

SYNTHESIS AND CHARACTERIZATION OF SOME NEW MONO- AND DIAMIDE COMPLEXES OF PLUTONIUM(IV) AND DIOXOURANIUM(VI) NITRATES

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(Received 5 August 1994; accepted 25 January 1995)

Abstract—Plutonium tetranitrato complexes with N,N'-dialkyl monoamides A [A = dibutyl derivatives of hexanamide (DBHA), octanamide (DBOA)] and tetraalkyl diamides B [B = tetrabutyl, tetraisobutyl and tetrahexyl malonamide (TBMA, TIBMA, THMA)] have been isolated and characterized as $\text{Pu}(\text{NO}_3)_4 \cdot 3\text{A}$ and $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{B}$, respectively. Complexes with diamides such as $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TBMA}$ and $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{TIBMA}$ were isolated as solids while all others were viscous liquids. Uranyl dinitrato-amide complexes with the above monoamides and diamides were synthesized and characterized as $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{A}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot \text{B}$. The IR and visible absorption spectra of the plutonium and uranium complexes indicate that they are O-bonded and the nitrate group acts as a bidentate group. The NMR spectra of the uranyl monoamide complexes indicate the existence of restricted rotation around the C—N bond, while thermal investigations reveal that decomposition proceeds through three exothermic steps corresponding to the release of amide and nitrate groups and finally leading to U_3O_8 .

Aliphatic monoamides are potential extractants for actinides^{1–3} and have been suggested as extractants for nuclear fuel reprocessing. The utility of diamides has assumed importance for the removal of actinides from high-activity waste solution.⁴ Numerous references are available in the literature where they have been used as synergistic donors,^{5,6} and in speciation studies,^{7,8} thermodynamic and spectral studies^{9–11} of actinides. However, there is little reported on the study of solid complexes except by Bagnall *et al.*,^{12–14} who isolated and characterized U^{IV} , U^{VI} , Pu^{IV} and Np^{IV} complexes with N,N'-dimethyl- and N,N'-di-isopropyl acetamide and many substituted amides from nitrate and chloride media and investigated their X-ray powder pattern, electronic absorption and IR spectra.

Musikas and Charpin^{15–17} have characterized uranyl complexes with N,N'-dibutyl dodecanamide and N,N'-di-n-butyl dimethyl-3,3-butanamide through crystal structure studies and spectral properties. Many solid synergistic uranyl and plutonyl pyrazolonate adducts with amides have been synthesized and characterized earlier in our laboratory.^{18,19}

In view of the importance of actinide nitrate-amide complexes in solvent extraction and their potential use in separation and recovery processes, the synthesis, characterization, spectral and thermal properties of solid Pu^{IV} and U^{VI} nitrate-amides have been investigated. The present paper deals with the characterization of complexes with symmetrical (DBHA = dibutyl hexanamide and DBOA = dibutyl octanamide), unsymmetrical (MBOA = methyl butyl octanamide) and branched chain (DBEHA = dibutyl ethylhexylamide and

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DIBEHA = di-isobutyl ethylhexylamide) amides and diamides (TBMA = tetrabutyl malonamide, TIBMA = tetraisobutyl malonamide and THMA = tetrahexyl malonamide), their absorption, ^1H NMR spectra and thermal behaviour.

EXPERIMENTAL

Preparation of ligands

N,N'-Dialkylamides: dibutyl derivatives of hexanamide (DBHA), ethylhexylamide (DBEHA), octanamide (DBOA), methylbutyl derivatives of octanamide (MBOA), and the di-isobutyl derivative of ethylhexylamide (DIBEHA) were synthesized by reacting their respective acyl chlorides with dialkylamine in ether.²⁰ Tetrabutyl (TBMA), tetraisobutyl (TIBMA) and tetrahexyl (THMA) derivatives of malonamides were also synthesized by reacting malonyl chloride with the respective dialkylamine. All the amides are yellow liquids and the purity of vacuum distilled products was ascertained by elemental analysis,²¹ IR and ^1H NMR spectra and amide contents.²²

Preparation of uranium(VI) complexes

The complexes were prepared by solvent extraction of aqueous uranium nitrate solution (10 cm^3 , 5 mol dm^{-6}) at $\text{pH} = 2$ with benzene (10 cm^3) containing 10 mol dm^{-6} of the respective amide. The organic layer was dried with anhydrous sodium sulphate, evaporated to dryness and repeatedly recrystallized from n-hexane (yield: 60–80%).

Preparation of plutonium(IV) complexes

^{239}Pu (5 g) was purified on a Dowex-1X4 anion exchange resin (100–200 mesh) from HNO_3 (7.5 mol dm^{-3}) followed by two peroxide precipitations. Finally, purified plutonium was precipitated as the hydroxide and converted to Pu^{IV} by dissolving in concentrated nitric acid. Tetravalency was maintained by the addition of a few drops of H_2O_2 and excess H_2O_2 was catalytically decomposed by swirling the solution around the platinum wire and checked spectrophotometrically for complete conversion to Pu^{IV} . The solution was made up in 3.5 mol dm^{-3} HNO_3 prior to solvent extraction.

An aliquot containing Pu^{IV} (100 mg) in HNO_3 (10 cm^3 , 3.5 mol dm^{-3}) was extracted with a benzene layer (10 cm^3) containing the required amount of the respective amide (pre-equilibrated with 3.5 mol dm^{-3} HNO_3). The brown-coloured benzene extract was washed twice with HNO_3 (10 cm^3 , 3.5 mol dm^{-3}) and reduced to 0.5 cm^3 by evaporation

under suction. The syrupy green liquid was agitated with n-hexane (5 cm^3) for 3 h (except for TBMA and TIBMA, which gave sticky dark tan solids). The syrupy green liquid was repeatedly washed with a 30:70 ratio of dichloromethane and n-hexane to remove impurities and finally air dried. Three purification steps were necessary to obtain the pure products (yield: 30–40%).

Characterization of uranium(VI) and plutonium(IV) complexes

Carbon and hydrogen were determined by the semi-micro empty-tube combustion method and nitrogen by Dumas' method. Melting points were determined using the automatic melting point apparatus (Mettler F.P-61). Most of the plutonium complexes were liquids at room temperature. All these analytical facilities were standardized and glove-box adapted for plutonium work. The plutonium and uranium contents were determined gravimetrically from the weights of the corresponding oxides (PuO_2 and U_3O_8) left behind after the combustion procedure (Tables 1 and 2). Uranium contents were also determined by the titrimetric method and plutonium contents by $4\pi\alpha$ -liquid scintillation counting (Table 1).

IR and electronic spectral measurements

The absorption spectra of complexes were recorded by redissolving them in tertiary butyl benzene and monitoring the peaks on a DU-7 Beckman spectrophotometer (Table 2). IR spectra were recorded in between CsI discs (for liquids) and in Nujol mulls (for sticky solids) using a Pye–Uicam 9512 IR spectrophotometer in the $4000\text{--}200\text{ cm}^{-1}$ range (Table 3). Absorption and IR spectra were recorded using spectrophotometers attached to a glove-box for handling radioactive samples.

RESULTS AND DISCUSSION

Electronic spectra

The prominent features of the spectra of uranyl and plutonium(IV) nitrate-amide complexes (dissolved in tertiary butyl benzene) are summarized in Table 2. The spectra of the uranium complexes (Fig. 1) are very similar to those observed by Musikas and co-workers.^{10,11} The extinction coefficient of the bands at 421, 428 and 441 and 456 nm were comparatively higher, while shifts in the bands of the uranium complexes from 416 (UO_2^{2+} in 3.5 mol dm^{-3} HNO_3) to 421 nm and the emergence of new peaks at 441 and 456 nm indicate bonding through

Table 1. Analytical data of plutonium(IV) nitrate-amide complexes

S. No.	Complex	Colour	M.p./B.p. (°C)	Yield (%)	Carbon	Hydrogen	Nitrogen Analysis (%) ^a	Gravimetric	Radiometric
1.	DBHA UO ₂ (NO ₃) ₂ ·2DBHA	Light Yellow Yellow	250–290 109	90 80	72.1(73.1) 39.9(39.8)	12.7(12.8) 6.9(6.6)	6.6(6.8) 6.6(6.6)	— 27.8(27.2)	— —
2.	Pu(NO ₃) ₄ ·3DBHA DBOA	Syrupy green Light yellow	^b 150–170 (2 mm)	40 90	43.4(43.1) 74.5(75.2)	7.2(7.4) 12.8(13.0)	8.1(8.4) 5.4(5.5)	20.5(20.4) —	20.6(20.4) —
3.	UO ₂ (NO ₃) ₂ ·2DBOA	Yellow	71.5	70	42.4(42.5)	7.1(7.4)	6.2(6.2)	26.0(26.3)	—
4.	Pu(NO ₃) ₄ ·3DBOA MBOA	Dark tan Colourless	^b 111 (0.1 mm)	50 80	46.0(46.1) 73.2(73.2)	5.6(5.6) 12.9(12.8)	7.7(7.8) 6.7(6.6)	18.4(19.1) —	19.4(19.1) —
5.	UO ₂ (MO ₃) ₂ ·2MBOA	Yellow	48.7	60	38.9(38.0)	6.9(6.6)	6.8(6.9)	28.4(29.0)	—
6.	Pu(NO ₃) ₄ ·3MBOA TBMA	Viscous green Brown	^b 160 (0.1 mm)	30 50	38.3(38.3) 69.4(69.9)	6.4(6.6) 12.0(11.7)	8.6(8.9) 8.5(8.6)	23.3(23.5) —	23.9(23.5) —
7.	UO ₂ (NO ₃) ₂ ·TBMA	Yellow	137.1	70	30.3(31.7)	5.4(5.3)	7.9(7.8)	33.2(33.1)	—
8.	Pu(NO ₃) ₄ ·2TBMA TIBMA	Dark Tan Syrupy crystals	^b 35.5	45 60	39.7(40.0) 69.6(69.9)	6.7(6.7) 11.2(11.7)	9.8(9.8) 8.5(8.76)	22.2(21.0) —	21.4(21.0) —
9.	UO ₂ (NO ₃) ₂ ·TIBMA	Yellow	188.4	80	31.6(31.7)	5.5(5.3)	7.7(7.8)	33.0(33.1)	—
10.	Pu(NO ₃) ₄ ·2TIBMA THMA	Dirty yellow Brown	167.1 150–170 (0.2 mm)	30 50	39.8(40.0) 73.7(74.0)	6.6(6.7) 11.8(12.3)	10.8(9.8) 6.8(6.4)	21.2(21.0) —	20.2(21.0) —
11.	UO ₂ (NO ₃) ₂ ·2THMA	Yellow	143.5	40	51.1(51.0)	8.6(8.6)	6.8(6.6)	19.5(19.1)	—
12.	Pu(NO ₃) ₄ ·2THMA DEBHA	Dark green Colourless	^b 125.4	40 80	47.2(47.5) 74.3(75.2)	8.0(7.9) 12.6(13.0)	8.4(8.2) 5.3(5.5)	17.3(17.5) —	17.9(17.5) —
13.	UO ₂ (NO ₃) ₂ ·2DBEHA DIBEHA	Yellow Yellow	115.7 122	70 80	42.4(42.5) 74.3(75.2)	7.5(7.3) 12.9(13.0)	6.4(6.2) 5.6(5.5)	26.2(26.3) —	— —
14.	UO ₂ (NO ₃) ₂ ·2DIBEHA	Light yellow	142.7	70	42.6(42.5)	7.5(7.3)	6.1(6.2)	26.3(26.3)	—

^aRequired values are given in parentheses.^bSyrupy liquids at room temperature.

Table 2. Principal features in electronic spectra of the complexes in tertiary butyl benzene

S. No.	Complex	Feature (nm) ^a
1.	UO ₂ (NO ₃) ₂ · 2DBHA	362 (11.0); 371 (w); 421 (18.6); 428 (18.7); 441 (15.2); 456 (8.5); 471 (w); 485 (w)
2.	Pu(NO ₃) ₄ · 3DBHA	432 (115.5); 498 (88.9); 556 (51.2); 643 (57.5); 661 (54.6)
3.	UO ₂ (NO ₃) ₂ · 2DBOA	361, 371, 421, 428, 440, 456, 471, 485
4.	Pu(NO ₃) ₄ · 3DBOA	432 (63.3); 497 (53.7); 557 (39.4); 641 (40.6); 663; 773 (45.9)
5.	UO ₂ (NO ₃) ₂ · 2MBOA	361, 371, 421, 428, 440, 456, 471, 485
6.	Pu(NO ₃) ₄ · 3MBOA	435 (41.6); 498 (44.1); 642; 662 (25.4); 791 (25.7)
7.	Pu(NO ₃) ₄ · 2TBMA	497(131.9); 535 (78.6); 654 (73.5); 790 (55.6)
8.	Pu(NO ₃) ₄ · 2TIBMA	495 (90.7); —; 659 (50.1); 797 (38.3); 850 (26.9)
9.	UO ₂ (NO ₃) ₂ · 2THMA	361; 420; 428; 441, 456, 471, 485
10.	Pu(NO ₃) ₄ · 2THMA	491 (10.6); —; 658 (6.4); 675 (6.4)
11.	UO ₂ (NO ₃) ₂ · 2DBEHA	363, 370, 411, 422, 444, 456, 475
12.	UO ₂ (NO ₃) ₂ · 2DI- BEHA	363, 372, 410, 421, 443, 458, 476

^a Figures in parentheses are extinction coefficients (mol⁻¹ dm⁻¹ cm⁻¹), w = weak

Table 3. Typical IR bands of U^{VI} and Pu^{IV} nitrato-amide complexes

Compound	ν(C=O) ^a	O—U—O		NO ₃ vibration (cm ⁻¹)					
		stretch	bending	τ ₄	τ ₂	τ ₆	τ ₃	Δν(C=O)	τ ₄ -τ ₂
1. UO ₂ (NO ₃) ₂ · 2DBHA	1570 (1642)	960	260	1285	1035	815	750	68	250
2. Pu(NO ₃) ₄ · 3DBHA	1610 (1642)	—	—	1295	1025	838	730	32	270
3. UO ₂ (NO ₃) ₂ · 2DBOA	1568 (1645)	940	260	1280	1035	815	750	77	245
4. Pu(NO ₃) ₄ · 3DBOA	1585 (1645)	—	—	1280	1030	820	735	40	250
5. UO ₂ (NO ₃) ₂ · 2DBEHA	1620 (1645)	980	260	1285	1035	815	752	25	250
6. UO ₂ (NO ₃) ₂ · 2DIBEHA	1620 (1645)	980	265	1285	1038	815	752	25	247
7. UO ₂ (NO ₃) ₂ · 2MBOA	1580 (1645)	945	262	1280	1035	820	755	65	245
8. Pu(NO ₃) ₄ · 3MBOA	1585 (1645)	—	—	1290	1030	835	735	40	260
9. UO ₂ (NO ₃) ₂ · TBMA	1575 (1635)	940	260	1280	1030	815	750	60	250
10. Pu(NO ₃) ₄ · 2TBMA	1610 (1640)	—	—	1310	1025	838	730	30	285
11. UO ₂ (NO ₃) ₂ · TIBMA	1580 (1635)	935	260	1285	1030	820	750	49	255
12. Pu(NO ₃) ₄ · 2TIBMA	1600 (1635)	—	—	1310	1025	838	730	40	285
13. UO ₂ (NO ₃) ₂ · 2THMA	1535 (1640)	948	270	1300	1040	830	765	105	260
14. Pu(NO ₃) ₄ · 2THMA	1600 (1640)	—	—	1300	1035	820	730	40	265

^a Figures in parentheses are stretching frequencies of the pure ligands.

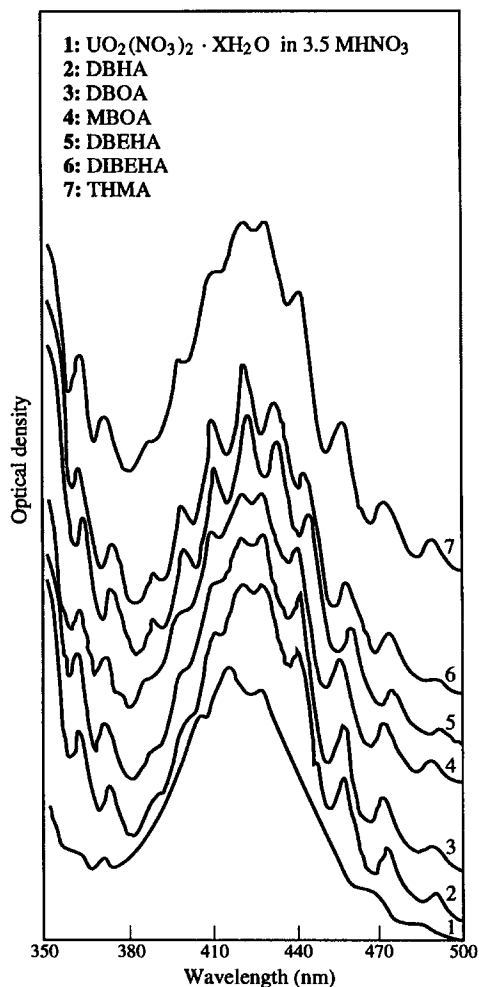


Fig. 1. Absorption spectra of the complexes: $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{A}$, curves 2–6 (monoamides); $\text{UO}_2(\text{NO}_3)_2 \cdot 1\text{A}$, curve 7 (diamides).

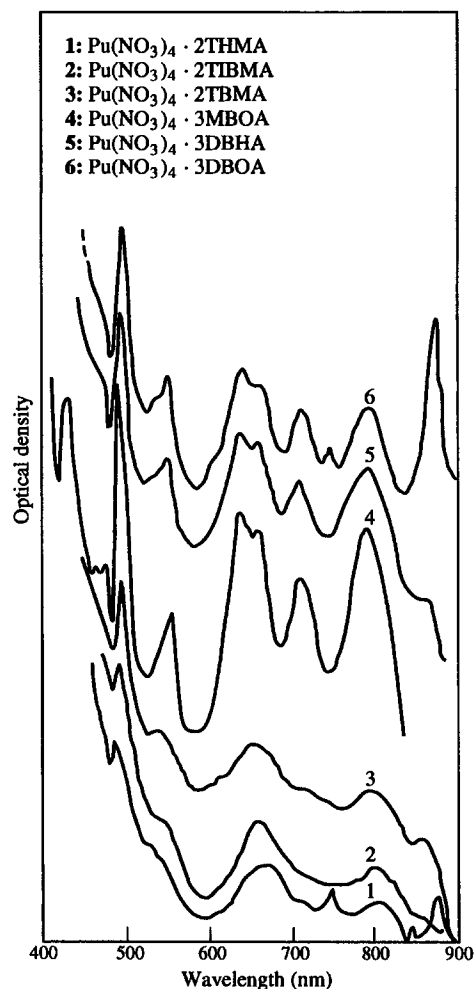


Fig. 2. Absorption spectra of the complexes $\text{Pu}(\text{NO}_3)_4 \cdot 3\text{A}$, curves 4–6 (monoamides) $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{A}$, curves 1–3 (diamides).

the oxygen of the amides. The bathochromic shifts observed from 476 (pure Pu^{IV} in $3.5 \text{ mol dm}^{-3} \text{ HNO}_3$) to around 497 nm were similarly attributed to the bonding of amide in plutonium(IV) complexes (Fig. 2). Extinction coefficients of monoamide complexes at main peaks around 432, 497, 556, 541, 642 and 791 nm and bands around 495, 655 and 790 nm in diamide complexes were comparatively higher. Although the spectra of uranium and plutonium complexes were found to be similar amongst themselves the symmetry of environment around these cations could not be assessed conclusively.

IR spectra

The nitrate and carbonyl group stretching frequencies appearing in the IR spectra of amide complexes are summarized in Table 3. In uranyl

complexes, the reduction of the stretching frequency of the carbonyl band of free amide from 1640 to around 1570 cm^{-1} indicates its coordination in the molecule. The average shift was observed to be 60 cm^{-1} , except for DBEHA and DIBEHA where it was 25 cm^{-1} , indicating the formation of weaker complexes. Four nitrate vibrations, τ_4 , τ_2 , τ_6 , τ_3 , have been identified and a large difference of $(\tau_4 - \tau_2)$ of around 250 cm^{-1} indicates the nitrate as the bidentate group. The O—U—O asymmetric stretch in uranyl complexes has been observed as a strong band around 950 cm^{-1} , indicating its coordination in the molecule.¹³

In plutonium(IV) complexes, the amides are coordinated to plutonium via the carbonyl group oxygen atom, and C=O stretching shifts to a lower frequency around 40 cm^{-1} for mono- and diamide molecules. The four NO_3 group vibrations (τ_4 , τ_2 , τ_6 , τ_3) were present and similarly identified as in

the case of uranyl complexes due to the bidentate nitrate group. However, in plutonium complexes a shoulder due to the τ_1 NO_3 vibration around 1510 cm^{-1} was also observed. The bidentate nature of the nitrate group in the complexes was further corroborated by the splitting of the band near 700 cm^{-1} into the two strong bands around 735 and 790 cm^{-1} (absent in the pure ligand), as suggested by Lever *et al.*²³ for the bidentate bonding of NO_3 . Distinct bands appearing around 460 cm^{-1} , which were absent in the free ligands have been identified as the Pu—O (amide) stretching frequency. Sharp bands at 1055 and 765 cm^{-1} were attributed to C—H in-plane and out-of-plane deformations of the acyl group (uranium and plutonium complexes), while weak and broad bands appearing in the $3400\text{--}3200\text{ cm}^{-1}$ region are attributed to O—H stretching, showing the hygroscopic nature of the plutonium complexes due to moisture pick-up during sample preparation. These bands are totally absent in the uranium complexes.

¹H NMR spectra

¹H NMR spectra of the uranyl complexes were recorded in CDCl_3 using TMS as an internal standard (Table 4). The bands corresponding to $\alpha\text{-CH}_2$ of butyl and $\alpha\text{-CH}_2$ of acyl groups, other $\alpha\text{-CH}_2$ as well as the methyl protons of butyl and acyl groups,

in the case of neat DBHA, DBOA and MBOA ligands, and their uranyl complexes have been assigned (Table 4). The presence of two clear triplets for the $\alpha\text{-CH}_2$ protons of the butyl group indicate that they are non-equivalent due to restricted rotation of the C—N bond, the triplets arising due to the associated coupling in the adjacent methylene protons. Methyl protons of the acyl group as well as the methyl of the butyl group in MBOA were observed as mostly shielded and appearing as triplets due to coupling by adjacent methylene protons.

Thermal studies

Thermal investigations revealed a dip around 100°C in a DTA-trace of uranyl monoamide complexes and around 140°C in diamide complexes, presumably due to phase changes that can be correlated with the complete removal of hindered rotation around the C—N bond. Two distinct plateaux in the TGA curves corresponding to the loss of amide and nitrate groups, respectively, were observed, except in the case of DBHA and DBOA complexes. This may be attributed to the release of two amide moieties and one NO_3 group around $225\text{--}290^\circ\text{C}$, $320\text{--}350^\circ\text{C}$ (simultaneously) and $400\text{--}500^\circ\text{C}$, corresponding to the final conversion into U_3O_8 , respectively. Exothermic loss of both nitrate

Table 4. ¹H NMR spectral data for $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{X}$ complexes and free amides (X = DBHA, DBOA, MBOA)

Band position	No. of protons	Band position	No. of protons	Assignments
DBHA ligand		$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DBHA}$		
3.32	4.1	3.57	8	α -Methylene of butyl group
2.32	2.1	2.70	4	α -Methylene of acyl group
—	—	1.66	16	Other CH_2 of butyl only
1.38	13.9	1.06	28	Other CH_2 of butyl and acyl
0.93	8.9	0.69	12	CH_3 of butyl and acyl
DBOA ligand		$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DBOA}$		
3.32	4.0	3.60	8	α -Methylene of butly group
2.32	2.1	2.68	4	α -Methylene of acyl group
—	—	1.68	16	Other CH_2 of butyl only
1.37	17.9	1.11	26	Other CH_2 of butyl and acyl
0.95	8.9	0.74	12	CH_3 of butyl and acyl
		$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MBOA}$		
		3.52	4	α -Methyl of butyl group
		3.21	5.8	N-Methyl
	N.R.	2.63	4	α -Methylene of acyl group
		1.63	8	Other CH_2 of butyl only
		1.09	19.6	Other CH_2 of acyl only
		0.56	12	CH_3 of acyl and butyl

N.R. = not recorded.

Table 5. Thermal data for uranyl nitrate-amide complexes

Description	UO ₂ (NO ₃) ₂ · 2DBHA	UO ₂ (NO ₃) ₂ · 2DBOA	UO ₂ (NO ₃) ₂ · 2MBOA	UO ₂ (NO ₃) ₂ · 2DBEHA	UO ₂ (NO ₃) ₂ · 2DIBEHA	UO ₂ (NO ₃) ₂ · TIBMA	UO ₂ (NO ₃) ₂ · TBMA
1. Molecular weight	848.8	904.8	820.8	904.8	904.8	720	720
2. Total loss of weight (%)	66.50 (66.90)	68.97 (70.16)	66.56 (67.11)	65.80 (70.16)	68.95 (70.16)	60.79 (62.50)	59.32 (62.50)
3. Phase change temperature (°C)	110	70	50	105	140		
4. % Uranium content	28.38 (28.17)	26.31 (26.31)	28.71 (28.99)	26.18 (26.31)	26.33 (26.31)	33.25 (33.04)	34.49 (33.04)
5. First step weight loss (%) (liberation of two amide molecules in monoamides and two in diamides)	53.50 (53.60)	58.89 (56.50)	51.68 (51.09)	56.64 (56.45)	55.56 (56.45)	43.28 (45.28)	42.99 (45.28)
6. Second step weight loss (%) (liberation of two NO ₃ groups)	6.5 (7.3) ^a	9.5 (6.9) ^a	14.47 (15.11)	12.57 (13.71)	13.39 (13.71)	16.52 (17.22)	16.33 (17.22)
7. First decomposition temperature Peak height temperature (°C)	225, 290	225, 270	225	220, 245	205, 245	235	240
Nature of peak	SE, WE	SE, WE	SE	SE, WE	SE, WE	SE	SE
8. Second decomposition temperature Peak height temperature (°C)	320	320	330	330	330	345	320
Nature of peak	SE	SE	SE	SE	SE	ME	ME
9. Third decomposition temperature Peak height temperature (°C)	440	460	400	—	—	500	500
Nature of peak	WE	WE	ME	—	—	SE	SE

^aComputed for liberation of one nitrate group.

SE = strong exothermic; WE = weak exothermic; ME = medium exothermic. Required values are given in parentheses.

and amide ligands simultaneously, around 290 °C, was observed only in the case of THMA.

Uranyl diamide complexes of the type $\text{UO}_2(\text{NO}_3)_2 \cdot \text{diamide}$ are also of the same type where uranium is coordinated by both the $\text{C}=\text{O}$ groups of one diamide molecule, except in the complex $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{THMA}$, where one more THMA molecule is attached and the absence of the free $\text{C}=\text{O}$ stretching vibration in the complex suggests that it is not the amide of crystallization but it is bonded due to interaction of uranyl-bonded THMA to another THMA, forming an outer-sphere complex of the type $[\text{UO}_2(\text{NO}_3)_2 \cdot \text{THMA}] \cdot \text{THMA}$. Such non-ideal behaviour (dipole-dipole interactions) were observed by Musikas and co-workers^{9,11} in a solvent extraction and thermodynamic study with amide systems. In tetranitrato plutonium(IV) complexes, $\text{Pu}(\text{NO}_3)_4 \cdot 3\text{amides}$ (monoamides) and $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{amide}$ (diamides) were obtained. Smaller average shifts of $\text{C}=\text{O}$ stretching (30 cm^{-1}) in both cases, as well as the absence of $\text{C}=\text{O}$ (free), is indicative of outer-sphere complexes of the type $[\text{Pu}(\text{NO}_3)_4 \cdot 2\text{amide}] \cdot \text{amide}$ (monoamides) and $[\text{Pu}(\text{NO}_3)_4 \cdot \text{amide}] \cdot \text{amide}$ (diamides). The higher positive charge on nitrogen, which confers a higher electron density on the carbonyl oxygen of the bonded amide, is responsible for this interaction. The X-ray powder patterns of the uranium complexes were similar to those reported by Charpin *et al.*¹⁵⁻¹⁷ while the solid plutonium-TIBMA complex was amorphous in nature.

Acknowledgements—The authors wish to express their sincere thanks to Dr R. H. Iyer, Head of Radiochemistry Division, for his keen interest and to Shri N. K. Kulkarni and Dr K. D. Singh of the Fuel Chemistry Division for recording the thermograms. The authors also thank Dr M. S. Subramanian for helpful discussions.

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