Dimethyl Sulphoxide Complexes of Some Actinoid Tetranitrates

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Complexes of some actinoid tetranitrates with dimethyl sulphoxide (dmso), $M(NO_3)_4,x$dmso [x = 6 (Th, Np, and Pu) and 3 (Th, U, Np, and Pu)] have been prepared by reactions in non-aqueous media. I.r. and Raman spectral results are reported for these complexes together with i.r. spectra of the hexanitrato-complexes $Cs_2[M(NO_3)_6]$ (M = Th and Np). *X*-Ray powder diffraction data are also presented together with details of the electronic spectra of the uranium, neptunium, and plutonium complexes.

COMPLEXES of thorium tetranitrate with dimethyl sulphoxide (dmso) $Th(NO_3)_4,x$dmso,yH_2O (x = 3, 4, 6, 9, and 12 for $y = 0$; x = 3, 7, and 8 for $y = 2$; $x = 11$, $y = 1$) and with diphenyl sulphoxide (dpso) $Th(NO_3)_4$,3dpso have been reported,[1-5] but analogous complexes of other actinoid tetranitrates have not been recorded. In fact very little is known about donor-ligand complexes of uranium, neptunium, and plutonium tetranitrates.[6,7] In the case of actinoid tetrachlorides it is known that the pentakis complexes MCl_4,5dmso become progressively easier to degrade to the tris complexes MCl_4,3dmso as the ionic radius of the actinoid element decreases from thorium to plutonium, the pentakis complex being unknown for the latter.[8] It was therefore of interest to prepare dmso complexes of some actinoid tetranitrates (Th, U, Np, and Pu) and examine their properties in order to ascertain whether a similar trend obtained, and to determine the mode of co-ordination of the nitrate groups and the sulphoxide ligand in these complexes.

RESULTS AND DISCUSSION

Stoicheiometry of the Complexes.—Reaction between thorium tetranitrate pentahydrate and a large excess of dimethyl sulphoxide (dmso) in acetone, followed by recrystallisation of the precipitate from acetone–dmso, resulted in formation of the complex $Th(NO_3)_4$,6dmso, whereas recrystallisation from acetone–2-methylbutane or acetone–ethyl acetate mixtures yielded the tris complex $Th(NO_3)_4$,3dmso in the α-crystal modification. This is metastable, slowly changing to the β-form which is also obtained on crystallisation from acetone. A third crystallographically distinct modification of the complex $Th(NO_3)_4$,3dmso was formed when the hexakis complex was treated with anhydrous carbon tetrachloride. Hexakis and tris complexes of neptunium tetranitrate were obtained in a similar manner from $Cs_2[Np(NO_3)_6]$ and dmso, whilst metathesis of $PuCl_4$,3dmso with silver nitrate in methyl cyanide–dmso yielded $Pu(NO_3)_4$,3dmso. A similar reaction involving $Cs_2[PuCl_6]$, a large excess of dmso, and the stoicheiometric quantity of silver nitrate yielded a complex of composition $Pu(NO_3)_4$,7·1dmso when the initial product was recrystallised from acetone. This phase lost dmso continuously when exposed to a vacuum (10^{-4} Torr), the final product after several hours being γ-$Pu(NO_3)_4$,3dmso. There was no evidence (weight against time plot) for formation of a stable hexakis complex. The complex $Np(NO_3)_4$,6dmso loses dmso relatively slowly at 10^{-4} Torr, 3 days being required for complete conversion to the tris complex, whilst $Th(NO_3)_4$,6dmso appears to be stable under such conditions. These stability trends are similar to those recorded earlier for the actinoid tetrachloride pentakis(dmso) complexes.

An unstable uranium tetranitrate tris complex could be prepared by metathesis of UCl_4,3dmso with silver nitrate in methyl cyanide provided that the product was isolated rapidly by the addition of diethyl ether. Slow crystallisation from acetone–2-methylbutane at ice temperature resulted in oxidation, yielding only $UO_2(NO_3)_2$,2dmso; the solid tris complex also underwent oxidation within a few hours with liberation of nitrogen dioxide and a foul-smelling organic material, which had

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[1] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.

[2] G. Gritzner, V. Gutmann, and M. Michlmays, *Z. analyt. Chem.*, 1967, **224**, 245.

[3] N. Gründüz, B. C. Smith, and M. A. Wasseff, *Comm. Fac. Sci. Univ. Ankara, ser B.*, 1969, 31.

[4] A. K. Molodkin, O. M. Ivanova, Z. V. Betyakova, and L. E. Kolesnikova, *Russ. J. Inorg. Chem.*, 1970, **15**, 1692.

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

[6] K. W. Bagnall, 'The Actinide Elements,' Elsevier, Amsterdam, 1972.

[7] D. Brown, 'Comprehensive Inorganic Chemistry,' Pergamon Press, Oxford, 1973, vol. 5, p. 277.

[8] K. W. Bagnall, D. Brown, D. G. Holah, and F. Lux, *J. Chem. Soc. (A)*, 1968, 465.

an odour resembling that of dimethyl sulphide. However, it is improbable that this sulphide is produced since it is known [9] to be oxidised to dmso by nitrogen dioxide. Attempted preparation of the complex $U(NO_3)_4$,6dmso was unsuccessful; the reaction product decomposed, even in a dry atmosphere, before it could be characterised.

In view of these observations on uranium tetranitrate complexes, and the fact that protactinium(IV) is appreciably less stable with respect to oxidation than is uranium(IV), preparation of protactinium tetranitrate complexes was not attempted. Considering the stability with respect to oxidation of the complex $U(NO_3)_4$,2·5dma [10] (dma = *NN*-dimethylacetamide) and oxidation of protactinium(IV) in the $PaCl_4$–dmso system,[8] it seems probable that the ligand rather than the nitrate ion is the oxidant in the uranium tetranitrate–dmso system. It would obviously be of interest to have information on other $U(NO_3)_4$–sulphoxide systems in order to help clarify this problem.

The dmso complexes identified during the present investigation are listed in Table 1. We observed no evidence for formation of the complex $Th(NO_3)_4$,4dmso, previously reported [2] to be formed when the tetranitrate pentahydrate was heated with dmso under reflux at 50 °C and 10^{-2} Torr. In view of our results, and the fact that Cotton and Francis [1] obtained the hexakis complex by vacuum evaporation of a dmso solution containing $Th(NO_3)_4,5H_2O$, it would appear probable that the tetrakis complex was a mixture of the 1 : 6 and 1 : 3 complexes rather than an individual complex. We have not attempted to repeat the preparation of the complexes $Th(NO_3)_4$,9dmso [4] and $Th(NO_3)_4$,12dmso.[3]

TABLE 1

Stoicheiometry of actinoid tetranitrate complexes with dimethyl sulphoxide

Th	U	Np	Pu
1 : 6	*a*	1 : 6	*b*
α-1 : 3			
β-1 : 3			
γ-1 : 3 [c]	γ-1 : 3	γ-1 : 3	γ-1 : 3

[a] Product rapidly oxidises to unidentified uranium(VI) species. [b] A relatively unstable phase (*ca.* 7·1dmso) was obtained which quickly lost dmso at 10^{-4} Torr to yield the 1 : 3 complex. [c] Tentatively called γ-$Th(NO_3)_4$,3dmso on the basis of the similarity between its *X*-ray powder pattern and those of the other γ-modifications. The possibility remains, however, that it is a fourth crystal form.

The hexakis complexes are moisture-sensitive and dissolve in solvents such as acetone, nitromethane, and methyl cyanide, but are insoluble in non-polar solvents such as 2-methylbutane and ethyl acetate. The tris complexes exhibit similar solubility properties but unlike the hexakis complexes they appear to be stable in the atmosphere.

X-Ray Crystallographic Studies.—Only one crystal modification (γ) was identified for tris(dmso) complexes of uranium, neptunium, and plutonium tetranitrate, despite the fact that all the complexes were obtained under conditions which resulted in formation of α-$Th(NO_3)_4$,3dmso. Slow crystallisation from acetone, which yielded β-$Th(NO_3)_4$,3dmso and resulted in oxidation of the uranium(IV) complex, was not studied with the remaining tris complexes which were available only in small quantities.

Single-crystal studies [11] have shown that the complex β-$Th(NO_3)_4$,3dmso possesses monoclinic symmetry, space group $P2_1/c$ with $a_0 = 15{\cdot}50$, $b_0 = 15{\cdot}71$, and $c_0 = 16{\cdot}16$ Å and β = 146·70°. Preliminary results indicate that the four nitrate groups are each bidentate and that all three dmso molecules are co-ordinated *via* the oxygen atom, the thorium atom being eleven-co-ordinate. The stereochemistry around each thorium atom is close to a singly capped pentagonal antiprism (D_{5d}) [*cf.* the arrangement in the $Th(NO_3)_4,3H_2O$ units shown [12] previously to exist in the complex $Th(NO_3)_4,5H_2O$]. An indexed powder pattern for this β-phase is to be found in Supplementary Publication No. SUP 20 814 (4 pp.).* The derived cell constants were identical with those obtained from the single-crystal study. Partial *X*-ray powder diffraction results for the complexes α-$Th(NO_3)_4$,3dmso and γ-$Np(NO_3)_4$,3dmso are also listed in SUP 20814 together with similar results for $Th(NO_3)_4$,6dmso with which the neptunium analogue is isostructural.

X-Ray powder studies indicate that the hexanitrato-complexes $Cs_2[Th(NO_3)_6]$ and $Cs_2[Np(NO_3)_6]$, which were employed as starting materials during this study, are isostructural. A partial *X*-ray powder pattern for the former complex is also shown in SUP 20814.

I.r. and Raman Spectra.—As observed previously for the actinoid tetrachloride dmso complexes, the sulphoxide ligand is co-ordinated to the tetranitrates *via* the oxygen atom, the S=O stretching vibration shifting to lower frequencies on co-ordination. In order to identify the S=O vibration in the spectra of the complexes, all of which exhibited two or three strong bands between 900 and 1 000 cm^{-1}, deuteriated hexakis and tris complexes of thorium tetranitrate were prepared and their i.r. spectra compared with those of the normal complexes. The results obtained for the hexakis complexes are shown in Table 2, from which it is apparent that the S=O stretching vibration occurs at 900 cm^{-1}. Positions for the remaining complexes are shown in Table 3. Δν(S=O) increases from thorium to plutonium for each series of complexes, but the differences between the values for the neptunium and plutonium complexes are relatively small. Such an increase can be attributed to the actinoid contraction resulting in a shortening of the metal–oxygen bond with decreasing ionic radius of M. The larger difference between thorium and uranium is compatible with the

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue (items less than 10 pp. are supplied as full size copies).

[9] C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 1956, 2705.

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

[11] A. J. Smith, personal communication. We are grateful to Dr. A. J. Smith for obtaining unit-cell dimensions of the complex β-$Th(NO_3)_4$,3dmso for us by single-crystal techniques.

[12] J. C. Taylor, M. H. Mueller, and R. L. Hitterman, *Acta Cryst.*, 1966, **20**, 842.

TABLE 2

I.r. spectra (cm^{-1}) of the complexes $Th(NO_3)_4$,6dmso and $Th(NO_3)_6$,6([$^2H_6$]dmso) in the range 4 000—700 cm^{-1}

$Th(NO_3)_4$,6dmso	Assignment [a]	$Th(NO_3)_4$,6([$^2H_6$]dmso)
3 008m	Asym. C–H(C–D) stretch	2 263m
2 921m	Sym. C–H(C–D) stretch	2 138m
1 490s	Bidentate nitrate stretch(ν_1)	1 490s
1 430s 1 411m	Asym. $CH_3(CD_3)$ deformation	1 028s
1 350s,b	Ionic nitrate stretch	1 350s,b
b	Sym. $CH_3(CD_3)$ deformation	1 052m
1 315s 1 295s 1 280 sharp	Covalent nitrate stretch (ν_4)	1 308s, sharp 1 289s, sharp
1 032 sharp	Covalent nitrate stretch (ν_2)	1 035s
1 000s 945s	$CH_3(CD_3)$ rock	794w 779m, sharp
960s	S=O stretch	960s,b
833m, sharp	Ionic nitrate out-of-plane bend	840s, sharp
814m, sharp	Covalent nitrate out-of-plane bend (ν_6)	820w, sharp [c]
739m, sharp [d] 722m [d]	Covalent nitrate in-plane bends (ν_3,ν_5)	744w, sharp [d] 728w [d]

s = Strong, m = medium, w = weak, and b = broad.

[a] Alkyl assignments are based on earlier results (F. A. Cotton, R. Francis, and W. D. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534.) [b] Masked by the strong covalent nitrate band, ν_4. [c] The CD_3 rocking mode probably contributes to this band. [d] There may be a contribution from the asym C–S stretch.

relative differences in ionic radii,[13] *viz.* Th^{4+} 0·984, U^{4+} 0·929, Np^{4+} 0·913, and Pu^{4+} 0·896 Å. It is interesting to note that although $\Delta\nu$(S=O) values are consistently greater for tris complexes than for hexakis complexes the differences (*ca.* 11 cm^{-1}) are relatively small. There are, in fact, no bands in the spectra of the latter series of complexes which can be associated with free or weakly bound ligand (*cf.* MCl_4,7dmso complexes [8]), but bands associated with ionic nitrate were observed (Tables 2 and 3). Without structural data for the hexakis complexes, it is not possible to discuss further the relative shifts in ν(S=O) which occur on co-ordination as the balance of attractive and repulsive forces will obviously be dependent on the respective co-ordination numbers of the actinoid(IV) ions as well as on their sizes.

Raman studies on randomly orientated crystals of the complex β-$Th(NO_3)_4$,3dmso showed that the relative intensities of the three highest nitrate frequencies are in accord with the suggestion [14] that the presence of bidentate nitrate groups can be deduced from the relative intensities of these three frequencies. The observed bands were ν_1 1 510w, ν_4 1 400vw, ν_2 1 040s, ν_6 820vw, ν_3 749w, and ν_5 29m cm^{-1}. The complex α-$Th(NO_3)_4$,3dmso gave a virtually identical Raman spectrum, ν(S=O) in each complex occurring at 950 cm^{-1}. I.r. assignments for the covalent nitrate bands of various tetranitrate dmso complexes, $Cs_2[Th(NO_3)_6]$, and $Cs_2[Np(NO_3)_6]$ (Table 3) are based on the presence of bidentate groups. This, on the evidence available, appears reasonable for the tris complexes and, by analogy with $(NH_4)_2[Ce(NO_3)_6]$ [15] and $Mg[Th(NO_3)_6]$,$8H_2O$,[16] for the hexanitrato-complexes. On the basis of the i.r. results the hexakis complexes contain both ionic and covalent nitrate groups (footnote *b*, Table 3).

TABLE 3

I.r. results (cm^{-1}) for the actinoid(IV) nitrate complexes

Complex	Colour	Nitrate vibrations [a] ν_1	ν_4	ν_2	ν_6	ν_3	ν_5	ν(S=O)	$\Delta\nu$(S=O)
$Cs_2[Th(NO_3)_6]$	White	1 550sh 1 527	1 276	1 206	805	738	702		
$Cs_2[Np(NO_3)_6]$	Pink	1 523	1 280	1 028	802	742	702		
$Th(NO_3)_4$,6dmso [b]	White	1 490	1 315 1 295 1 280	1 032	814	739	722	960	96
$Np(NO_3)_4$,6dmso [b]	Green	1 487	1 308 1 297 1 276	1 206	805	732	715	951	105
$Pu(NO_3)_4$,*x*dmso [b,c]	Red-orange	1 510	1 313 1 278	1 029	808	737	722	950	106
β-$Th(NO_3)_4$,3dmso [d]	White	1 502	1 316 1 289	1 037	818 812	756 748	728	956	100
$U(NO_3)_4$,3dmso	Green	1 515	1 287	1 037	812	753	726	937	119
$Np(NO_3)_4$,3dmso	Grey-green	1 510	1 283	1 026	802	742	715	939	117
$Pu(NO_3)_4$,3dmso	Green	1 515	1 284	1 031	805	747	718	937	119

[a] Assignments are those recommended for bidentate nitrate groups (R. W. Hester and W. L. Grossman, *Inorg. Chem.*, 1966, **5**, 1308; J. L. Bullock, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2257). [b] Ionic nitrate vibrations were observed at 1 350 and 833, 1 345 and 827, and 1 350 and 831 cm^{-1}, respectively, for the Th, Np, and Pu complexes. [c] $x = ca.$ 7·1. [d] Virtually identical band positions were observed for the α- and γ-modifications although $\Delta\nu$(S=O) increased to 105 cm^{-1}.

Molodkin *et al.*[4] published similar results for the complex $Th(NO_3)_4$,6dmso whilst our own studies were in progress, and also reported the presence of ionic nitrate groups in the 1 : 9 dmso complex. Thorium tetranitrate–urea complexes have similarly been shown [17] to contain ionic

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[13] J. R. Peterson and B. B. Cunningham, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 327.

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

[15] T. A. Beineke and J. Delgaudio, *Inorg. Chem.*, 1968, **7**, 715.

[16] S. Šćavničar and B. Prodič, *Acta Cryst.*, 1964, **18**, 698.

[17] A. K. Molodkin, O. M. Ivanova, and L. E. Kozina, *Russ. J. Inorg. Chem.*, 1968, **13**, 1192.

nitrate when four or more ligand molecules are coordinated to the thorium atom.

Comparison of the far i.r. spectra of the dmso complexes (700—225 cm^{-1}) with that of the free ligand did not permit assignment of metal–oxygen (ligand) or metal–oxygen (nitrate) stretching frequencies. However strong features at 232 and 237 cm^{-1} in the spectra of the complexes $Cs_2[Th(NO_3)_6]$ and $Cs_2[Np(NO_3)_6]$, respectively, can probably be assigned to metal–oxygen (nitrate) stretching vibrations. Bands at similar frequencies have been assigned [18] to metal–oxygen vibrations in the complexes $Th(NO_3)_4,5H_2O$ and $Th(NO_3)_4,4H_2O$.

Visible Spectra.—The spectrum of solid γ-$U(NO_3)_4$,3dmso (400—800 nm) is virtually identical with that observed for a solution of the complex in anhydrous methyl cyanide, with bands at 435, 485, 555, 614, and 664 nm, suggesting that the probably eleven-co-ordinate species in the solid also exists in this solvent. The spectra of certain other complexes are listed in Table 4, from which it can be seen that the two neptunium tetranitrate dmso complexes in nitromethane exhibit spectra which differ only in a few respects from that of the presumably twelve-co-ordinate hexanitratoneptunate(IV) in methanol. The similarity of the spectra of the tris and hexakis dmso complexes suggests that on dissolution in anhydrous nitromethane dmso is released from the latter complex and, since solid-state and solution spectra of the complex γ-$U(NO_3)_4$,3dmso are the same, the ionic nitrate presumably becomes covalent. The fact that no ionic nitrate band was observed around 830 cm^{-1} (the higher-frequency band occurred in the region of strong solvent absorption) in the i.r. spectrum of the complex $Th(NO_3)_4$,6dmso in nitromethane supports this view. The covalent nitrate band, ν_6, occurred at *ca.* 810 cm^{-1} (*cf.* Table 3) for both the tris and hexakis complexes in this solvent.

TABLE 4

Visible and near i.r. spectral results

$Cs_2[Np(NO_3)_6]$ [a]		$Np(NO_3)_4$,6dmso [b]		$Np(NO_3)_4$,3dmso [b]		$Pu(NO_3)_4$,3dmso [c]	
λ/nm	ε/l mol^{-1} cm^{-1}	λ/nm	ε/l mol^{-1} cm^{-1}	λ/nm	ε/l mol^{-1} cm^{-1}	λ/nm	ε/l mol^{-1} cm^{-1}
422	15	423	25	424	21	502	s
467	11	473	14	473	12	548	m
502	16	504	18	504	16	608	w
535	13	530	14	530	12	654	m
583	10	602	11	602	11	682	s
630	8					741	m
718	34	718	46	718	40	800	m
735	35	736	48	736	42	1 070	m
770	25	767	27	767	24		
833	31	849	37	849	33		
892	40						
965	28	984	29	985	25		
997	17						
1 116	6	1 143	6	1 143	5		
1 170	6	1 162	7	1 161	5		

[a] In methanol. [b] In nitromethane. [c] Solid-state transmission spectrum, relative intensities given as s = strong, m = medium, and w = weak.

EXPERIMENTAL

Reagents.—Thorium tetranitrate hydrate (B.D.H. Ltd.) was used as supplied. The complexes $Cs_2[Th(NO_3)_6]$ and $Cs_2[Np(NO_3)_6]$ were prepared according to available methods,[10] as were UCl_4,3dmso and $PuCl_4$,3dmso.[8] Dimethyl sulphoxide was flushed with nitrogen and stored over molecular sieves (5A) in a nitrogen-atmosphere box. The deuteriated ligand was prepared as described previously.[19] The complexes were prepared and handled in dry-atmosphere boxes (water $\leqslant$20 p.p.m., oxygen $\leqslant$20 p.p.m.) to afford protection against atmospheric moisture and the radiation emitted by the radioactive isotopes ^{237}Np and ^{239}Pu.

Thorium Tetranitrate–Dimethyl Sulphoxide (1/6).—A large excess of dmso (35·24 mmol; 2·5 cm^3) was added, with stirring, to a solution of the complex $Th(NO_3)_4,5H_2O$ (1·37 mmol, 779·2 mg) in acetone. The white, deliquescent crystalline *product* was recrystallised from acetone–dmso (3 cm^3), washed with chloroform (2 cm^3), and vacuum dried (10^{-4} Torr) for several hours (yield 80%). The deuteriated complex was prepared by the same procedure.

Neptunium Tetranitrate–Dimethyl Sulphoxide (1/6).—dmso (2·82 mmol, 0·2 cm^3) Was added to a suspension of the complex $Cs_2[Np(NO_3)_6]$ (0·43 mmol, 374 mg) in acetone (2 cm^3). The mixture was stirred vigorously and the supernatant liquid removed after centrifugation. Addition of dmso (14·1 mmol, 1 cm^3) to this solution and the combined acetone washings (2 cm^3) of the precipitated $CsNO_3$ yielded a hygroscopic, lime-green, crystalline *product* which was washed with acetone (2 cm^3) and vacuum dried (10^{-4} Torr) for 2 h. This material, which was slightly ligand-deficient, was treated with a solution of dmso (1·5 mmol, 0·11 cm^3) in acetone (1 cm^3) for 3 days and a pure product isolated as before (yield 80%).

Thorium Tetranitrate–Dimethyl Sulphoxide (1/3).—Dimethyl sulphoxide (8·8 mmol, 0·63 cm^3) was added to the tetranitrate pentahydrate (1·47 mmol, 840·3 mg) in acetone (5 cm^3). The white, non-hygroscopic *product* obtained by addition of 2-methylbutane and cooling at ice temperature for 1 day was recrystallised from acetone–2-methylbutane, washed with 2-methylbutane, and vacuum dried (10^{-4} Torr). This procedure, and a similar one involving acetone–ethyl acetate, resulted in formation of the metastable α-*modification* (yields *ca.* 80%). Recrystallisation from acetone yielded the β-*modification*, whilst the third crystal form (γ)

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[18] J. Ferraro and A. Walker, *J. Chem. Phys.*, 1966, **45**, 550.

[19] F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, jun., and M. A. Nelson, *J. Chem. Soc.*, 1959, 4138.

was obtained when the complex $Th(NO_3)_4$,6dmso was degraded with dry carbon tetrachloride.

Uranium Tetranitrate–Dimethyl Sulphoxide (1/3).—A solution of silver(I) nitrate (3·82 mmol, 648 mg) in methyl cyanide (5 cm^3) was mixed with powdered UCl_4,3dmso (0·95 mmol, 586 mg). The supernatant liquid was removed after 5 min by centrifugation and diethyl ether (20 cm^3) added to it to yield an oil which, on grinding under the solution, yielded a pale green *solid*. This was washed with diethyl ether (5 cm^3) and vacuum dried (10^{-4} Torr) for 1 h (yield 60%). Slow recrystallisation from acetone–2-methylbutane at ice temperature resulted in formation of the hexavalent *complex*, $UO_2(NO_3)_2$,2dmso.

Neptunium Tetranitrate–Dimethyl Sulphoxide (1/3).—The initial product (in acetone, 4 cm^3), from a reaction analogous to that described above for preparation of the complex $Np(NO_3)_4$,6dmso, was precipitated by addition of 2-methylbutane (10 cm^3). The pale green solid was dissolved in acetone (2 cm^3), insoluble caesium nitrate separated by centrifugation, and the *product* isolated by addition of 2-methylbutane (8 cm^3). This was washed with 2-methylbutane and vacuum dried (yield 90%). Alternatively, the same crystal modification (γ) was obtained when the hexakis complex was exposed to a non-static vacuum (10^{-4} Torr) for *ca.* 3 days.

Plutonium Tetranitrate–Dimethyl Sulphoxide (1/3).—A reaction analogous to that described for the tris uranium tetranitrate complex yielded an oil on vacuum evaporation of the initial methyl cyanide supernatant liquid and washings. This was dissolved in acetone and traces of silver(I) chloride removed by centrifugation, following which the oil was reformed by the addition of 2-methylbutane. After four such cycles the oil was allowed to solidify under 2-methylbutane; the resulting solid was washed with this solvent and vacuum dried (yield 60%). Alternatively, a phase of composition $Pu(NO_3)_4$,7·1dmso, obtained during attempts to prepare the hexakis complex {$Cs_2[PuCl_6]$ plus an excess of dmso and the stoicheiometric amount of silver(I) nitrate in methyl cyanide} was pumped at 10^{-4} Torr for several hours, during which time dmso was lost continuously until the tris complex was formed.

Thorium, uranium, neptunium, and plutonium were determined as described previously [20] and nitrate was precipitated and weighed as the Nitron complex.[21] Results are shown in Table 5 together with those for carbon, nitrogen, sulphur, and hydrogen, determined by standard combustion techniques, for selected complexes. I.r. spectra (4 000—225 cm^{-1}), visible and near i.r. spectra (400—1 200 nm), and *X*-ray powder diffraction patterns were obtained as described recently.[20] Raman spectra of randomly oriented crystals were recorded using a Spex 1401 spectrometer with a photon counting unit and an excitation frequency of 5 145 Å provided by a 250 mW argon–ion laser.

TABLE 5

Analytical results (%)

(*a*) Metal and Nitrate

	Found		Calc.		
Complex	M	NO_3	M	NO_3	Yield
$Th(NO_3)_4$,6dmso	24·5	25·9	24·5	26·2	80
$Np(NO_3)_4$,6dmso	25·1	25·9	24·9	26·0	80
$Th(NO_3)_4$,3dmso	32·7	34·6	32·5	34·7	80
$U(NO_3)_4$,3dmso	33·1		33·0		60
$Np(NO_3)_4$,3dmso	32·9	34·4	32·9	34·5	90
$Pu(NO_3)_4$,3dmso	Identified by *X*-ray powder results				60

(*b*) Carbon, hydrogen, nitrogen, and sulphur

	Found				Calc.			
Complex	C	H	N	S	C	H	N	S
$Th(NO_3)_4$,6dmso	15·3	4·1			15·2	3·8		
$Th(NO_3)_4$,3dmso	10·6	2·8			10·1	2·5		
$U(NO_3)_4$,3dmso	10·0	2·5	7·8	13·7	10·0	2·5	7·8	13·4

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

[21] A. I. Vogel, ' Textbook of Quantitative Analysis,' 3rd edn., Longmans, London, 1961.