Phosphine Oxide Complexes of Thorium(IV), Uranium(IV), Neptunium(IV), and Dioxouranium(VI) Nitrates

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Complexes of the actinoid tetranitrates with phosphine oxides, $M(NO_3)_4,xR_3PO$ (R = Me(tmpo), M = Th, U, X = 4 and M = Th, Np, x = 3; R = Pr^n(tprpo), M = Th, U, Np, x = 2·67; R = Bu^n(tbpo) M = Th, x = 4; R = Me_2N-(hmpa), M = Th, U, Np, x = 2; R = Ph(tppo), M = Np, x = 2) and with the bidentate phosphine oxides, octamethylpyrophosphoramide(ompa), $Th(NO_3)_4$,2·5ompa and $M(NO_3)_4$,1·5ompa (M = Th, U, Np), bis(diphenylphosphinyl)methane (ppm), $Th(NO_3)_4$,1·5ppm and bis(diphenylphosphinyl)ethane, $Th(NO_3)_4$,2ppe, have been prepared, along with the uranium(VI) analogues $UO_2(NO_3)_2,xL$ (L = tprpo, x = 2; L = ppm, x = 1·5). The i.r., Raman, and electronic spectra of these complexes are discussed.

ALTHOUGH phosphine oxides have been investigated as possible alternatives to tri-n-butyl phosphate in the chemical processing of neutron-irradiated uranium by solvent extraction from nitrate media, relatively few complexes of the actinoid nitrates have been characterised, for the isolation of the complexes formed in these processes has been of secondary importance compared to the extractive properties of the ligands. The only recorded anhydrous complexes of the tetranitrates appear to be the bis triphenylphosphine oxide compounds, $M(NO_3)_4$,2tppo (M = Th,[1,2] U,[3] Pu[4]), $U(NO_3)_4$,$x$hmpa (x = 2,4[3]), $[U(NO_3)_3(hmpa)_4]BPh_4$,[3] and the (diethylphosphinyl)ethane (epe) complex, $Th(NO_3)_4$,3epe, which appears [5] to be ionic, $[Th(NO_3)_2(epe)_3]^{2+}$ $(NO_3)_2^-$. The lack of information on the uranium(IV) and neptunium(IV) complexes of these ligands is a reflection of the instability of the nitrates of these two elements with respect to oxidation of uranium(IV) [6] and neptunium(IV).[7] In contrast, several bis phosphine oxide complexes have been recorded for uranyl nitrate, $UO_2(NO_3)_2$,2R_3PO (R = Me,[8] Bu^n,[9-11] Ph,[8,9,12,13] Me_2N [14]) and the ompa complex, $UO_2(NO_3)_2$,ompa, is also known.[15] It was therefore of interest to investigate the possibility of isolating uranium(IV) and neptunium(IV) nitrate complexes with a variety of phosphine oxides in order to ascertain whether the size of the alkyl or aryl substituents had any marked influence on the stoicheiometry of the complexes that might be obtained, and to compare the products with their thorium(IV) analogues where known, or to prepare the latter if not, in order to see whether there were any observable trends that could be ascribed to the decreasing radius of the central atom along the series. In those instances where the stoicheiometries of the actinoid(IV) species appeared to be unusual, the uranyl(VI) analogue was also prepared. Trimethyl (tmpo), tri-n-propyl (tprpo), tri-n-butyl (tbpo), and triphenyl (tppo) phosphine oxides, hexamethylphosphoramide (hmpa), octamethylpyrophosphoramide (ompa), bis(diphenylphosphinyl)-methane (ppm) and -ethane (ppe) were selected for this study.

Because i.r. spectroscopic information is available only for $Th(NO_3)_4$,2tppo,[2] $UO_2(NO_3)_2$,2tbpo,[10] $UO_2(NO_3)_2$,2tppo,[16] and, to a very limited extent, $UO_2(NO_3)_2$,2hmpa,[14,15] and $UO_2(NO_3)_2$,ompa,[15] the i.r. and Raman spectra were recorded for both the previously known and new phosphine oxide complexes in an attempt to ascertain the bonding mode of the nitrate groups in them.

The Complexes.—The thorium tetranitrate and uranyl(VI) nitrate compounds were prepared by treating the hydrated nitrates with the ligand in a suitable solvent. The uranium(IV) and neptunium(IV) analogues were obtained in a similar manner from the hexanitratocomplexes, $Cs_2M(NO_3)_6$, the only problems being the elimination of the liberated caesium nitrate and, more serious, the ready oxidation of several of the resulting uranium(IV) complexes to the corresponding uranyl(VI) compound. The first problem was easily overcome by the selection of a suitable solvent system in which the required complex would dissolve and the unwanted materials would not, but because of differences between the solubilities of the various complexes, it was not possible to use a single solvent system throughout. The oxidation of uranium(IV) could not be circumvented in the attempted preparations of the complexes of uranium tetranitrate with tbpo, tppo, ppe, or ppm, although in the last instance some preparations gave a green solid which dissolved in chloroform, the resulting solution yielding a green precipitate of approximate composition $U(NO_3)_4$,1·67ppm on the addition of 2-methylbutane. However, most of the attempted preparations yielded $UO_2(NO_3)_2$,1·5ppm.

tmpo and tbpo Complexes.—The stoicheiometries of the products obtained with the monodentate phosphine oxides depended to a considerable extent on the size of the ligand; with the smallest of the ligands, tmpo, thorium and uranium tetranitrates formed the tetrakis complexes, $M(NO_3)_4$,4tmpo. Although the mother liquor from the recrystallization of the thorium complex yielded a small amount of the corresponding tris complex, the uranium tris complex could not be isolated and, in contrast, under similar conditions neptunium tetranitrate formed only the tris complex. The i.r. spectra (Table 1) of the tris complexes indicated that all the nitrate groups were covalently bound (the assignments in Table 1 refer to bidentate nitrate groups), whereas additional modes that could be assigned to ionic nitrate were present in the spectra of the tetrakis tmpo and tbpo complexes (Table 2). This suggests that they are probably of the form $[M(NO_3)_3(R_3PO)_4]^+(NO_3)^-$ and the molar conductivities of the tetrakis complexes in nitromethane (Table 3) are consistent with 1 : 1 electrolyte behaviour. A somewhat similar ionic structure has been reported [17] for the dimethyl sulphoxide (dmso) complex $ThCl_4$,5dmso, which is an ion pair, $[ThCl_3(dmso)_5]^+Cl^-$ in the solid state.

It has been suggested [18] that the sequence of relative intensities of the three highest frequency features in the Raman spectra of nitratocomplexes should provide a means of distinguishing between unidentate and bidentate nitrato-groups. In particular, the second highest frequency in the spectra of the former is strong, or very strong, whereas in the spectra of the latter it is weak. Using this criterion, it appears from the Raman spectra of randomly oriented crystals of the compounds that the

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covalent nitrato-groups in the tetrakis actinoid(IV) and bis dioxouranium(VI) nitrate complexes are bidentate, whereas some or all of the nitrato-groups appear to be unidentate in $Np(NO_3)_4$,3tmpo. The method does not distinguish between symmetrical and bridging bidentate groups, but the former are the more likely. Because of the oxidation of the uranium(IV) complexes in the laser beam, observations were restricted to the thorium(IV), neptunium(IV), and dioxouranium(VI) compounds.

TABLE 1

Infrared spectra of the nitrate complexes cm^{-1}

Compound	Colour	Nitrate vibrations ν_1	ν_4	ν_2	ν_6	ν_3/ν_5	ν(P=O)	$\Delta\nu$(P=O)
$Th(NO_3)_4$,3tmpo	White	1513s, br	1283m	1033m	813w	762w	1083s	80
$Th(NO_3)_4$,4tmpo	White	1512m	1287s	1030m	820m, 813w	760m	1085s	78
$U(NO_3)_4$,4tmpo	Green	1510w, sh	1292s	1035m, sh	820w	764w, 750vw	1087s	76
$Np(NO_3)_4$,3tmpo	Dark green	1502s, 1495s	1278s	1024m	820m, 805m	760m, 752m	1073s	90
$UO_2(NO_3)_2$,2tmpo	Yellow	1505s, 1495w, sh	1299s, 1290s	1040s	816w	764w	1091s	72
$Th(NO_3)_4$,2·67tprpo	White	1520s, 1496s	1299s, 1282s	1042m, 1032s	815w, sh	745w, 739w	1102s 1095s	68, 75
$U(NO_3)_4$,2·67tprpo	Green	1515s 1495s	1298m, sh 1285s	1029s	809w	747w	1092s	78
$Np(NO_3)_4$,2·67tprpo	Greenish-yellow	1518s, 1496s	1282s, 1292w, sh	1031m	805w	744w	1086s	84
$UO_2(NO_3)_2$,2tprpo	Yellow	1510s, 1490m, sh	1291s	1036m	805w	750m	1095s, 1080m, sh	75 90
$Th(NO_3)_4$,4tbpo	White	1504s, 1509w, sh	1295s	1032m	815m	740m	1102s, 1083s	68, 87
$UO_2(NO_3)_2$,2tbpo	Yellow	1513s, 1530w, sh	1283s	1032w	816w		1111s, 1098s	59, 72
$Th(NO_3)_4$,2tppo	White	1530s, 1540m, sh	1283m	1027s	808m		1062s	128
$Np(NO_3)_4$,2tppo	Greenish-yellow	1546s, 1528s	1268m, 1277w, sh	1020sh, w (?) 1014m	800w	740w	1056s	134
$UO_2(NO_3)_2$,2tppo	Yellow	1520s, 1526vw	1283vs	1034s, 1030m	812w	762m	1081s, 1133s	109, 57
$Th(NO_3)_4$,2hmpa	White	1528s	1286s	1027s	812m	767m	1066s	142
$U(NO_3)_4$,2hmpa	Green	1525s, (1545, 1510w, sh)	1293s	1024s	814w		1050s	158
$Np(NO_3)_4$,2hmpa	Green	1524s (1548, 1505w, sh)	1280s (1300, 1255w, sh)	1057s (?) 1024w, sh	805w	760s	1052s	156
$UO_2(NO_3)_2$,2hmpa	Yellow	1515s	1293s	1037m	817w	768s	1100s	98
$Th(NO_3)_4$,2·5ompa	White	1510s	1289s	1029m	807w	760m	1174s, br	61
$Th(NO_3)_4$,1·5ompa	White	1513s	1290s, br	1028s	813m	750m	1166s, br	69
$U(NO_3)_4$,1·5ompa	Green	1513s	1285s	1029m	808w	745m	1155s	80
$Np(NO_3)_4$,1·5ompa	Green	1515s	1283s	1030m, sh	805w	744m	1154s	81
$UO_2(NO_3)_2$,ompa	Yellow	1518s, br	1293s	1033m	814m	750m	1188s	47
$Th(NO_3)_4$,1·5ppm	White	1516s, (1546m, sh, 1526vw)	1293s, (1282m, sh)	1027m	810w	obs	1140s (1160w, sh, 1150vw, sh)	44
$UO_2(NO_3)_2$,1·5ppm	Yellow	1521s, 1512w, sh	1287s	1035w, 1030w, sh	810vw	obs	1135s (1160w, sh)	49
$Th(NO_3)_4$,2ppc	White	1515m, 1536w, sh	1290m, 1280m	1025m	808w		1131s (1182w, 1142w, sh)	51

obs = Obscured by ligand vibration.

tprpo Complexes.—This ligand consistently yielded complexes of composition $M(NO_3)_4$,2·67tprpo (M = Th, U, Np), a stoicheiometry which was not found with any other ligand in this investigation. Their i.r. spectra (Table 1) indicated that all nitrate groups were covalent and the Raman spectra (Th, Np, Table 4) were consistent with the presence of bidentate nitrato-groups. The splitting observed in the nitrate features in both sets of spectra probably arises from vibrational coupling. It is likely that the complexes are ionic, possibly $[M(NO_3)_3(tprpo)_4]^+{}_2[M(NO_3)_6]^{2-}$, analogous to the cationic species suggested for the tetrakis complexes. The conductivity results (Table 3) are, however, inconclusive. It is difficult to reconcile the formation of a neptunium complex of this stoicheiometry with the formation of $Np(NO_3)_4$,3tmpo in preference to $Np(NO_3)_4$,4tmpo, which could not be prepared, and a structural investigation of these complexes is clearly desirable. In contrast to the tetranitrates, dioxouranium(VI) nitrate formed only the common bis complex with tprpo, and this behaved as a non-electrolyte in nitromethane; its Raman spectrum (Table 4) is again consistent with the presence of bidentate nitrato-groups.

hmpa and tppo Complexes.—Only the bis complexes $M(NO_3)_4,2R_3PO$ were obtained with these more bulky ligands. The Raman spectra of these and of $UO_2(NO_3)_2$,$2R_3PO$ were consistent with the presence of bidentate nitrato-groups and the molar conductivities (Table 3) were low, indicating non-electrolyte behaviour. The tetranitrate complexes and $UO_2(NO_3)_2$,2hmpa are probably similar in structure to $[Th(NO_3)_4(tppo)_2]$ [2] and $[UO_2(NO_3)_2(tppo)_2]$ [19] respectively.

TABLE 2

Vibrations arising from ionic nitrate (cm^{-1})

Compound		E' (ν_3)	A_2'' (ν_2)
$Th(NO_3)_4$,4tmpo	I.r.	1365m, sh	830w
	Raman	1365vw	
$U(NO_3)_4$,4tmpo	I.r.	1350s, 1365m, sh	832vw
$Th(NO_3)_4$,4tbpo	I.r.	1343s	830w, sh
	I.r.[a]	1355m	835w, sh
	Raman	1360w, 1310m (?)	
$Th(NO_3)_4$,2·5ompa	I.r.	1352s, 1334s, 1314s	832w

[a] Carbon tetrachloride solution.

TABLE 3

Molar conductivities of some nitrate complexes in nitromethane at 20 °C

	Λ_{500}	Λ_{1000}	Electrolyte
Compound	Ω^{-1} cm^{-2} mol^{-1}	Ω^{-1} cm^2 mol^{-1}	type
$Th(NO_3)_4$,4tmpo	72·4	75·6	1 : 1
$U(NO_3)_4$,4tmpo	63·5	67·7	1 : 1
$Th(NO_3)_4$,4tbpo	55·5	56·9	1 : 1
$Th(NO_3)_4$,2·67tprpo *	52·5	59·1	?
$Th(NO_3)_4$,2hmpa	11·2	12·1	Non-electrolyte
$2Th(NO_3)_4$,3ompa	72·4	73·8	1 : 1
$2Th(NO_3)_4$,5ompa		293	?

* Plot of $\Lambda - \Lambda_e$ *vs.* $\sqrt{c}$ was non-linear.

TABLE 4

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

	ν_1	ν_4	ν_2	ν_6	ν_3/ν_5
$Th(NO_3)_4$,4tmpo	1500vw	1300vw	1056s, 1045s		775m, 728m
$Np(NO_3)_4$,3tmpo		1296m-s	1048w, sh	810s	795m,sh
$UO_2(NO_3)_2$,2tmpo	1500vw	1275vw	1040m, 1028w		770w
$Th(NO_3)_4$,2·67tprpo	1520w	1316w, 1282vw	1040vs		753w
$Np(NO_3)_4$,2·67tprpo	1520w	1300w, 1260w		810w	
$UO_2(NO_3)_2$,2tprpo	1520w		1041s		
$Th(NO_3)_4$,4tpbo	1510w	1310w (?), 1270w	1040s		
$UO_2(NO_3)_2$,2tbpo	1510w		1030w		
$Th(NO_3)_4$,2hmpa	1530w (1545m, 1496m)	1320vw, 1290vw	1034s		762w
$UO_2(NO_3)_2$,2hmpa	1505w, sh 1490s		1035vs		750w
$Th(NO_3)_4$,1·5ompa	1520m (1552m, 1625w)		1040vs		760w, sh, 710w
$UO_2(NO_3)_2$,ompa	1535w	1280vw, 1320vw	1033s		755w
$Th(NO_3)_4$,1·5ppm	1530w (1510w, 1590w)		*		*
$UO_2(NO_3)_2$,1·5ppm	1530w		1034vs (?) *		*
$Th(NO_3)_4$,2tppo	1540w, 1563w		*		752w, 740w

* Obscured by ligand absorptions.

Bidentate Phosphine Oxides.—Complexes of stoicheiometry $M(NO_3)_4$,1·5L were obtained with ompa and ppm, and a second ompa complex, $Th(NO_3)_4$,2·5ompa, was also obtained. The Raman spectra of $Th(NO_3)_4$,1·5ompa, $UO_2(NO_3)_2$,ompa, and $Th(NO_3)_4$,1·5ppm are consistent with the presence of bidentate nitrato-groups and the i.r. spectrum (Table 2) of $Th(NO_3)_4$,2·5ompa also showed that ionic nitrate was present in this complex. The same 2 : 3 stoicheiometry was found for the dioxouranium(VI) nitrate complex with ppm, whereas ompa only forms [15] a 1 : 1 complex. The two thorium tetranitrate–ompa complexes behave as electrolytes (Table 3) although there is no ionic nitrate in solid $Th(NO_3)_4$,1·5ompa. The ompa complexes of the actinoid tetrachlorides also have the 2 : 3 stoicheiometry,[20] and presumably all of these compounds are dimeric, but their structures are unknown. In contrast, ppe forms the bis complex, $Th(NO_3)_4$,2ppe, in which covalent nitrato-groups are probably present (Table 1); there is, however, no evidence to show whether ppe is behaving as a uni- or bi-dentate ligand in the complex.

Ligand Infrared Spectra.—The shifts in the P=O stretching frequencies in the i.r. spectrum are shown in Table 1; tmpo, tprpo, and tbpo all exhibit similar shifts on co-ordination as might be expected from the similar electronegativities of the substituent groups. The effect of electron withdrawal from the P=O group by the metal atom is felt throughout the small tmpo molecule and this is reflected in the i.r. spectra of its complexes, in which all of the ligand skeletal modes are shifted or split compared with those in the free ligand; this effect is much less marked in the longer chain tprpo and tbpo. There is very little difference in the magnitudes of the shifts in a set of complexes (Th, U, Np) or between the complexes $M(NO_3)_4$,xL and $M(NO_3)_4$(x + 1)L. A small splitting of the P=O mode in $Th(NO_3)_4$,4tbpo was observed both for the solid and for solutions in carbon tetrachloride; this may indicate more than one environment of the ligands. The shifts in the P=O stretching frequencies for the hmpa and tppo complexes are very much larger than those for the trialkylphosphine oxides, as has been observed for the corresponding complexes of the tetrachlorides.[21,22]

Electronic Spectra.—The diffuse reflectance spectra of the uranium(IV) complexes (Table 5) show a number of internal resemblances; that of $U(NO_3)_4$,1·5ompa is extremely simple, but it provides little evidence on which to base a structure. The reflectance spectrum of $U(NO_3)_4$,2·67tprpo is more revealing in that there are absorptions corresponding to those in the spectra of both $U(NO_3)_4$,2hmpa and $Cs_2U(NO_3)_6$, but the evidence is insufficiently strong to establish the structure. The solution spectra of $U(NO_3)_4$,2hmpa and $U(NO_3)_4$,4tmpo

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are very similar, with the extinction coefficients of the latter much larger than those of the former, as might be expected for the probable near centrosymmetric structure of $U(NO_3)_4$,2hmpa, which should be similar to that[2] of $Th(NO_3)_4$,2tppo. The spectra of the analogous neptunium(IV) complexes were also recorded but did not provide useful structural evidence.

X-Ray Diffraction.—Partial *X*-ray powder diffraction photographs indicated that $M(NO_3)_4$,2·67tprpo (M = Th, Np) were isomorphous; two other sets of complexes are probably isomorphous, $Th(NO_3)_4$,2tppo and $Np(NO_3)_4$,2tppo, and $Th(NO_3)_4$,2hmpa and $Np(NO_3)_4$,2hmpa. Although there were some similarities in the powder photographs of the tmpo complexes, $M(NO_3)_4$,3tmpo, and of the ompa analogues, they were insufficiently marked to indicate isomorphism.

TABLE 5

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

$Cs_2U(NO_3)_6$	$U(NO_3)_4$,2·67tprpo	$U(NO_3)_4$,2hmpa		$U(NO_3)_4$,4tmpo		$U(NO_3)_4$,1·5ompa
DSR[b]	DSR[b]	DSR[b]	MeCN	DSR[b]	MeCN	DSR[b]
				386w		377w
405w	402w			397w		
	425m	420m		415m	420 (19)	422w
	438m	428sh	427 (10)			433w
		456sh	457 (11)	453m	458 (15)	
468m	478s	473m	480 (17)		477 (13)	479m
		490sh		495m	495 (13)	
		503sh				
525m	520m	528w	537 (2)	520m	530 (6)	
560w	548m			586m		546w
	595m	595sh		602m	596 (10)	
608w					618 (14)	
633m	633s, 635m	643s	650 (17)	650s	655 (46)	655s
		668sh	673 (11)		670 (26)	
		733w				
	828m	828w		775w		
	902m			905m		
995m, br				970m		
	1063s	1038s, br		1068m, br	1050 (10)	
	1115s	1118s, br	1100 (5)	1100s, br		1090s
1183m, br	1162s					

[a] Extinction coefficients mol^{-1} l cm^{-1} in brackets. [b] DSR = Solid reflectance spectra.

EXPERIMENTAL

All complexes were prepared and handled in dry nitrogen atmosphere glove-boxes to afford protection against atmospheric moisture and oxygen as well as against the radioactive hazards associated with ^{237}Np.

Reagents.—Thorium nitrate hydrate (B.D.H., Ltd.) was used as supplied and uranyl nitrate hydrate (B.D.H., Ltd.) was converted to the dihydrate by the published method;[23] NpO_2 was supplied by British Nuclear Fuels, Ltd. $Cs_2U(NO_3)_6$ was prepared by the published method,[6] which was also applied to the preparation of $Cs_2Np(NO_3)_6$. tmpo, tprpo, and tbpo were prepared by a published method;[24] tppo (B.D.H., Ltd.) was recrystallized twice from ethyl acetate; hmpa and ompa (Koch–Light, Ltd.) were dried over type 5A molecular sieves. ppm and ppe were supplied to the authors by Mr. S. Todd of this department.

All solvents were dried over type 4A molecular sieves, distilled and then stored over molecular sieves. Solvents were purged with nitrogen before using them for uranium(IV) preparations.

Preparations.—The thorium tetranitrate and dioxouranium(VI) nitrate complexes were prepared by treating the hydrated nitrates with the ligand (10—100% excess for the stoicheiometry of the product) in a suitable solvent; the uranium and neptunium tetranitrate complexes were prepared in a similar manner from $Cs_2M(NO_3)_6$. In some instances [tmpo(U), tppo(Np), hmpa(U,Np), ompa(Np)] the complex that resulted from this procedure was insoluble, or had a low solubility, in the solvent medium in the cold, but in all such cases the complex dissolved on heating, permitting its separation from the insoluble caesium nitrate. Because of differences in the solubilities of the various complexes, it was not possible to use a common solvent system throughout and the various solvent systems that were used in this work are summarised in Table 6. One example each of the preparation of a thorium and a neptunium complex is given below to typify the procedures used. All products were vacuum dried (10^{-2} to 10^{-3} torr) for 8—16 h.

$Th(NO_3)_4$,4tmpo *and* $Th(NO_3)_4$,3tmpo.—Hydrated $Th(NO_3)_4$ (0·649 g, 1·16 mmol) and tmpo (0·812 g, 8·8 mmol) were dissolved in acetone (20 ml) and heated under reflux (1 h). The acetone was distilled off, leaving a white, waxy solid which was recrystallized from ethanol (4×) to yield $Th(NO_3)_4$,4tmpo (42%). Evaporation of the mother liquor, and subsequent recrystallization of the residue from ethanol yielded $Th(NO_3)_4$,3tmpo (10%, m.p. 262—264 °C).

$Np(NO_3)_4$,3tmpo.—A suspension of $Cs_2Np(NO_3)_6$ (0·126 g, 0·14 mmol) in chloroform (4 ml) was mixed with a solution of tmpo (0·080 g, 0·87 mmol) in the same solvent (4 ml). Addition of 2-methylbutane to the green filtrate yielded the dark green *complex* which was recrystallized from ethanol [yield 74%, m.p. 188—189 °C (d)].

Analyses.—Thorium, uranium, and neptunium were determined as described previously.[25] C, H, and N were determined by combustion using a Technicon CHN analyser,

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[23] B. M. Gatehouse and A. E. Comyns, *J. Chem. Soc.*, 1958, 3965.

[24] A. B. Burge and W. E. McKee, *J. Amer. Chem. Soc.*, 1951, **73**, 4590.

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

and nitrate was weighed as the nitron salt [26] (Th, U only) or by reduction to ammonia with Devarda's alloy,[27] a method which was unsatisfactory for the hmpa and ompa complexes. Phosphorus was determined colorimetrically as vanadium phosphatomolybdate following upon the decomposition of the complex by digestion with a mixture of perchloric and sulphuric acids.[28] The analytical results are summarised in Table 7.

TABLE 6

Solvent systems, yields, and m.p.'s of the nitrate complexes

Compound	Solvent used for Preparation: Metal nitrate	Solvent used for Preparation: Ligand	Solvent used for Recrystallization	Yield (%)	M.p. (t/°C)
$Th(NO_3)_4$,4tmpo	Acetone	Acetone	Ethanol (4 ×)	42	200—260
$Th(NO_3)_4$,2·67tprpo	Water	Ethanol	Acetone (2 ×)	58	169—170
$Th(NO_3)_4$,4tbpo	TEF [a,b]	TEF [a,b]	Diethyl ether	71	109—110
$Th(NO_3)_4$,2hmpa	MeCN	MeCN	MeCN	76	185
$Th(NO_3)_4$,1·5ompa	MeCN	None	MeCN	75	205·5 (d)
$Th(NO_3)_4$,2·5ompa [c]	MeCN	None	MeCN	*ca.* 10	129
$Th(NO_3)_4$,1·5ppm	Acetone	Acetone	None	57	276 (d)
$Th(NO_3)_4$,2ppe	Ethanol	Mixed [d]	Mixed [d]	70	245—246
$U(NO_3)_4$,4tmpo	Ethanol [e]	Ethanol	Ethanol	53	174—175 (d)
$U(NO_3)_4$,2·67tprpo	None [f]	Acetone [b]	Ethanol	22	96—98 (d)
$U(NO_3)_4$,2hmpa	None [f]	Ethanol	Ethanol	53	125 (d)
$U(NO_3)_4$,1·5ompa	None [f]	Methanol [g]	Mixed [h]	70	135 (d)
$Np(NO_3)_4$,3tmpo	Chloroform [e]	Chloroform [b]	Ethanol	74	188—189
$Np(NO_3)_4$,2·67tprpo	Ethanol [e]	Ethanol	Ethanol	67	144—145
$Np(NO_3)_4$,2tppo	Chloroform [e]	Chloroform [b]	Benzene	50	>206
$Np(NO_3)_4$,2hmpa	Ethanol [e]	None	Ethanol	61	171—172 (d)
$Np(NO_3)_4$,1·5ompa	Ethanol [e]	None [b]	Acetone	40	152—153
$UO_2(NO_3)_2$,2tprpo	Water	Ethanol	None	53	97—98
$UO_2(NO_3)_2$,1·5ppm	Acetone	Acetone	None	95	278—279

[a] TEF = Triethyl formate. [b] Complex precipitated on addition of, or to, 2-methylbutane. [c] Solution of metal nitrate added dropwise to the ligand. [d] 2 : 1 v/v Ethanol–chloroform. [e] Slurry of $Cs_2M(NO_3)_6$. [f] Solid $Cs_2M(NO_3)_6$ added to the solution of the ligand. [g] $CsNO_3$ precipitated from the solution on the addition of 2-methylbutane. [h] 1 : 1 v/v Ethanol–chloroform. (d) = Decomposed vigorously.

TABLE 7

Analytical results

Compound	Metal (%) Required	Metal (%) Found	Carbon (%) Required	Carbon (%) Found	Hydrogen (%) Required	Hydrogen (%) Found	Nitrogen (%) Required	Nitrogen (%) Found	Phosphorus (%) Required	Phosphorus (%) Found
$Th(NO_3)_4$,4tmpo	27·4	27·5	17·0	17·0	4·3	4·2	6·6	6·7	14·6	15·0
$Th(NO_3)_4$,3tmpo	30·7	30·4	14·3	13·9	3·6	3·4	7·4	7·6	12·3	12·0
$U(NO_3)_4$,4tmpo	27·9	27·8	16·9	17·2	4·25	4·5	6·6	6·3	14·5	15·0
$Np(NO_3)_4$,3tmpo	31·1	31·4					32·6 [a]	32·4 [a]		
$Np(NO_3)_4$,2tppo	22·8	22·5								
$Th(NO_3)_4$,2·67tprpo	24·4	24·3	30·3	30·2	5·9	5·8	5·9	6·0	8·7	8·9
$U(NO_3)_4$,2·67tprpo	24·9	24·9	30·1	30·2	5·9	5·0	5·9	5·5		
$Np(NO_3)_4$,2·67tprpo	24·8	25·0					26·0 [a]	25·9 [a]		
$UO_2(NO_3)_2$,2tprpo	31·9	31·7	28·9	29·0	5·6	5·8	3·8	3·7	8·3	8·6
$Th(NO_3)_4$,4tbpo	17·2	17·0	42·6	42·6	8·0	8·1	4·1	4·2	9·2	9·7
$Th(NO_3)_4$,2hmpa	27·7	27·9	17·2	17·4	4·3	4·3	16·7 [b]	16·8 [b]	7·4	7·4
$U(NO_3)_4$,2hmpa	28·2	28·5	17·1	17·3	4·3	4·3	16·6 [c]	16·5 [c]		
$Np(NO_3)_4$,2hmpa	28·1	28·0								
$Th(NO_3)_4$,2·5ompa	19·4	19·6	20·1	20·0	5·0	5·2	16·4	15·8		
$Th(NO_3)_4$,1·5ompa	25·5	25·1	15·8	15·5	4·0	3·9	15·4	15·0		
$U(NO_3)_4$,1·5ompa			15·7	15·5	3·9	4·0	15·3	15·0		
$Np(NO_3)_4$,1·5ompa	25·9	25·7								
$Th(NO_3)_4$,1·5ppm			40·8	40·9	3·0	2·8	5·1	4·8	8·4	8·0
$UO_2(NO_3)_2$,1·5ppm	23·4	23·0	44·2	44·6	3·2	3·5	2·8	2·9	9·1	7·3
$Th(NO_3)_4$,2ppe	17·3	17·6	46·6	46·1	3·6	3·6	4·2	3·9	9·3	9·8

[a] NO_3^- Content. [b] NO_3^- Analysis: required 29·6, found 29·3%. [c] NO_3^- Analysis: required 28·2, found 28·5%.

Physical Measurements.—I.r. spectra were recorded using a Perkin-Elmer 257 or 225 spectrometer with samples mounted as mulls in Nujol or hexachlorobutadiene between NaCl plates. In the case of the neptunium samples the plate holder was enclosed in an airtight box with Polythene windows, the design being based on that used at Harwell,[29] and a similar cell was placed in the reference beam of the spectrometer for balance. Raman spectra of powdered solids were recorded using a Cary 82 and a Cary 83 laser Raman spectrometer and electronic spectra (200—700 nm) were recorded for solutions using a Unicam SP 200 spectrophotometer or (350—2400 nm) a Beckman DK 2A instrument. Solid reflectance spectra (350—2400 nm) were recorded with the latter. The Raman and electronic spectra of the neptunium compounds were taken with the sample holders enclosed in Polythene bags. Electrical conductivities were measured for nitromethane solutions of the complexes at room temperature using a dipping cell and a

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[26] A. I. Vogel, ' A Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961, p. 583.

[27] Ref. 26, p. 248.

[28] R. S. Young, ' Chemical Analysis in Extractive Metallurgy,' London, Griffin, 1971, p. 271.

[29] D. Brown, personal communication.

Phillips conductivity bridge. M.p.s were determined using a Gallenkamp apparatus. *X*-Ray powder diffraction photographs were obtained as described previously.[25]

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