Sulphoxide Complexes of the Actinoid(IV) Nitrates

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Complexes of the actinoid tetranitrates with sulphoxides, $M(NO_3)_4 \cdot xR_2SO$ [R = Et (deso), M = Th, U, or Np, $x = 3$; R = Ph (dpso), M = Th, U, or Np, $x = 3$ and M = Th, U, Np, or Pu, $x = 4$; R = α-$C_{10}H_7$ (naphthyl, dnso), M = Th, $x = 3$] have been prepared. The i.r., Raman, and electronic spectra of the complexes are discussed.

DIMETHYL SULPHOXIDE (dmso) complexes of the actinoid tetranitrates, $M(NO_3)_4 \cdot x$dmso, where $x = 6$ (Th, Np, or Pu) and 3 (Th, U, Np, or Pu) have been reported in an earlier communication[1] in which attention was drawn to the instability of $U(NO_3)_4$–dmso complexes relative to the other actinoid(IV) nitrate–dmso complexes. The only actinoid(IV) nitrate complex with another sulphoxide is[2] $Th(NO_3)_4 \cdot 3$dpso (dpso = Ph_2SO), whereas complexes of the actinoid tetrachlorides with diethyl (deso; Th,[3] U,[3,4] Np,[3] or Pu[3]), diphenyl (dpso; Th,[2-5]

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[1] P. J. Alvey, K. W. Bagnall, and D. Brown, *J.C.S. Dalton*, 1973, 2326.

[2] B. C. Smith and M. A. Wassef, *J. Chem. Soc. (A)*, 1968, 1817.

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

[4] P. Gans and J. W. Marriage, personal communication.

[5] V. V. Savant and C. C. Patel, *J. Less-Common Metals*, 1971, **24**, 459.

U,[3,4,6] Np,[3] or Pu [3]), and di-α-naphthyl (dnso; Th,[3] U [3,4]) sulphoxides are now known. In these tetrachloride complexes, the expected trend, namely a decrease in co-ordination number with increasing size of the ligand and, across the series, with decreasing radius of the metal atom, was not well defined. It was, therefore, of interest to examine the corresponding complexes of the tetranitrates in order to ascertain whether this trend became more marked, as is the case with the phosphine oxide complexes [7] of these nitrates, and also whether it was possible to obtain more stable uranium tetranitrate complexes with other sulphoxide ligands.

RESULTS AND DISCUSSION

The Complexes.—The thorium tetranitrate tris-complexes separated as crystals (dpso), or as oils which ultimately crystallised (deso, dnso), when the ligand (deso, dpso) was added to a solution of the hydrated tetranitrate in a nonaqueous solvent or when the latter was added to the solid ligand (dnso). The solvated complex, $Th(NO_3)_4$·3dnso·EtOAc, resulted when the dnso complex was prepared in ethyl acetate solution, but the other ligands did not yield solvates when prepared from this solvent. Prolonged exposure to vacuum (10^{-4} Torr) slowly removed the ethyl acetate from the solvate.

The uranium(IV) and neptunium(IV) tris-deso complexes were prepared by treating the hexanitrato-complex, $Cs_2M(NO_3)_6$, with the ligand in acetone. However, the reaction was very slow with diaryl sulphoxides, even under reflux, resulting in extensive oxidation to dioxoactinoid-(V) or -(VI) species. Thus, $Np(NO_3)_4$·3dpso was obtained in only 16% yield by this procedure.

The tris-complex $U(NO_3)_4$·3dpso and the tetrakis-complexes $M(NO_3)_4$·4dpso (M = Th, U, Np, and Pu) were prepared by metathesis of the corresponding actinoid tetrachloride complex with silver nitrate in methyl cyanide. The main problem with this method is the slight solubility of the silver halide in methyl cyanide, its complete elimination requiring repeated vacuum evaporation of the solution of the complex and redissolution in small quantities of methyl cyanide or other organic solvents. This preparative method failed in the case of the $U(NO_3)_4$–dnso system owing to the spontaneous decomposition of the green primary product, with oxidation to uranium(VI), and the oily product obtained by this route in the $Pu(NO_3)_4$–deso system could not be induced to crystallise. The tris-complex $U(NO_3)_4$·3dpso was also obtained by addition of the ligand to uranium(IV) in 8M-HNO_3 containing sulphamic acid to prevent oxidation. Similarly the neptunium analogue and $Pu(NO_3)_4$·4dpso were prepared by the addition of 2—6M-HNO_3 to stoicheiometric mixtures of the ligand and the appropriate hexanitrato-complex, the initial oily product being dissolved in dichloromethane and reprecipitated by the addition of 2-methylbutane.

In addition to 1 : 3 complexes, 1 : 6 and 1 : 4 complexes also exist with dmso and dpso, respectively, as the ligand, whereas only 1 : 3 complexes have been obtained with deso. Unsuccessful attempts to obtain $Th(NO_3)_4$·4deso included reaction between $Th(NO_3)_4·5H_2O$ and a large excess of deso in acetone [*cf*. the preparation [1] of $Th(NO_3)_4$·6dmso by this route] followed by prolonged cooling in an ice-bath, and treatment of $Th(NO_3)_4$·3deso with an excess of ligand either alone or in dichloromethane, again at 0 °C. The oils isolated from these reaction mixtures by the addition of 2-methylbutane were induced to solidify by prolonged contact with this solvent or by washing with ether, but in all instances the product was $Th(NO_3)_4$·3deso.

In some cases products of very variable composition resulted. For example, the initial oily product obtained in the attempted preparations of $Pu(NO_3)_4$·3dpso could not be characterised satisfactorily and the $Np(NO_3)_4$–dnso system yielded a solid of approximate composition $Np(NO_3)_4$·2·7dnso. These neptunium and plutonium products were possibly mixtures of complexes of different stoicheiometry.

All of the complexes obtained are non-hygroscopic. The uranium tetranitrate–deso and –dpso complexes are more stable with respect to oxidation than the dmso complexes investigated previously [1] and although they decompose slowly at room temperature they remain unchanged when stored at ice temperature for several weeks. They are particularly unstable to heat, the 1 : 3 complexes decomposing, with oxidation to uranium(VI), at 64—68 °C, and $U(NO_3)_4$·4dpso at 93 °C. The molar conductivities (Λ_{1000}) of $Th(NO_3)_4$·3deso, $Th(NO_3)_4$·3dpso, and $Th(NO_3)_4$·3dnso in nitromethane were 39·8, 38·1, and 37·0 Ω^{-1} cm^{-2} mol^{-1}, respectively, very similar to the values found for β-$Th(NO_3)_4$·3dmso (34·6) and $Th(NO_3)_4$·6dmso (34·1). Consequently no conclusions could be drawn from these measurements.

I.r. and Raman Spectra.—The nitrate and sulphoxide group features in the i.r. spectra of the complexes are given in Table 1. The ligands are co-ordinated to the metal atom *via* the sulphoxide oxygen atom, with the S=O stretching vibration shifted to lower frequency to approximately the same extent as in the corresponding complexes of the actinoid tetrachlorides.[3] There is no clear cut trend in any of these series of nitrate complexes. The S=O stretching mode is split in the thorium and uranium tris-complexes, whereas the mode in the corresponding tetrakis-complexes appears as a much broader feature, the envelope of which is superposible on the combined split mode observed for the tris-complexes. It would clearly be of interest to obtain full structural data on selected compounds in the various series. The nitrate groups are covalently bound and features assignable to ionic nitrate were not observed in any of the spectra.

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[6] J. Selbin, M. Schober, and J. D. Ortego, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1385.

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

The Raman spectra of the solid thorium tetranitrate complexes were recorded in an attempt to ascertain whether the nitrate groups were uni- or bi-dentate in these compounds, using the suggested criterion[8] that the second-highest-frequency N–O feature in the Raman spectrum is strong, or very strong, in the former case but is weak in the latter case. Since ν_4 was too weak to be discerned in the spectra of the deso and dpso complexes (Table 2), it is reasonable to conclude that the nitrate groups are bidentate in these complexes, and the i.r. spectra (Table 1) are assigned[9] on this basis. Owing to fluorescence, ν_4 could not be observed in the case of $Th(NO_3)_4 \cdot 3dnso$ and the uranium(IV) compounds were too unstable thermally for Raman spectra to be obtained.

TABLE 1

I.r. spectra of the sulphoxide complexes (cm^{-1})

		Nitrate vibrations[a]							
Compound	Colour	ν_1(s)	ν_4(s)	ν_2(m)	ν_6(m)	ν_3(m)	ν_5(w)	ν(S=O)	$\Delta\nu$(S=O)
$Th(NO_3)_4 \cdot 3deso$	White	1497	1307	1030	811	741	722	951s	108
$U(NO_3)_4 \cdot 3deso$	Green	1520	1287	1040	812	750		960s	99
$Th(NO_3)_4 \cdot 4dpso$	White	1505	1315sh, 1290	1025	809	*b*	*b*	967s, b	72
$Th(NO_3)_4 \cdot 3dpso$	White	1512	1300sh, 1290	1025	805	*b*	*b*	960s, 935s	79, 114
$U(NO_3)_4 \cdot 4dpso$	Green	1510	1300, 1290	1030	810	*b*	*b*	945s, b	94
$U(NO_3)_4 \cdot 3dpso$	Green	1520	1290b	1030	810	*b*	*b*	958s, 935sh	81, 114
$Np(NO_3)_4 \cdot 4dpso$	Green	1510	1277b	1015	800	*b*	*b*	940s, b	99
$Np(NO_3)_4 \cdot 3dpso$	Green	1512	1280b	1028	802	*b*	*b*	942s, b	97
$Pu(NO_3)_4 \cdot 4dpso$	Brown	1510	1282	1028	802	*b*	*b*	945s	94
' $Pu(NO_3)_4 \cdot 3dpso$ '[c]	Brown	1515	1280	1020	805	*b*	*b*	962s	77
$Th(NO_3)_4 \cdot 3dnso$	White	1535sh, 1515, 1505sh	1300sh, 1285	1026	806	*b*	*b*	977s, 946s	65, 96
$Th(NO_3)_4 \cdot 3dnso \cdot EtOH$	White	1535sh, 1515, 1505sh	1300sh, 1285	1026	806	*b*	*b*	979s, 949s	63, 93
' $Np(NO_3)_4 \cdot 3dnso$ '[d]	Grey-green	1530	1288sh, 1275, 1265sh	1021		*b*	*b*	977s, 945s	65, 97

[a] Assigned as bidentate nitrate groups, following ref. 9. [b] Obscured by ligand vibrations. [c] Product not obtained pure; results refer to composition $Pu(NO_3)_4 \cdot 2{\cdot}8dpso$. [d] Product not obtained pure; results refer to composition $Np(NO_3)_4 \cdot 2{\cdot}7dnso$. s = Strong; m = medium; w = weak; b = broad; sh = shoulder.

TABLE 2

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

	ν_1	ν_4	ν_2	ν_6	ν_3/ν_5
$Th(NO_3)_4 \cdot 3deso$	1528w, 1468w, 1408w		1036s		755w, 745w, 720w
$Th(NO_3)_4 \cdot 3dpso$	1529vw, 1546vw		1035m		744w
$Th(NO_3)_4 \cdot 3dnso$	*a*	*a*	1038m	820w	

[a] Obscured by fluorescence.

Electronic Spectra.—The spectra of $U(NO_3)_4 \cdot 3dpso$ (400—1600 nm) and $U(NO_3)_4 \cdot 3deso$ (400—800 nm) in acetone were very similar to those of γ-$U(NO_3)_4 \cdot 3dmso$[1] and $U(NO_3)_4 \cdot 4tmpo$,[7] and those of $Np(NO_3)_4 \cdot 3deso$ (in nitromethane); $Pu(NO_3)_4 \cdot 2{\cdot}8dpso$ and $Pu(NO_3)_4 \cdot 4dpso$ (solid transmission) were likewise virtually identical to the spectra of the corresponding tris-dmso complexes.[1] These spectra were of no assistance in determining the symmetry of the environment of the metal atom in these complexes.

EXPERIMENTAL

The complexes were prepared and handled in dry-nitrogen atmosphere glove-boxes (water <20 p.p.m.; oxygen <20 p.p.m.) to afford protection against atmospheric moisture and the radiation emitted by the α-active isotopes ^{237}Np and ^{239}Pu.

Reagents.—Thorium tetranitrate hydrate (B.D.H., Ltd.) and dpso (Ralph N. Emmanuel, Ltd.) were used as supplied. $Cs_2U(NO_3)_6$,[10] $Cs_2Np(NO_3)_6$,[10] $Cs_2Pu(NO_3)_6$,[10] the actinoid tetrachloride–sulphoxide complexes,[3] deso,[11] and dnso[4] were prepared by published methods. All organic solvents and deso were distilled, freed from dissolved oxygen by purging with nitrogen, and stored over molecular sieves (type 5A).

Preparations.—Because of differences in the tractability of the various complexes, it was not possible to use a common solvent system throughout, and the various systems used are summarised in Table 3. One example each of the preparation of a thorium and a uranium complex is given below to typify the procedures used. All products were vacuum dried (10^{-4} Torr) for 1—24 h.

$Th(NO_3)_4 \cdot 4dpso$. Silver nitrate (0·1332 g, 0·78 mmol) in methyl cyanide (2 ml) was added to $ThCl_4 \cdot 4dpso$ (0·2307 g, 0·195 mmol) and the mixture was stirred for 10 min. The AgCl precipitate was washed with methyl cyanide (1 ml) and the combined supernatant liquid and methyl cyanide wash was evaporated under vacuum to yield a white oil.

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[8] C. C. Addison, M. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, 1971, **25**, 289.

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

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

[11] N. J. Leonard and C. R. Johnson, *J. Amer. Chem. Soc.*, 1962, **84**, 3701.

dpso (0·020 g, 0·1 mmol) In methyl cyanide (1 ml) was added to the oil and the resulting solution was centrifuged to remove traces of AgCl. The solvent was removed by evaporation under vacuum and carbon tetrachloride (2 ml) was added to the resulting oil, which became crystalline after 3 days. The *product* was washed with carbon tetrachloride (yield 90%).

$U(NO_3)_4$·3deso. deso (0·5 ml, 6·2 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 insoluble material was washed with acetone (3 ml) and 2-methylbutane (10 ml) was added to the combined supernatant liquid and washings to yield a green oil. This was dissolved in acetone (5 ml), filtered to remove $CsNO_3$, and reprecipitated with 2-methylbutane. This cycle was repeated (×3); the resulting green oil became crystalline after 3 days at room temperature. The product was washed with diethyl ether (yield 67%).

Analysis.—Thorium, uranium, neptunium, and plutonium were determined as described previously;[3] nitrate was precipitated and weighed as nitron nitrate.[12] Carbon, hydrogen, nitrogen, and sulphur were determined by combustion for selected thorium and uranium complexes. The analytical results are summarised in Table 4.

TABLE 3

Preparative solvent systems and yields for the nitrate complexes

Compound	Solvents used for preparation			Yield
	Metal nitrate	Ligand	Product wash	(%)
$Th(NO_3)_4$·3deso (i)	EtOAc (hot) ^{a}	None	EtOAc	90
(ii)	Me_2CO ^{b,e}	None	2-Methylbutane	90
$Th(NO_3)_4$·3dpso	EtOAc ^{d}	EtOAc	EtOAc	80
$Th(NO_3)_4$·4dpso	MeCN ^{e,f,g}	MeCN	CCl_4	90
$Th(NO_3)_4$·3dnso	$MeNO_2$ (hot) ^{c,h}	None	$MeNO_2$	65
$Th(NO_3)_4$·3dnso·EtOH	EtOAc (hot) ^{i}	None	(1) EtOAc, (2) 2-Methylbutane	90
$U(NO_3)_4$·3deso	None ^{j}	Me_2CO (0 °C) ^{b,k,l}	Et_2O	67
$U(NO_3)_4$·3dpso (i)	Me_2CO (0 °C) ^{b,e,l}	None	Et_2O	61
(ii)	UCl_4 in 8M-HNO_3 (0 °C) ^{g,h,m}	8M-HNO_3 (0 °C)	CCl_4	72
$U(NO_3)_4$·4dpso	MeCN ^{e,f,g}	MeCN	2-Methylbutane (0 °C)	67
$Np(NO_3)_4$·3deso	None ^{j}	Me_2CO ^{b,l,n}		70
$Np(NO_3)_4$·3dpso ^{q} (i)	None ^{j,p}	Me_2CO (hot) ^{o}		16
(ii)	None ^{j}	6M-HNO_3 ^{g,b,l}		75
$Np(NO_3)_4$·4dpso	MeCN ^{e,f,r}	MeCN	CCl_4	51
$Pu(NO_3)_4$·3dpso	None ^{j}	2M-HNO_3 ^{s}		

[a] Oil precipitated which became crystalline on grinding under the hot supernatant liquid. [b] Oil precipitated from reaction solution by 2-methylbutane. [c] Oil crystallised on standing under 2-methylbutane overnight. [d] Crystals separated on slow evaporation of the solvent. [e] Corresponding chloride complex with methyl cyanide solution of silver(I) nitrate. [f] Oil obtained by vacuum evaporation of the solvent. [g] Oil crystallised on standing under carbon tetrachloride (3 days). [h] Oil separated at 0 °C. [i] Oil solidified at 0 °C after 10 h. [j] $Cs_2M(NO_3)_6$ (M = U, Np, or Pu as appropriate). [k] Oil became crystalline on standing at room temperature (3 days). [l] Oil redissolved in acetone, filtered, and reprecipitated with 2-methylbutane (×3). [m] Saturated with sulphamic acid. [n] Oily product became a gum on grinding under 2-methylbutane (4 days) and solidified on standing under carbon tetrachloride (2 days). [o] Boiled for 2 × 30 min. [p] Oil solidified on grinding under 2-methylbutane. [q] Attempted preparation from $NpCl_4$·3dpso (footnote *e*) gave '$Np(NO_3)_4$·2·6dpso' (90% yield). [r] Initial oily product dissolved in a dichloromethane solution of dpso. [s] Brown oil formed on heating; dissolved in dichloromethane and reprecipitated therefrom with 2-methylbutane. Oil solidified on standing under 2-methylbutane with intermittent grinding (several days).

TABLE 4

Analytical results

Compound	M.p.	Metal (%)		Carbon (%)		Hydrogen (%)		Nitrogen (%)		Sulphur (%)	
	(t/°C) ^{b}	Found	Req.	Found	Req.	Found	Req.	Found	Req.	Found	Req.
$Th(NO_3)_4$·3deso	116	29·0	29·1	18·0	18·1	3·9	3·8	7·1	7·0	12·1	12·2
$U(NO_3)_4$·3deso	68(d)	29·9	29·6	17·0	17·9	3·5	3·7	6·0	6·9		
$Np(NO_3)_4$·3deso		30·1	29·5					30·8 ^{a}	30·9 ^{a}		
$Th(NO_3)_4$·4dpso	53—55	17·8	18·0	44·1	44·6	3·0	3·7	18·9 ^{a}	19·2 ^{a}		
$U(NO_3)_4$·4dpso	93 (d)	19·5	18·4					20·1 ^{a}	19·3 ^{a}		
$Np(NO_3)_4$·4dpso		18·5	18·3					19·2 ^{a}	19·2 ^{a}		
$Pu(NO_3)_4$·4dpso		18·8	18·4					20·8 ^{a}	19·2 ^{a}		
$Th(NO_3)_4$·3dpso	165	21·5	21·4	39·5	39·8	3·0	2·8	5·2	5·2	8·7	8·8
$U(NO_3)_4$·3dpso	64 (d)	21·5	21·8	39·5	39·6	2·9	2·7	4·9	5·1		
$Np(NO_3)_4$·3dpso		20·7	21·7					22·6 ^{a}	22·7 ^{a}		
$Th(NO_3)_4$·3dnso	180 (d)	16·7	16·7					17·7 ^{a}	17·9 ^{a}		
$Th(NO_3)_4$·3dnso·MeCOOEt	180 (d)	15·7	15·7					16·7 ^{a}	16·8 ^{a}		

[a] NO_3^- content. [b] d = decomposition temperature.

Physical Measurements.—I.r. and electronic spectra, conductivities, and *X*-ray powder-diffraction patterns were obtained as described previously;[3] Raman spectra of powdered solids were recorded using a Cary 83 Raman Spectrometer.

The authors thank Mr. M. A. Hart for the microanalyses, (C, H, N, and S) and Mrs. K. M. Glover and Mr. F. J. G. Rogers for assistance with α-spectrometry and α-counting. Two of us (K. W. B., P. J. A.) are indebted to the UKAEA, AERE, Harwell and to the S.R.C. for the research grants which supported this work and another (O. V. L.) is indebted to the Overseas Development Administration for the award of a technical assistance scholarship.

[4/2043 *Received, 4th October,* 1974]

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