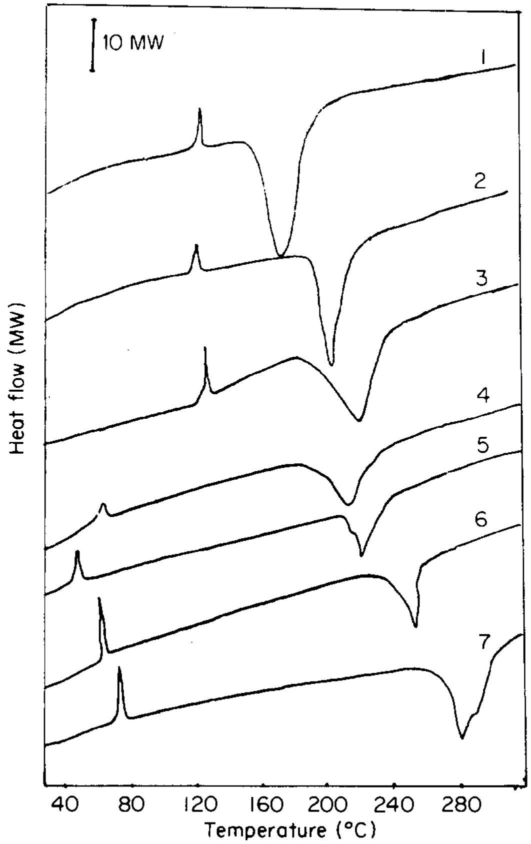

Fig. 2. DSC curves for complexes 1–7.

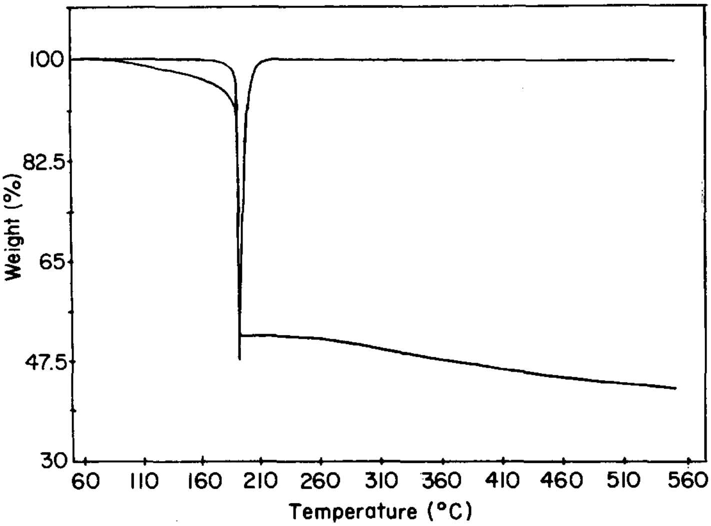

Fig. 3. TG–DTG curve for complex 1.

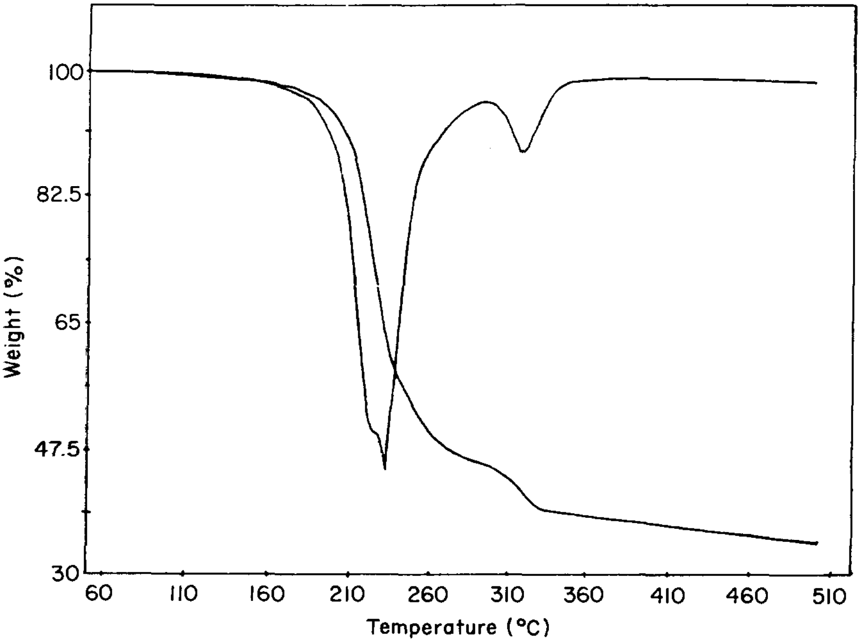

Fig. 4. TG–DTG curve for complex 5.

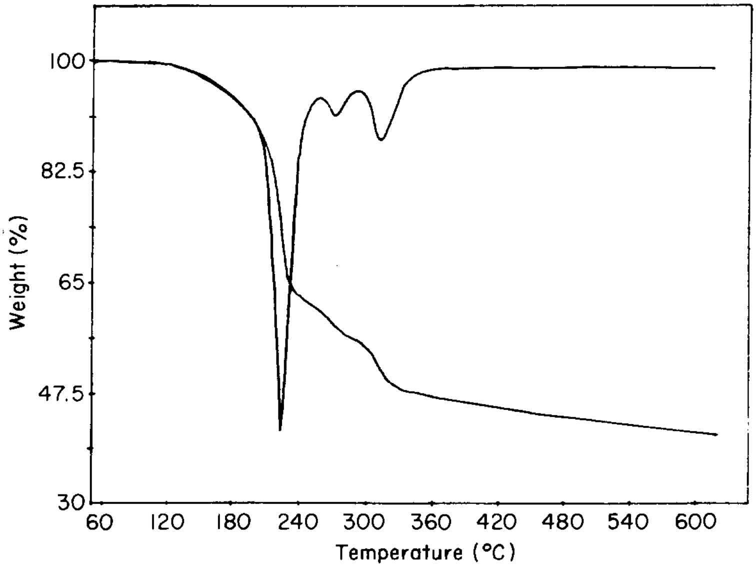

Fig. 5. TG–DTG curve for complex 2.

nitrate moieties. Complexes 2–4 decompose in three steps: release of organic ligand first, then oxygen, followed by nitrogen dioxide. It is, however, worth mentioning that, in the case of the three-step mode, the latter two stages are not clearly distinguishable, but just faintly recognizable. Figures 3–5 show the DTG curves of the above three respective patterns.

It is revealed by analysis of the mass losses that, for all the complexes studied, the final residue at the end of decomposition is U_3O_8, which is in accordance with predictions from earlier literature [13, 14].

CONCLUSIONS

Summing up our discussions, we consider that the following points should be underlined.

(1) In their complexes with uranyl nitrate the *N*-alkylcaprolactams coordinate to the uranium atom through the carbonyl groups. The complexes have an approximately hexagonal bipyramid structure.

(2) By comparison, decomposition temperatures for the free ligands, represented by the DTG peak temperatures, are lower than those for the corresponding ligands in the complexes, which implies that the coordinated ligands are stabilized by coordination.

(3) The decomposition scheme for the complexes studied is either by the release of the organic ligand first, in the range 120–300°C, then immediate release of nitrate up to 630°C, or by release of both organic ligand and nitrate groups almost simultaneously. Finally, the residue U_3O_8

is obtained. The scheme may be summarized as

$$3UO_2(NO_3)_2L_2 \rightarrow 6L + 2O_2 + 6NO_2 + U_3O_8$$

where L is the organic ligand, namely *N*-alkylcaprolactam.

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