# The Chemistry of Uranium. Part XII. Nitrate Complexes of Uranium(IV) and Thorium(IV)

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The behaviour of $[NO_3]^-$ as anionic ligand towards $Th^{IV}$ and $U^{IV}$ in the presence of various amounts of trimethylphosphine and tris(dimethylamino)phosphine oxides has been studied in non-aqueous media by conductometric, spectroscopic, and enthalpimetric methods. The relation between species present in solution and solids isolated and the influence of cation-and neutral-donor ligand size on the action of nitrate as a donor have been investigated.

THE behaviour of nitrate as an anionic ligand towards uranium(IV) in the presence of a strong large phosphoryl-oxygen donor ligand, *viz.* tris(dimethylamino)phosphine oxide (tdpo) in acetone solution, has previously been discussed by us.[1] Additional solution chemical and solid-state properties of the $U[NO_3]_4$–tdpo system are

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[1] J. G. H. du Preez and C. P. J. van Vuuren, *J. Inorg. Nuclear Chem.*, 1974, **36**, 81.

now reported. The system has also been generalized to become $\mathrm{M[NO_3]_4}$–neutral oxygen-donor ligand–acetone [M = U and Th; tdpo and trimethylphosphine oxide (tmpo) are the neutral ligands]. The object was to determine how the size of the metal cation and neutral ligand influence the metal–nitrate interactions in the solid state and in solution. The solid complexes isolated are $\mathrm{Th[NO_3]_4{\cdot}3tdpo}$, $\mathrm{Th[NO_3]_4{\cdot}4tdpo}$, and $\mathrm{M[NO_3]_4{\cdot}}x\mathrm{tmpo}$ (M = U and Th; $x = 3$ and 5). The preparation of $\mathrm{M[NO_3]_4{\cdot}4tmpo}$ (M = Th and U) in alcohol solutions has recently been reported.[2] These could not be prepared by us from acetone solutions. Conductometric and enthalpimetric titrations provided evidence for the existence of the 3tmpo and 5tmpo species. In contrast to $\mathrm{U^{IV}}$, autoionized species of $\mathrm{Th[NO_3]_4}$ are prominent in acetone solutions with these ligands if the ligand to metal ratio is relatively low.

## EXPERIMENTAL

*Materials.*—The salts $\mathrm{Cs_2[U(NO_3)_6]}$ [3] and $\mathrm{Th[NO_3]_4{\cdot}5OH_2}$ were used as starting materials for the preparation of the complexes. Tris(dimethylamino)phosphine oxide (tdpo) (Fluka) was used as supplied while trimethylphosphine oxide (tmpo) was prepared as previously reported.[4]

*Preparations.*—The preparations of $\mathrm{U[NO_3]_4{\cdot}2tdpo}$ and $\mathrm{U[NO_3]_4{\cdot}4tdpo}$ were reported earlier.[1]

*Uranium tetranitrate–trimethylphosphine oxide* (1/3), $\mathrm{U[NO_3]_4{\cdot}3tmpo}$. Tmpo (0.32 g) dissolved in methyl cyanide (5 cm$^3$) was added to a suspension of $\mathrm{Cs_2[U(NO_3)_6]}$ (1 g) in methyl cyanide (15 cm$^3$). The dark green solution obtained on stirring was filtered and concentrated *in vacuo* to a small volume (*ca.* 5 cm$^3$) and ethyl acetate (*ca.* 3 cm$^3$) was added. The dark green *crystals* which formed were washed with isopentane and dried *in vacuo*.

*Uranium tetranitrate–trimethylphosphine oxide* (1/5), $\mathrm{U[NO_3]_4{\cdot}5tmpo}$. Excess of tmpo dissolved in acetone was added to an acetone solution (10 cm$^3$) of $\mathrm{U[NO_3]_4{\cdot}3tmpo}$ (1—2 g). The light green solid which formed immediately was crystallized from hot methyl cyanide containing excess of tmpo. The resulting *solid* was washed with acetone, isopentane, and dried *in vacuo*.

*Thorium tetranitrate–tris(dimethylamino)phosphine oxide* (1/3), $\mathrm{Th[NO_3]_4{\cdot}3tdpo}$. The salt $\mathrm{Th[NO_3]_4{\cdot}5OH_2}$ (1 g) was dissolved in acetone (10 cm$^3$) which contained tdpo (1 g). On addition of isopentane (3 cm$^3$) and subsequent cooling the white solid *product* formed.

*Thorium tetranitrate–trimethylphosphine oxide* (1/3), $\mathrm{Th[NO_3]_4{\cdot}3tmpo}$. The salt $\mathrm{Th[NO_3]_4{\cdot}3OH_2}$ (1 g) was dissolved in methyl cyanide (10 cm$^3$). Tmpo (0.5 g) dissolved in the same solvent was added and the solution concentrated to a small volume (*ca.* 5 cm$^3$). On addition of ethyl acetate (*ca.* 5 cm$^3$) and subsequent cooling the white solid *product* formed.

*Thorium tetranitrate–tris(dimethylamino)phosphine oxide* (1/4) *and –trimethylphosphine oxide* (1/5), $\mathrm{Th[NO_3]_4{\cdot}4tdpo}$, *and* $\mathrm{Th[NO_3]_4{\cdot}5tmpo}$. These complexes were prepared from $\mathrm{Th[NO_3]_4{\cdot}3L}$ (L = tdpo and tmpo) following the same procedure as used for the preparation of their uranium analogues.[1]

The $\mathrm{U[NO_3]_4}$ solutions used in the conductometric titrations were prepared from cold acetone solutions (0 °C) of $\mathrm{UCl_4}$ according to reaction (1). After precipitation of

$$\mathrm{UCl_4 + 4Ag[NO_3] \longrightarrow U[NO_3]_4 + 4AgCl}\downarrow \qquad (1)$$

the AgCl, the supernatant solution was quickly made up to 250 cm$^3$ with the required solvent (acetone or methyl cyanide). The solution was then standardized (uranium determination). The conductometric titration was then made immediately at 0 °C.

*Analyses.*—Uranium [1] and thorium [5] were determined as described previously. Nitrate was weighed as Nitron nitrate. The results are given in Table 1.

TABLE 1

Analyses (%) *

| Complex | U | $\mathrm{NO_3}$ |
|---|---|---|
| $\mathrm{U[NO_3]_4{\cdot}2tdpo}$ | 28.3 (28.2) | 29.6 (29.4) |
| $\mathrm{U[NO_3]_4{\cdot}4tdpo}$ | 19.9 (19.8) | 20.4 (20.6) |
| $\mathrm{U[NO_3]_4{\cdot}3tmpo}$ | 31.3 (31.2) | 33.0 (32.5) |
| $\mathrm{U[NO_3]_4{\cdot}5tmpo}$ | 25.3 (25.2) | 26.0 (26.2) |
| $\mathrm{Th[NO_3]_4{\cdot}3tdpo}$ | 22.9 (22.8) | 24.5 (24.4) |
| $\mathrm{Th[NO_3]_4{\cdot}4tdpo}$ | 19.7 (19.4) | 20.9 (20.7) |
| $\mathrm{Th[NO_3]_4{\cdot}3tmpo}$ | 30.9 (30.7) | 32.5 (32.8) |
| $\mathrm{Th[NO_3]_4{\cdot}5tmpo}$ | 24.9 (24.7) | 26.6 (26.4) |

* Calculated values are given in parentheses.

*Physical Measurements.*—I.r. spectra were obtained from Nujol and hexachlorobutadiene mulls between NaCl plates with a Perkin-Elmer 457 spectrophotometer. Conductivity measurements were made with a Metrohm Konduktoskop. Enthalpimetric titrations were carried out using an Aminco Titra-Thermosmat titrimeter. The experimental procedure was described previously.[6] Each titration was made at least six times.

## RESULTS AND DISCUSSION

$\mathrm{M[NO_3]_4}$–*tdpo Systems.*—The conductometric titration of $\mathrm{U[NO_3]_4}$ with tdpo in acetone solution [Figure, curve (*a*)] is in agreement with earlier observations, namely that an un-ionized $\mathrm{U[NO_3]_4{\cdot}2tdpo}$ complex is formed (minimum at mol ratio 2 : 1) and that ionization takes place at higher tdpo to uranium ratios.[1] The $\mathrm{Th[NO_3]_4}$ titration curve differed [Figure, curve (*b*)] in so far that autoionization was more pronounced in the earlier stages of the titration and ionization was also greater, as for $\mathrm{U[NO_3]_4}$, when tdpo : $\mathrm{Th[NO_3]_4}$ ratios were greater than 2 : 1. In the initial stages of the conductometric titration of tdpo against $\mathrm{Th[NO_3]_4}$ the increase in conductivity must be ascribed to enhanced autoionization {formation of $\mathrm{[Th(NO_3)_3{\cdot}2tdpo{\cdot}S]^+}$ and $\mathrm{[Th(NO_3)_5{\cdot}S]^-}$ (S = solvent)}. After this period the most important reaction will be that of complex formation (*e.g.* $\mathrm{Th[NO_3]_4{\cdot}2tdpo{\cdot}OCMe_2}$). Further addition of tdpo leads to a gradual increase in the extent of ionization. The percentage ionization of $\mathrm{Th[NO_3]_4{\cdot}4tdpo}$ is greater than that of $\mathrm{Th[NO_3]_4{\cdot}3tdpo}$ when excess of tdpo is present.

No solid $\mathrm{Th[NO_3]_4{\cdot}2tdpo}$ could be prepared from acetone solutions, even when a $\mathrm{Th[NO_3]_4}$ : tdpo mol

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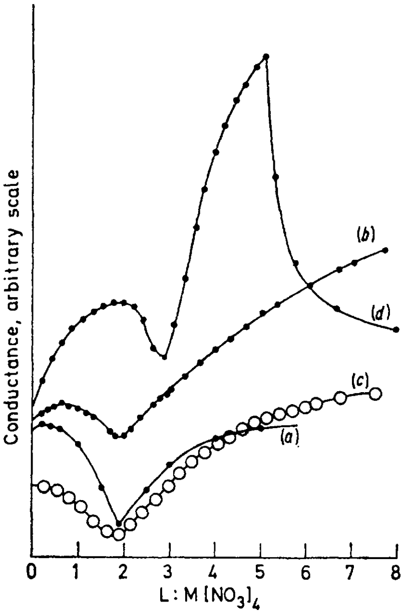
[2] K. W. Bagnall and M. W. Wakerley, *J.C.S. Dalton*, 1974, 889.

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

[4] P. Gans, Ph.D. Thesis, London University, 1964.

[5] A. I. Vogel, 'Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1964.

[6] J. G. H du Preez and J. Koorts, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 99.



Conductometric titration curves of M[NO$_3$]$_4$ with tmpo and tdpo (*a*) M = U, L = tdpo; (*b*) M = Th, L = tdpo; (*c*) M = U, L = tmpo; and (*d*) M = Th, L = tmpo

ratio of 1 : 2 was used, but only Th[NO$_3$]$_4$·3tdpo. This fact, and the relatively lesser pronounced minimum at a mol ratio of 2 : 1 in the case of thorium, suggests that the neutral complex (Th[NO$_3$]$_4$·2tdpo) is less stable relative to autoionized and ionized species than in the case of uranium. The i.r. spectrum (mull) of the latter complex contains all six fundamental modes of co-ordinated nitrate (see Table 2) and a band split by 42 cm$^{-1}$ in the 1 700—1 800 cm$^{-1}$ region which suggested bidentate co-ordinated nitrato-groups.[1] Although somewhat obscured by a co-ordinated nitrato-absorption ($\nu_2$), a peak at 1 040 cm$^{-1}$ was interpreted as indicating bonded P=O of tdpo. The molar conductivity of Th[NO$_3$]$_4$·3tdpo in nitromethane indicated that it is a weak electrolyte, although stronger than U[NO$_3$]$_4$·2tdpo. When a nitromethane solution of Th[NO$_3$]$_4$·3tdpo was titrated conductometrically with Na[BPh$_4$] the ionized nitrate was precipitated as Na[NO$_3$] and an end-point was obtained at a Th[NO$_2$]$_4$·3tdpo to Na[BPh$_4$] ratio of 1 : 0.14. An approximate constant can now be calculated for the ionization of Th[NO$_3$]$_4$·3tdpo if it is assumed that [Th(NO$_3$)$_3$·3tdpo$^+$] = [NO$_3^-$] = 0.14 times the total thorium concentration. A value of 1 × 10$^{-3}$ mol l$^{-1}$ is obtained. The corresponding value for U[NO$_3$]$_4$·2tdpo is 1 × 10$^{-4}$ mol l$^{-1}$. Solid Th[NO$_3$]$_4$·4tdpo was very similar to the corresponding uranium(IV) complex with respect to its molar conductance and i.r. spectra.[1]

When Th[NO$_3$]$_4$·4tdpo was warmed *in vacuo* at 50 °C Th[NO$_3$]$_4$·3tdpo was formed. On heating the latter to 150 °C *in vacuo* Th[NO$_3$]$_4$·2tdpo was formed. Similarly U[NO$_3$]$_4$·2tdpo could be prepared by warming U[NO$_3$]$_4$·4tdpo *in vacuo* at 80 °C. Oxidation of the former only starts at *ca.* 115 °C. In the enthalpimetric titration curve of Th[NO$_3$]$_4$ with tdpo in acetone solution, inflection points were present at mol ratios of 2 : 1 and 3 : 1. The most important reaction taking place initially will be (2). The enthalpy for this reaction is only

$$\mathrm{Th[NO_3]_5{\cdot}\mathit{x}OCMe_2 + 2tdpo \longrightarrow Th[NO_3]_4{\cdot}2tdpo{\cdot}OCMe_2 + (\mathit{x} - 1)Me_2CO} \quad (2)$$

31 kJ mol$^{-1}$ whereas that of the next reaction, (3), is

$$\mathrm{Th[NO_3]_4{\cdot}2tdpo{\cdot}OCMe_2 + tdpo \longrightarrow Th[NO_3]_4{\cdot}3tdpo + Me_2CO} \quad (3)$$

36 kJ mol$^{-1}$. This relatively smaller enthalpy per tdpo [equation (2)] can be explained by a larger entropy contribution to the free energy as compared to equation (3) if $x > 3$ in (2) which is almost certainly the case. The gradual increase after a mol ratio of 3 : 1 can be explained in terms of a gradual ionization.

M[NO$_3$]$_4$–tmpo *Systems*.—The minimum at a tmpo : U[NO$_3$]$_4$ mol ratio of 2 : 1 in the conductometric titration of an ice-cold solution of U[NO$_3$]$_4$ in acetone with tmpo [Figure, curve (*c*)] suggests that a U[NO$_3$]$_4$·2tmpo complex is formed. Solid U[NO$_3$]$_4$·2tmpo could not be isolated. Even at mol ratios of 2 : 1, U[NO$_3$]$_4$·3tmpo crystallized instead. It is therefore assumed that the species in solution is U[NO$_3$]$_4$·2tmpo·OCMe$_2$.

TABLE 2

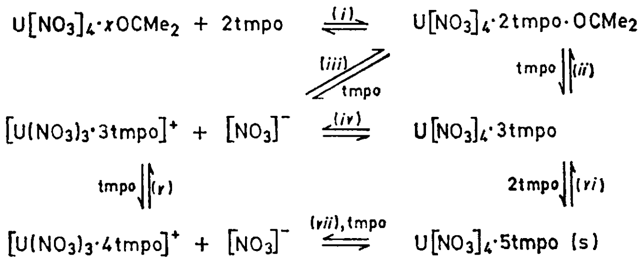
Nitrate i.r. absorption bands (cm$^{-1}$)

| Complex | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_6$ | ($\nu_2 + \nu_3$) | ($\nu_2 + \nu_5$) | Δ | ($\nu_1 + \nu_2$) | ($\nu_2 + \nu_4$) | Δ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cs$_2$[U(NO$_3$)$_6$] [a] | 1 525br | 1 030 | 742 | 1 282 | 705 | 808 | 1 780 | 1 738 | 42 | 2 550 | 2300 | 250 |
| U[NO$_3$]$_4$·3tmpo | 1 500br | 1 030 | 746 | 1 290 | 705(sh) | 810 | 1 775 | 1 740 | 35 | 2 520 | 2 320 | 200 |
| U[NO$_3$]$_4$·5tmpo | 1 470 | *b* | 740 | 1 295 | *c* | 820 | 1 715, 1 745, 1 765 | | | 2 510, 2 400, 2 280 | | |
| | 1 390 | *b* | *b* | | | 825 | | | | | | |
| Th[NO$_3$]$_4$·3tdpo | 1 510br | *b* | *b* | 1 300 | 711 | 820 | 1 770 | 1 728 | 42 | 2 550 | 2 315 | 235 |
| Th[NO$_3$]$_4$·4tdpo | 1 480br [d] | *b* | *b* | 1 310 | 712 | 818 | 1 718, 1 741, 1 773 | | | 2 530, 2 380, 2 370 | | |
| | 1 500 [e] | *b* | *b* | 1 300 | *c* | 818 | *c* | *c* | | *c* | *c* | |
| Th[NO$_3$]$_4$·3tmpo | 1 500br | 1 037 | 742 | 1 290 | 710 | 820 | 1 775 | 1 740 | 35 | 2 530 | 2 320 | 210 |
| Th[NO$_3$]$_4$·5tmpo | 1 390br | *b* | 740(sh) | 1 300 | *c* | 827 | 1 715, 1 740, 1 770 | | | 2 395, 2 320, 2 275 | | |
| | 1 470 | *b* | | | | | | | | | | |

br = Broad and sh = shoulder.

[a] Ref. 1. [b] Could not be assigned due to ligand interference. [c] Very weak and difficult to assign. [d] Solid. [e] Solution.

The i.r. spectrum of U[NO$_3$]$_4$·3tmpo indicated that all the nitrato-groups are bidentate (Table 2). The P=O stretching band was lowered by 108 cm$^{-1}$. The broad P=O absorption suggests that the bonded tmpo molecules are non-equivalent. The complex U[NO$_3$]$_4$·3tmpo behaves as a weak electrolyte in nitromethane solution. When U[NO$_3$]$_4$·3tmpo was titrated conductometrically with tmpo in acetone the conductivity increased until precipitation of $U[NO_3]_4\cdot 5tmpo$ occurred at a mol ratio of 1 : 5. In methyl cyanide solution the conductivity levelled off at a mol ratio of 1 : 5, but no solid was precipitated. These facts can be interpreted with the aid of the Scheme. Here reaction (*i*) represents complex formation. This is followed by (*ii*) although (*iii*) is also significant. Ionization (*v*) becomes more important with increasing amounts of tmpo until precipitation (*vii*) takes place. Reaction (*vi*) is the overall reaction or the 3tmpo to the 5tmpo species.



SCHEME

The i.r. spectrum of solid $U[NO_3]_4\cdot 5tmpo$ differed from that of $U[NO_3]_4\cdot 3tmpo$ in that, apart from the bidentate nitrato-frequencies, an ionic peak at 1 400 $cm^{-1}$ was exhibited. It was recently shown that the solid $U[NO_3]_4\cdot 4tmpo$, isolated from alcohol solution, contains ionic nitrate groups and behaves as a 1 : 1 electrolyte.[2] It was not possible to distinguish between the nitrate frequency ($\nu_2$) at 1 030 $cm^{-1}$ and the P=O stretching frequency since only one broad absorption band centred at *ca.* 1 070 $cm^{-1}$ was observed. A band at 1 170 $cm^{-1}$ was indicative of weakly co-ordinated tmpo.

When the molar conductance of $U[NO_3]_4\cdot 5tmpo$ was plotted against $c^{\frac{1}{2}}$ ($c$ = concentration), $\lambda$ decreased with dilution. This unusual behaviour is explained in terms of formation of complexes of $U[NO_3]_4\cdot 3tmpo$ or even $U[NO_3]_4\cdot 2tmpo$, *i.e.* the reverse of reactions (*vi*), (*iv*), and (*v*).

Enthalpimetric titration of $U[NO_3]_4\cdot 3tmpo$ with tmpo indicates that the sum of the enthalpy of reactions (4)

$$U[NO_3]_4\cdot 3tmpo + tmpo \rightleftharpoons [U(NO_3)_3\cdot 4tmpo]^+ + [NO_3]^- \quad (4)$$

and (5) is 60 kJ $mol^{-1}$. Precipitation starts after the

$$[U(NO_3)_3\cdot 4tmpo]^+ + tmpo \rightleftharpoons [U(NO_3)_3\cdot 5tmpo]^+ + [NO_3]^- \quad (5)$$

addition of 2 mol excess of tmpo (overall tmpo : U = 5 : 1). The heat evolved afterwards, *i.e.* from 2 to 13 mol excess of tmpo when the curve levels off ($U[NO_3]_4\cdot 5tmpo$ completely precipitated), is mainly the heat of precipitation of the latter (*ca.* 210 kJ $mol^{-1}$).

Both solid $Th[NO_3]_4\cdot 3tmpo$ and $Th[NO_3]_4\cdot 5tmpo$ could be isolated from acetone solutions (see Experimental section). The i.r. spectra of these were very similar to those of the corresponding uranium analogues (Table 2). This also applies to their non-aqueous conductivities. The bonding of nitrate and tmpo are also similar, therefore.

Constants were determined for the precipitation reaction (6) for M = U and Th in acetone solution at

$$M[NO_3]_4\cdot 3tmpo + 2tmpo \overset{\beta}{\rightleftharpoons} M[NO_3]_4\cdot 5tmpo\ (s) \quad (6)$$

25 °C. When $[M(NO_3)_4\cdot 3tmpo]^{-1}$ was plotted against $[tmpo]^2$ in each case, straight lines were obtained the gradient of which gave values for $\beta = \{[M(NO_3)_4\cdot 3tmpo][tmpo]^2\}^{-1}$.[1] $\{[M(NO_3)_4\cdot 3tmpo] = [M^{4+}]$. In acetone solution, [tmpo] = (concentration of excess of tmpo in solution less the amount of tmpo precipitated).$\}$ Values of $3 \times 10^6$ and $4 \times 10^5$ $l^2$ $mol^{-2}$ were obtained for the uranium and thorium analogues, respectively. The greater insolubility of the uranium complex is clearly illustrated.

Conductometric titration of $Th[NO_3]_4$ with tmpo in acetone solution [curve (*d*), Figure] clearly illustrates that $Th[NO_3]_4$ reacts differently with tmpo in acetone solution than $U[NO_3]_4$ [curve (*c*)]. The initial increase in conductivity to a maximum at a tmpo : $Th[NO_3]_4$ mol ratio of 2 : 1 can be interpreted in terms of enhanced autoionization according to equation (7). This is followed

$$2Th[NO_3]_4 + 4tmpo \rightleftharpoons [Th(NO_3)_4\cdot 4tmpo]^+ + [Th(NO_3)_4\cdot OCMe_2]^- \quad (7)$$

by a decrease in conductivity and a minimum at a mol ratio of 3 : 1, which suggests that complexes of $Th[NO_3]_4\cdot 3tmpo$ are formed. The very rapid increase in conductivity in the region of 3—4 mol tmpo added can only partly be explained in terms of ionization. Autoionization, *i.e.* the formation of species $[Th(NO_3)_3\cdot 5tmpo]^+$ and $[Th(NO_3)_5\cdot tmpo]^-$, must make significant contributions to the conductivity. When a mol ratio of 4 : 1 is exceeded, ionization becomes relatively more important again.

The enthalpy of the reaction $Th[NO_3]_4$ with tmpo in acetone solution increased almost linearly up to a mol ratio of 3 : 1 when a value of 110 kJ $mol^{-1}$ was obtained. After 3 mol of tmpo had been added a smaller $\Delta H$ value per additional mol tmpo was obtained. This latter increase must be ascribed to the heat of the ionization reactions (17.5 kJ per mol tmpo added) and the former linear section to the ultimate formation of a $Th[NO_3]_4\cdot 3tmpo$ complex (36.6 kJ per mol tmpo added). After a mol ratio of 5 : 1 had been reached, slow precipitation occurred. The heat given off in this region is therefore the heat of precipitation.

The magnetic properties of the nitrato-complexes of $U^{IV}$ were investigated. All these are temperature dependent to a greater or lesser degree and typical of $U^{IV}$ complexes of high co-ordination number.

*Conclusions*.—The donor action of $[NO_3]^-$ as a ligand to $U^{IV}$ and $Th^{IV}$ is very similar under the conditions studied here and previously.[1] The fact that autoionization takes place more readily with $Th[NO_3]_4$ than $U[NO_3]_4$ when titrated with tdpo and tmpo, and that autoionization of $UCl_4$ takes place frequently but

$ThCl_4$ very seldom,[7,8] seems to suggest that the larger nitrate ion forms more stable anionic thorium nitrate than chloride species, whereas in the case of the smaller $U^{IV}$ chlorides form equally readily. The fact that solid hexanitratothorate, *e.g.* $Cs_2[Th(NO_3)_6]$, species can be prepared much more readily than the hexachlorothorate analogues, which are more readily solvated, is in agreement with this. In the case of uranium, both $Cs_2[U(NO_3)_6]$ and $Cs_2[UCl_6]$ can readily be prepared from aqueous acidic solution.

Previous research suggested that tdpo is a stronger ligand than tmpo if the enthalpy of their reactions with monobasic acids (phenol or $SbCl_5$), where stereochemical factors can be ignored, are compared.[9] This work indicated that tmpo is a stronger ligand than tdpo for $Th[NO_3]_4$. {Enthalpies of 75 and 30 kJ $mol^{-1}$ were obtained for the species $Th[NO_3]_4 \cdot 2L$, respectively.} This phenomenon is almost certainly due to the smaller size of tmpo, which can lead to more intense metal–phosphoryl-oxygen donor-atom interaction, when compared to that of tdpo. This effect will lead to a greater extent of metal–nitrate bond weakening and, therefore, ionization in complexes of tmpo, even where the stoicheiometry of the tmpo and tdpo complexes is the same. The higher molar conductivity of $Th[NO_3]_4 \cdot 3$tmpo as compared to $Th[NO_3]_4 \cdot 3$tdpo is in agreement with this. Apart from this effect, however, a larger tmpo : $M[NO_3]_4$ mol ratio is possible in lattice-stabilized complexes than for tdpo, *e.g.* $M[NO_3]_4 \cdot 4$tdpo but $M[NO_3]_4 \cdot 5$tmpo can be isolated. This will enhance the previous effect. This work, therefore, indicates how stereochemical effects can alter the donor strength of neutral ligands. This fact may be of special significance in applied chemical processes, for example solvent extraction of a neutral species will be hampered by a neutral ligand which will cause ionization.

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