Amide Complexes of Thorium(IV), Uranium(IV), and Dioxouranium(VI) Nitrates

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Complexes of thorium tetranitrate, $Th(NO_3)_4 \cdot xL$ (x = 3, L = MeCONHMe; x = 2.5, L = $MeCONEt_2$, $EtCONMe_2$, or $Me_3C \cdot CONMe_2$; x = 2, L = $MeCONPh_2$), uranium tetranitrate, $U(NO_3)_4 \cdot 2.5L$ (L = $MeCONEt_2$ or $EtCONMe_2$), and dioxouranium(VI) nitrate, $UO_2(NO_3)_2 \cdot 2L$ (all above $R'CONR''_2$), have been prepared. Their i.r., Raman, and electronic spectra are discussed.

THE only amide complexes of the actinoid nitrates so far recorded are the *NN*-dimethylacetamide (dma) compounds, $M(NO_3)_4 \cdot 2.5$dma (M = Th,[1] U,[2] or Np[3]) and the *NN*-dimethylformamide (dmf) complex,[4] $UO_2(NO_3)_2 \cdot 2$dmf. The stoicheiometry of the complexes formed with amides by thorium or uranium tetrachloride varies markedly[5] with the bulk of the substituents R in the ligands $R^1CONR^2R^3$ and we have, therefore, extended this investigation to the corresponding actinoid(IV) nitrate systems in order to ascertain whether similar changes in stoicheiometry result with the smaller, potentially bidentate nitrate ion, as well as to compare the products with those obtained in actinoid tetranitrate–R_3PO systems.[6]

The amide ligands used in this work, and the abbreviations used for them, were as follows:

$R^1CONR^2R^3$

R^1 = Me, R^2 = H, R^3 = Me (nma)
R^1 = Me, R^2 = R^3 = Et (dea), Ph (dpha)
R^1 = Et (dmpa), Pr^n (ba), Me_2CH (iba), Bu^n (va), Me_2CHCH_2 (iva), Me_3C (pva), R^2 = R^3 = Me

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[1] K. W. Bagnall, D. Brown, P. J. Jones, and P. S. Robinson, *J. Chem. Soc.*, 1964, 2531.

[2] K. W. Bagnall, P. S. Robinson, and M. A. A. Stewart, *J. Chem. Soc.*, 1961, 4060.

[3] J. B. Laidler, *J. Chem. Soc.* (*A*), 1966, 780.

[4] A. S. Solokin, K. A. Rybakov, and A. M. Pantaleeva, *Russ. J. Inorg. Chem.*, 1969, **14**, 1362.

[5] K. W. Bagnall, J. G. H. du Preez, and (in part) J. Bajorek, L. Bonner, H. Cooper, and G. Segal, *J.C.S. Dalton*, 1973, 2682.

[6] K. W. Bagnall and M. W. Wakerley, *J.C.S. Dalton*, 1974, 889.

The Complexes.—The thorium tetranitrate and dioxouranium(VI) nitrate complexes were prepared by treating the hydrated nitrates with the ligands in acetone or ethanol. In some instances (ba, iba, va, and iva) the thorium(IV) products were oils that could not be solidified. The uranium tetranitrate complexes (dea, dmpa) were prepared in the same way from $Cs_2U(NO_3)_6$ but at 0 °C to minimise oxidation to uranium(VI); dpha did not react with $Cs_2U(NO_3)_6$ and pva reacted only slowly, no pure product being obtained. An alternative route, reaction of $UCl_4{\cdot}2pva$ with silver nitrate in methyl cyanide at 0 °C, yielded an unidentified green oil which evolved oxides of nitrogen when set aside, the uranium(IV) being oxidised to uranium(VI).

TABLE 1

Molar conductivities ($\Lambda_{1000}/\Omega^{-1}$ cm^2 mol^{-1}) of some nitrate complexes in nitromethane at 20 °C

Ligand, L						
nma	$Th(NO_3)_4{\cdot}3L$	57.5				
dmpa	$Th(NO_3)_4{\cdot}2.5L$	39.5	$U(NO_3)_4{\cdot}2.5L$	46.2	$UO_2(NO_3)_2{\cdot}2L$	38.6
dea	$Th(NO_3)_4{\cdot}2.5L$	43.7	$U(NO_3)_4{\cdot}2.5L$	25.0	$UO_2(NO_3)_2{\cdot}2L$	46.7
pva	$Th(NO_3)_4{\cdot}2.5L$	35.2			$UO_2(NO_3)_2{\cdot}2L$	43.7
dpha	$Th(NO_3)_4{\cdot}2L$	56.0			$UO_2(NO_3)_2{\cdot}2L$	50.7
ba					$UO_2(NO_3)_2{\cdot}2L$	40.3
iba					$UO_2(NO_3)_2{\cdot}2L$	39.2
va					$UO_2(NO_3)_2{\cdot}2L$	44.4
iva					$UO_2(NO_3)_2{\cdot}2L$	41.0

TABLE 2

Infrared spectra of the nitrate complexes (in cm^{-1}): nitrate vibrations [a]

Compound	Colour	ν_1	ν_4	ν_2	ν_6	ν_3	ν_5	$\nu_{C=O}$	$\Delta\nu_{C=O}$
$Th(NO_3)_4{\cdot}3nma$	White	1 500m, sh	1 285s	1 035s	810m	743m	725w	1 618s	42
$Th(NO_3)_4{\cdot}2.5dea$	White	1 515vs	1 280vs	1 028s	808m	741s	710w	1 590s	57
$U(NO_3)_4{\cdot}2.5dea$	Green	1 522vs	1 290vs	1 040s	812m	750s	718m	1 608s	39
$UO_2(NO_3)_2{\cdot}2dea$	Yellow	1 515vs	1 285vs	1 030s	810m	742m	710m	1 600s	47
$Th(NO_3)_4{\cdot}2.5dmpa$	White	1 500s, sh	1 280vs	1 033s	812m	746s	722m	1 610s	32
$U(NO_3)_4{\cdot}2.5dmpa$	Green	1 525vs	1 285vs	1 035s	815m	751s	725m	1 610s	32
$UO_2(NO_3)_2{\cdot}2dmpa$	Yellow	1 510vs, sh	1 270vs	1 025vs	810w	743m	710s	1 565s	77
$Th(NO_3)_4{\cdot}2.5pva$	White	1 520vs	1 275vs	1 035s	813m	748s	720s	1 583s	49
$UO_2(NO_3)_2{\cdot}2pva$	Yellow	1 500vs, sh	1 275vs	1 025vs	806s	740vs	703w	1 592s	40
$UO_2(NO_3)_2{\cdot}2iva$	Yellow	1 500vs, sh	1 270vs	1 025vs	804s	740vs	710s	1 590s	60
$UO_2(NO_3)_2{\cdot}2va$	Yellow	1 500vs, sh	1 270vs	1 025vs	808m	740vs	700w	1 596s	48
$Th(NO_3)_4{\cdot}2dpha$	White	1 495s, sh	1 285s	1 035s	814m	748s	720m	1 608m	67
$UO_2(NO_3)_2{\cdot}2dpha$	Yellow	1 530s	1 280s	1 030m	805m	742w	710w	1 605s	70
$UO_2(NO_3)_2{\cdot}2ba$	Yellow	1 515s	1 275vs	1 028s	804m	741s	718w	1 595s	50
$UO_2(NO_3)_2{\cdot}2iba$	Yellow	1 505s	1 280s	1 028s	808m	740s	715w	1 584s	64

[a] Assigned on the basis of the presence of bidentate nitrate groups.[7]

s = strong; m = medium; w = weak; sh = shoulder; v = very.

TABLE 3

Raman spectra of the thorium tetranitrate complexes (in cm^{-1})

	ν_1	ν_4	ν_2	ν_6	ν_3	ν_5
$Th(NO_3)_4{\cdot}3nma$	1 523w	1 315w	1 038vs		750w	705vw
$Th(NO_3)_4{\cdot}2.5dea$	1 490s, (1 455s)	1 290w	1 031vs, 1 026vs		747m	714s
$Th(NO_3)_4{\cdot}2.5dmpa$	1 500w, (1 460w)		1 033vs	815w	745w	720w, 705vw
$Th(NO_3)_4{\cdot}2.5pva$	1 509w, (1 449w)		1 040vs, 1 030vs	830w	750w	722m
$Th(NO_3)_4{\cdot}2dpha$	1 490m, (1 470m)		1 029s		745w	712m

s = strong; m = medium; w = weak; v = very.

With nma as ligand the tris-complex, $Th(NO_3)_4{\cdot}3nma$, was obtained, in contrast to the 1 : 2.5 stoicheiometry of the dea, dmpa (Th,U), and pva (Th) complexes. The behaviour of pva with thorium tetranitrate was surprising because dpha formed only the bis-complex with thorium tetranitrate and pva, a bulky ligand, is known to form only bis-complexes with thorium or uranium tetrachloride.[4] The known dma complexes [1-3] of the actinoid tetranitrates also have the 1 : 2.5 stoicheiometry, but their structures have not been recorded. Dioxouranium(VI) nitrate formed only bis-complexes with the di-*N*-substituted amides used in this work.

One possible formulation for the complexes of 1 : 2.5 stoicheiometry would be an ionic species of the type $[M(NO_3)_2 5L]^{2+}[M(NO_3)_6]^{2-}$; the molar conductivities (Λ_{1000}) of the complexes in nitromethane at 20 °C (Table 1) ranged from 25.0 [$U(NO_3)_4{\cdot}2.5dea$] to 57.5 Ω^{-1} cm^2 mol^{-1} [$Th(NO_3)_4{\cdot}3nma$], most of them being below 47 Ω^{-1} cm^2 mol^{-1}. The plots of Λ against $\sqrt{c}$ were moderately linear, but no conclusions as to the ionic species present, if any, could be drawn from the results.

The thorium(IV) and dioxouranium(VI) nitrate complexes were not hygroscopic; all the complexes were soluble in common organic solvents, such as acetone, ethanol, methyl cyanide, and nitromethane, and were insoluble in hydrocarbons, diethyl ether, or carbon tetrachloride.

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[7] R. W. Hester and W. L. Grossman, *Inorg. Chem.*, 1966, **5**, 1308.

Vibrational Spectra.—The nitrate and carbonyl group features in the i.r. spectra of the complexes are given in Table 2. The ligands are co-ordinated to the metal atom *via* the amide carbonyl-group oxygen atom, the shifts to lower frequency in the C=O stretching mode ranging from 32 to 77 cm^{-1} (comparable with the shifts observed in the corresponding amide complexes of the tetrachlorides).

Ionic nitrate groups are absent, all being covalently bound, and although the features of the Raman spectra of the thorium tetranitrate complexes (Table 3) were badly obscured because of fluorescence, ν_4 usually being too weak to be discerned, ν_2 could be seen easily as a very strong feature. It has been suggested[8] that ν_4 in the Raman spectrum would be a strong or very strong feature if the nitrate groups were unidentate. Consequently it is reasonable to conclude that the nitrate groups are bidentate in these complexes, and the i.r. spectra have been assigned[7] on this basis. The uranium(IV) compounds were too unstable thermally for the Raman spectra to be obtained.

TABLE 4

Electronic spectra of the uranium(IV) complexes (in nm [a])

$U(NO_3)_4 \cdot 2.5$dea	$U(NO_3)_4 \cdot 2.5$dmpa
	387 (5.6)
423 (1.8)	424 (6.9)
434 (7.2)	434 (6.0)
474 (14.4)	474 (13.1)
538 (3.4)	538 (2.8)
618 (4.3)	
656 (17.2)	656 (15.2)
960 (3.6)	965 (2.0)
1 055 (6.6)	1 055 (2.1)sh
1 089 (7.2)	1 089 (3.3)
1 160 (4.9)	1 165 (3.3)
	1 380 (5.1)
	1 505 (5.1)
	1 615 (3.2)
1 690 (6.2)	1 695 (4.9)
	1 725 (5.6)
	1 900 (2.2)
2 090 (4.6)	2 100 (2.2)

[a] Extinction coefficients, mol^{-1} l cm^{-1}, in parentheses; solvent, acetone; sh = shoulder.

TABLE 5

Analytical results, yields, and melting points

	Metal (%)		Carbon (%)		Hydrogen (%)		Nitrogen (%)			
Compound	Required	Found	Required	Found	Required	Found	Required	Found	Preparative yield (%)	M.p. (t/°C) *
$Th(NO_3)_4 \cdot 3$nma	33.2	33.1	15.4	15.5	3.0	3.1	14.0	14.1	80	139d
$Th(NO_3)_4 \cdot 2.5$dea	30.2	30.6	23.5	24.5	4.2	4.4	11.9	11.5	70	93d
$U(NO_3)_4 \cdot 2.5$dea	30.8	31.4	23.3	24.0	4.2	4.3	11.8	11.4	65	70—73d
$UO_2(NO_3)_2 \cdot 2$dea	38.1	38.9	23.1	23.4	4.2	4.3	9.0	9.5	78	110
$Th(NO_3)_4 \cdot 2.5$dmpa	31.7	30.4	20.5	21.4	3.8	3.8	12.4	12.3	76	111—113d
$U(NO_3)_4 \cdot 2.5$dmpa	32.3	33.2	20.3	20.7	3.7	3.8	12.3	11.7	74	76—77d
$UO_2(NO_3)_2 \cdot 2$dmpa	40.0	39.5	20.1	20.2	3.7	3.7	9.4	9.3	90	210
$Th(NO_3)_4 \cdot 2.5$pva	28.9	30.5	26.2	24.9	4.7	4.5	11.3	10.2	55	127—129d
$UO_2(NO_3)_2 \cdot 2$pva	36.5	36.2	25.8	25.8	4.6	4.6	8.6	8.6	83	119
$UO_2(NO_3)_2 \cdot 2$iva	36.5	37.4	25.8	25.2	4.6	4.5	8.6	8.6	76	90
$UO_2(NO_3)_2 \cdot 2$va	36.5	37.6	25.8	25.3	4.6	4.6	8.6	8.5	75	125
$Th(NO_3)_4 \cdot 2$dpha	25.7	24.7	37.2	38.0	2.9	2.9	9.3	9.5	60	195—196d
$UO_2(NO_3)_2 \cdot 2$dpha	29.2	28.7	41.2	40.6	3.2	3.1	6.9	6.5	84	196
$UO_2(NO_3)_2 \cdot 2$ba	38.1	38.0	23.1	23.2	4.2	4.3	9.0	9.0	63	148
$UO_2(NO_3)_2 \cdot 2$iba	38.1	37.5	23.1	23.3	4.2	4.2	9.0	9.3	71	169

* d = decomposed.

Electronic Spectra.—The spectra of the two uranium tetranitrate complexes (Table 4) in acetone were somewhat similar to those of the recently recorded phosphine oxide complexes,[6] but they did not provide evidence concerning the symmetry of the environment(s) of the metal atoms in these complexes.

EXPERIMENTAL

The complexes were prepared and handled in dry nitrogen atmosphere glove-boxes to afford protection against atmospheric moisture and oxygen.

Reagents.—Thorium tetranitrate hydrate (Fisons, Ltd.), uranyl nitrate hydrate (B.D.H., Ltd.), and dpha (Kodak, Ltd.) were used as supplied. Uranium tetra-acetate[9] and $Cs_2U(NO_3)_6$[2] were prepared by published methods, the latter using uranium tetra-acetate as the starting material. The compounds dmpa, ba, iba, va, iva, and pva were prepared by amidation of the acids with hexamethylphosphoric triamide,[10] and nma and dea by reaction of the acyl chloride with the amine in ether. The ligands were redistilled under reduced pressure before use and both they and the solvents used were freed from dissolved oxygen by purging with nitrogen, after which they were stored over molecular sieves (ligands, type 4A; solvents, type 5A).

Preparation of Thorium Tetranitrate Complexes.—The ligand (12—15 mmol), either alone (nma, dea, dmpa, pva) or in acetone (10 ml; dpha), was added to a solution of the hydrated tetranitrate (1—3 g, 1.3—5 mmol) in acetone (20 ml). The crude products were precipitated as colourless oils on the addition of 2-methylbutane (nma, dea, dmpa) or ether (pva), or isolated as a solid (dpha) by evaporating the acetone solution. The crude products were redissolved in acetone and reprecipitated with 2-methylbutane (×6; nma, dea); the oily products so obtained were either vacuum dried, ground with ethyl acetate, then recrystallised from hot ethyl acetate and vacuum dried (nma, dea complexes), or dissolved in ethyl acetate, from which the solid complexes (dmpa, pva) separated on the addition of diethyl ether or (dpha) when

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[8] C. C. Addison, M. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 321.

[9] D. Gredenic and B. Korpar-Colig, *J. Inorg. Chem.*, 1968, **30**, 1751.

[10] J. Kopecky and J. Smejkal, *Chem. and Ind.*, 1966, 1529.

set aside at 0 °C (48 h). The oily products obtained by the above methods with ba, iba, va, and iva could not be induced to solidify.

Preparation of Uranium Tetranitrate Complexes.—The ligand (dea or dmpa; 5—6 mmol) was added to a suspension of $Cs_2U(NO_3)_6$ (0.876 g, 1 mmol) in acetone (5 ml) at 0 °C; the filtrate was evaporated under vacuum to small bulk, diluted with dichloromethane and filtered to remove residual $CsNO_3$. Addition of diethyl ether (5 ml) precipitated a green oil which became crystalline when set aside at 0 °C (2 d). The crystals were washed with diethyl ether (2 × 2 ml), redissolved in dichloromethane (10 ml), reprecipitated with diethyl ether (5 ml), washed with the same solvent (3 × 5 ml), and vacuum dried (10^{-3} Torr, 6 h).

Preparation of Dioxouranium(VI) *Nitrate Complexes.*—The ligand (6—10 mmol, dea, dmpa, ba, iba, va, iva, and pva) or the stoicheiometric amount (dpha) was added to a solution of the hydrated nitrate (2.36—4.6 mmol) in ethyl acetate (10 ml). Yellow crystals of the bis-complexes separated on the addition of a few drops of 2-methylbutane (dea, dmpa, ba, iba, iva, and pva) or diethyl ether (ba, iba, iva, and pva), or of a larger volume (5 ml) of the latter (va and dmpa). The complexes were washed with ethyl acetate (5 ml; all), followed by diethyl ether (2 × 5 ml; ea, ipa, dmpa, and va) or a second wash with ethyl acetate (others), and were vacuum dried (10^{-3} Torr, 1 h).

Analysis.—Thorium and uranium were determined as described previously; [11] thorium was also determined volumetrically using EDTA.[12] C, H, And N were determined by combustion and the analytical results are summarised in Table 5.

Physical Measurements.—Vibrational and electronic spectra, electrical conductivities, and melting points were obtained as described previously.[6]

The authors thank Mr. M. A. Hart for the microanalyses (C, H, N, Th, U) and one of us (O. V. L.) is indebted to the Overseas Development Administration for the award of a technical assistance scholarship.

[5/199 *Received*, 30*th January*, 1975]

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[11] P. J. Alvey, K. W. Bagnall, D. Brown, and J. Edwards, *J.C.S. Dalton*, 1973, 2308.

[12] A. I. Vogel, 'A Text-book of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961, p. 444.