

Spectrophotometric study of the formation of adducts between $\text{Np}(\text{TTA})_4$ and some neutral donors

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MS received 19 February 1981

Abstract. The formation of adducts between $\text{Np}(\text{TTA})_4$ and neutral donors TOPO, TPPO, DBBP, DOSO and TBP in benzene medium has been studied by spectrophotometry and the presence of 1:1 adducts is shown. From the spectral changes observed, the adduct formation constants were evaluated and found to be 1.85×10^4 (TPPO), 4.72×10^3 (DBBP) and 2.12×10^3 (DOSO). The spectra indicated that adduct formation increases the coordination number of $\text{Np}(\text{IV})$ from 8 in $\text{Np}(\text{TTA})_4$ to 9 in the adducts formed. Data obtained using the solvent extraction method to evaluate the adduct formation constant of $\text{Np}(\text{TTA})_4$ with TPPO are also included.

Keywords. Solvent extraction; synergism; $\text{Np}(\text{TTA})_4$ -neutral donor adducts; coordination.

1. Introduction

In the solvent extraction of metal ions from aqueous media by mixtures of a β -diketone (HA) and a neutral donor (S), in organic solvents, an enhancement in the extraction has been observed as compared to using either extractant alone (Marcus and Kertes 1969). This enhancement in the extraction, known as synergism, is attributed to the formation of adducts in the organic phase between the metal β -diketonate and the neutral donor. Such adducts have been reported in the case of tetravalent actinides for $\text{Th}(\text{IV})$ (Healy 1961; Sekine and Dyrssen 1967; Patil *et al* 1981), $\text{U}(\text{IV})$ (Patil and Ramakrishna 1979), $\text{Np}(\text{IV})$ (Ramanujam *et al* 1979), and $\text{Pu}(\text{IV})$ (Patil *et al* 1980a). The stoichiometry of the adduct and their formation constants have been determined by a method in which the distribution ratio of the metal, kept at trace concentration, has been determined as a function of one of the variables,

$$[\text{HA}]_{(\text{org})}, [\text{H}^+]_{(\text{aq})} \text{ and } [\text{S}]_{(\text{org})},$$

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keeping the other two constant. As the adduct formation between a metal β -diketonate and a neutral donor occurs in the organic phase, it was felt that the spectrophotometric method could conveniently be employed for studying the same. The adduct formation of $\text{U}(\text{TTA})_4$ with various neutral donors has been studied (Patil *et al* 1979a; Patil and Ramakrishna 1979; Ramakrishna *et al* 1980) by the spectrophotometric method. The adduct formation constants between $\text{Pu}(\text{TTA})_4$ and TBP obtained by spectrophotometry were found to be in good agreement with those obtained using solvent extraction methods (Ramakrishna *et al* 1979), thus proving the reliability of the spectrophotometric method. No such data has been reported on $\text{Np}(\text{IV})$ although changes in the absorption spectrum of $\text{Np}(\text{TTA})_4$ in benzene upon addition of TBP was reported (Ramanujam *et al* 1979). In the present work, the adduct formation of $\text{Np}(\text{TTA})_4$ with the neutral donors tri-*n*-octylphosphine oxide (TOPO), triphenyl phosphine oxide (TPPO), di-*n*-butyl *n*-butyl phosphonate (DBBP), di-*n*-octyl sulphoxide (DOSO) and tri-*n*-butyl phosphate (TBP) was studied from the spectral changes and the results obtained are compared with those obtained earlier (Patil *et al* 1980b, d; Sajun *et al* 1981) by solvent extraction.

Since no data on the synergistic extraction of $\text{Np}(\text{IV})$ by mixtures of HTTA and TPPO are available in literature, it was felt desirable to obtain such data and compare the adduct formation constant obtained by solvent extraction method with that obtained by the spectrophotometric method. These data are also included here.

2. Experimental

2.1. Materials

^{237}Np and ^{238}Np were obtained and purified as described earlier (Ramanujam *et al* 1979). HTTA and TOPO obtained from M/s E. Merck, Germany and TPPO obtained from M/s Fluka, Switzerland were vacuum dried over P_2O_5 . The solution of HTTA in benzene was pre-equilibrated with dilute perchloric acid for a few hours to allow its hydration. TBP obtained from M/s Monsanto Chem., USA was purified (Alcock *et al* 1956). DBBP, procured from M/s K and K Labs., USA was purified by the same method as that used for the purification of TBP (Alcock *et al* 1956; Healy *et al* 1977). DOSO was synthesized and purified as described (Mohanty and Reddy 1975). All other reagents were of AR grade.

2.2. Procedure

2.2a. *Absorption spectra*: $\text{Np}(\text{IV})$ was prepared by taking an appropriate amount of ^{237}Np (~ 100 mg) in $\sim 3\text{M}$ HNO_3 containing $\sim 0.05\text{M}$ hydrazine and heating on a water bath for 2 hr. The acidity was then adjusted to $\sim 0.5\text{M}$ and $\text{Np}(\text{IV})$ was extracted into a suitable aliquot of $\sim 0.5\text{M}$ HTTA in benzene which was subsequently diluted with benzene to give a solution with the required concentration of neptunium and HTTA.

Several solutions of $\text{Np}(\text{TTA})_4$ in benzene containing excess (~ 10 times as compared with [S]) HTTA and suitable concentrations of the desired neutral donor were prepared such that the resulting solutions were having varying ratios

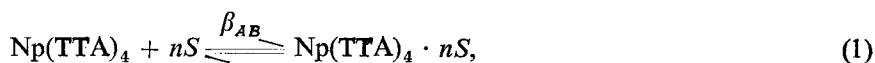
of $[S]/[Np(IV)]$ but the same concentration of $Np(IV)$. The absorption spectra of these solutions were recorded using a Cary-14 recording spectrophotometer with 5 cm path length cells, using benzene as the blank. HTTA and the neutral donors, at the concentrations used, were not found to absorb in the wavelength region studied. Scanning speeds of 0.5 Å/sec and 2.5 Å/sec were used and the absorbance values in the wavelength region 730–745 nm, recorded at 0.5 Å/sec scan speed, were read from the spectral records.

2.2b. *Solvent extraction*: The experimental procedure for the measurement of the distribution ratios of neptunium is generally the same as described earlier (Ramanujam *et al* 1979). The assay of neptunium, in both phases at the end of equilibration, was done by gamma counting of ^{238}Np using a well-type NaI(Tl) scintillation detector. The distribution ratio measurements were done in triplicate and the agreement between the values was usually within $\pm 2\%$.

3. Results

3.1. Absorption spectral studies

The formation of adducts between $Np(TTA)_4$ and a neutral donor S can be represented by

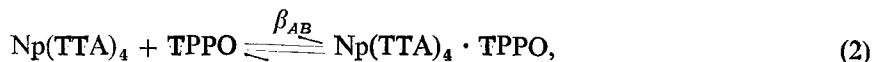


where n represents the number of neutral donor molecules present in the adduct. As the addition of S to a solution of $Np(TTA)_4$ in benzene results in appreciable changes in the absorption spectrum of $Np(TTA)_4$, the spectral changes can be conveniently used for studying the above equilibrium by the method described earlier (Patil *et al* 1979a; Patil and Ramakrishna 1979; Ramakrishna *et al* 1980).

3.1a. *Adduct formation between $Np(TTA)_4$ and TOPO*: The changes in the absorption spectrum of $Np(TTA)_4$ observed in the presence of varying concentrations of TOPO are shown in figure 1. The well-defined isosbestic points indicate the presence of two absorbing species. The variation of the absorbance with $[TOPO]/[Np(IV)]$ is shown in figure 2, from which it is apparent that $Np(TTA)_4$ forms a 1:1 adduct with TOPO. From figure 2 it can be concluded that when $[TOPO]/[Np(IV)] < 1$, the added TOPO is almost completely consumed in the adduct formation which is complete when the ratio is equal to unity. This suggests that the β_{AB} value in this case is extremely high and its calculation is not feasible from the observed spectral changes.

3.1b. *Adduct formation between $Np(TTA)_4$ and TPPO, DBBP or DOSO*: The changes in the absorption spectrum of $Np(TTA)_4$ upon addition of the donors TPPO, DBBP or DOSO were identical to those shown in figure 1, from which it was concluded that all these donors also form 1:1 adducts with $Np(TTA)_4$.

The procedure used for calculating the equilibrium constant β_{AB} for adduct formation is explained with TPPO as a typical example. The adduct formation reaction can be represented by



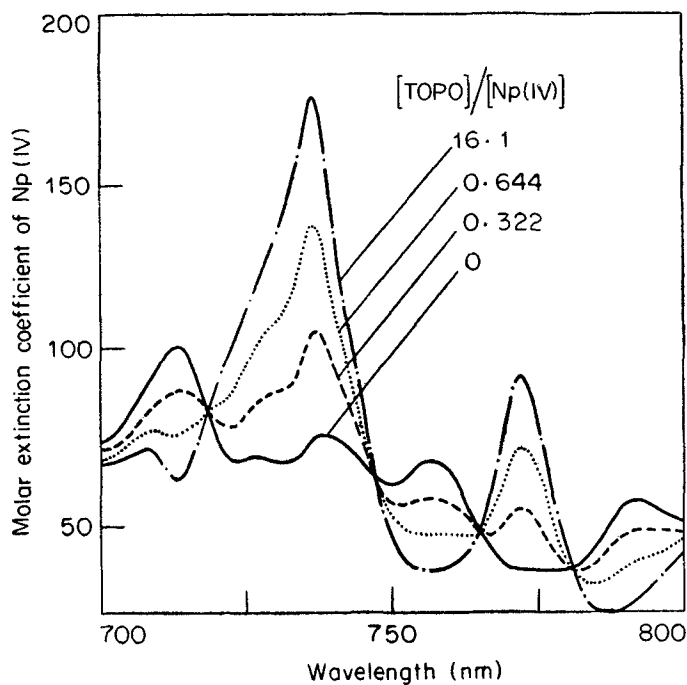


Figure 1. Absorption spectra of benzene solutions of $\text{Np}(\text{TTA})_4$ and the changes caused to it by the addition of TOPO.

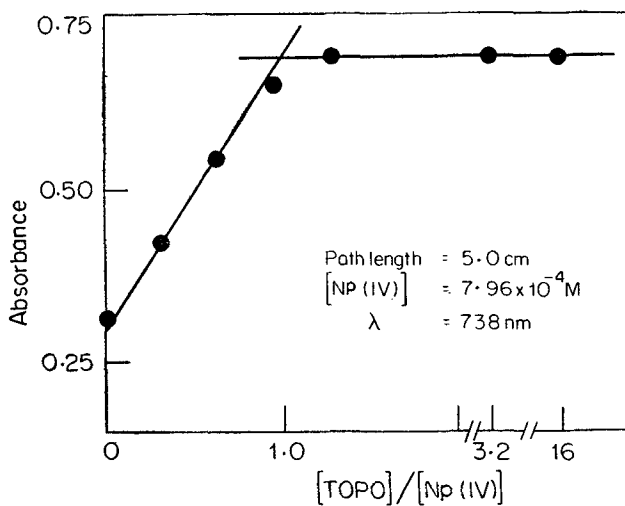


Figure 2. Variation of the absorbance value of $\text{Np}(\text{IV})$ with $(\text{TOPO})/[\text{Np}(\text{IV})]$.

and the equilibrium constant for this reaction is given by

$$\beta_{AB} = \frac{[\text{Np}(\text{TTA})_4 \cdot \text{TPPO}]}{[\text{Np}(\text{TTA})_4][\text{TPPO}]} \quad (3)$$

As only two absorbing species, *viz.* $\text{Np}(\text{TTA})_4$ and $\text{Np}(\text{TTA})_4 \cdot \text{TPPO}$ are responsible for the given absorption spectrum, the observed molar extinction coefficient (E) at a particular wavelength can be given by the relation

$$EC = E_1C_1 + E_2C_2, \quad (4)$$

where E_1 = molar extinction coefficient of $\text{Np}(\text{TTA})_4$, E_2 = molar extinction coefficient of $\text{Np}(\text{TTA})_4 \cdot \text{TPPO}$, C = total concentration of $\text{Np}(\text{IV})$, C_1 = concentration of $\text{Np}(\text{TTA})_4$ and C_2 = concentration of $\text{Np}(\text{TTA})_4 \cdot \text{TPPO}$, and C , C_1 and C_2 are related by

$$C = C_1 + C_2. \quad (5)$$

Using (4) and (5), C_1 and C_2 can be expressed in terms of C , E , E_1 and E_2 . Thus,

$$C_1 = (E - E_2) C / (E_1 - E_2) \quad (6)$$

and $C_2 = (E_1 - E) C / (E_1 - E_2). \quad (7)$

On substituting these values of C_1 and C_2 in (3), (8) is obtained

$$\beta_{AB} = \frac{C_2}{C_1 [\text{TPPO}]_{\text{free}}} = \frac{(E_1 - E)}{(E - E_2)} \times \frac{1}{[\text{TPPO}]_{\text{free}}}. \quad (8)$$

The equilibrium concentration of TPPO, $[\text{TPPO}]_{\text{free}}$, is given by

$$\begin{aligned} [\text{TPPO}]_{\text{free}} &= [\text{TPPO}]_{\text{total}} - C_2 \\ &= [\text{TPPO}]_{\text{total}} - \frac{(E_1 - E) C}{(E_1 - E_2)}. \end{aligned} \quad (9)$$

When C and path length of the cell are kept constant, E , E_1 and E_2 are proportional to A , A_1 and A_2 respectively where A is the observed absorbance at a particular wavelength, A_1 the absorbance of $\text{Np}(\text{TTA})_4$ at the same wavelength and A_2 the absorbance of $\text{Np}(\text{TTA})_4 \cdot \text{TPPO}$, also at the same wavelength. Thus by knowing the values of C , $[\text{TPPO}]_{\text{total}}$, A , A_1 and A_2 , the values of β_{AB} can be calculated using eqn. (10)

$$\beta_{AB} = \frac{(A_1 - A)}{(A - A_2)} \times \frac{1}{[\text{TPPO}]_{\text{free}}}, \quad (10)$$

where $[\text{TPPO}]_{\text{free}} = [\text{TPPO}]_{\text{total}} - \frac{(A_1 - A) C}{(A_1 - A_2)}. \quad (11)$

The values of A_1 were obtained from the absorption spectrum of $\text{Np}(\text{TTA})_4$ in the absence of S , and the values of A_2 from the spectrum of $\text{Np}(\text{IV})$ at $[S]/[\text{Np}(\text{IV})] = 31.4, 33.3$ and 69.2 for TPPO, DBBP and DOSO respectively, as any further increase in the $[S]/[\text{Np}(\text{IV})]$ ratio did not result in any observable change in the spectrum, thereby suggesting the complete conversion of $\text{Np}(\text{TTA})_4$ to $\text{Np}(\text{TTA})_4 \cdot S$ under these conditions. For calculating $[S]_{\text{free}}$ using (11), the interaction between HTTA and S was neglected as it was expected to be much weaker as compared with the adduct formation constant. The values of A_1 , A_2 and A obtained at different wavelengths and the values of β_{AB} calculated

from them, for a few wavelengths, are given in tables 1-3. The β_{AB} values obtained at different wavelengths agree well with each other, the average values being $(1.85 \pm 0.21) \times 10^4$ (TPPO), $(4.72 \pm 0.19) \times 10^3$ (DBBP) and $(2.12 \pm 0.07) \times 10^3$ (DOSO).

3.1c. *Adduct formation between $Np(TTA)_4$ and TBP*: The evaluation of the adduct formation constant of $Np(TTA)_4$ with TBP was attempted by the spectrophotometric method. From the solvent extraction studies a value of $\beta_{AB} = 565$ has been reported (Ramanujam *et al* 1979). This suggested that much higher

Table 1. Spectrophotometric data on the adduct formation between $Np(TTA)_4$ and TPPO.

$$[Np(IV)] = 7.96 \times 10^{-4} \text{ M}$$

[TPPO]/[Np(IV)]	Absorbance at wavelength (nm)				
	730	733	736	739	742
0 (A_1)	0.281	0.278	0.298	0.313	0.302
0.628	0.442	0.476	0.566	0.575	0.431
0.942	0.502	0.550	0.680	0.646	0.453
1.26	0.540	0.590	0.722	0.722	0.502
1.57	0.543	0.597	0.737	0.733	0.500
3.14	0.562	0.618	0.770	0.763	0.520
31.4 (A_2)	0.577	0.636	0.788	0.793	0.533
Avg. $\beta_{AB} \times 10^{-4}$	1.69	2.16	1.96	1.60	1.83

Table 2. Spectrophotometric data on the adduct formation between $Np(TTA)_4$ and DBBP.

$$[Np(IV)] = 7.80 \times 10^{-4} \text{ M}$$

[DBBP]/[Np(IV)]	Absorbance at wavelength (nm)				
	730	734	738	742	773
0 (A_1)	0.280	0.280	0.309	0.302	0.145
0.412	0.356	0.377	0.431	0.361	0.218
0.833	0.418	0.457	0.534	0.406	0.275
1.25	0.461	0.516	0.602	0.437	0.315
1.67	0.482	0.543	0.634	0.451	0.328
2.08	0.493	0.557	0.649	0.462	0.344
33.3 (A_2)	0.542	0.620	0.730	0.497	0.388
Avg. $\beta_{AB} \times 10^{-3}$	4.62	4.59	4.68	4.83	4.79

Table 3. Spectrophotometric data on the adduct formation between $\text{Np}(\text{TTA})_4$ and DOSO.

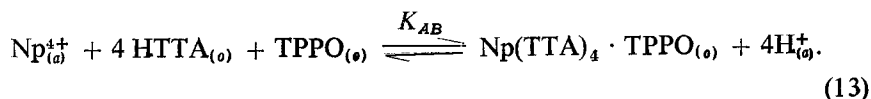
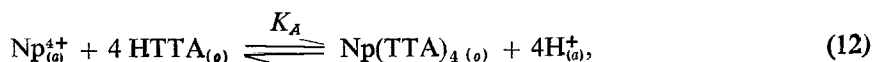
$$[\text{Np}(\text{IV})] = 7.80 \times 10^{-4} \text{ M}$$

[DOSO]/[Np(IV)]	Absorbance at wavelength (nm)				
	730	734	738	742	745
0 (A_1)	0.277	0.278	0.311	0.296	0.277
0.433	0.340	0.360	0.413	0.353	0.319
0.865	0.400	0.434	0.502	0.403	0.358
1.29	0.433	0.483	0.565	0.436	0.387
1.73	0.460	0.515	0.605	0.454	0.402
2.17	0.488	0.544	0.641	0.477	0.423
4.33	0.521	0.590	0.693	0.503	0.442
69.2 (A_2)	0.563	0.646	0.758	0.542	0.477
Avg. $\beta_{AB} \times 10^{-3}$	2.12	2.10	2.23	2.19	1.93

concentrations of TBP, relative to the concentrations of neutral donors studied, earlier, have to be used to get measurable changes in the absorption spectrum of $\text{Np}(\text{TTA})_4$. Attempts to measure the absorption spectra using such concentrations of TBP revealed that under these conditions $\text{Np}(\text{IV})$ is partially oxidised. Even by using too much excess of HTTA, which aids the stabilization of the oxidation state, this difficulty could not be overcome. No adduct formation constant could be calculated for this system although the spectral changes did indicate adduct formation.

3.2. Solvent extraction of $\text{Np}(\text{IV})$ by HTTA and HTTA + TPPO in benzene

The extraction of $\text{Np}(\text{IV})$ from perchlorate medium by solutions of HTTA and mixtures of HTTA and TPPO is given by (12) and (13) respectively



The concentration equilibrium constants K_A and K_{AB} are given by

$$K_A = \frac{[\text{Np}(\text{TTA})_4] [\text{H}^+]^4}{[\text{Np}^{4+}] [\text{HTTA}]^4} = D_A \frac{[\text{H}^+]^4}{[\text{HTTA}]^4}, \quad (14)$$

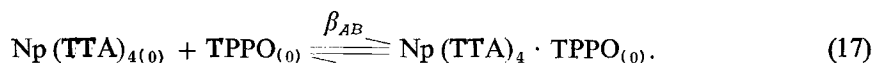
where $D_A = [\text{Np}(\text{TTA})_4]/[\text{Np}^{4+}]$ is the distribution ratio of $\text{Np}(\text{IV})$ with solutions of HTTA alone and

$$K_{AB} = \frac{[\text{Np}(\text{TTA})_4 \cdot \text{TPPO}] [\text{H}^+]^4}{[\text{Np}^{4+}] [\text{HTTA}]^4 [\text{TPPO}]} = D_{AB} \frac{[\text{H}^+]^4}{[\text{HTTA}]^4 [\text{TPPO}]}, \quad (15)$$

where $D_{AB} = D - D_A$, and D is the observed distribution ratio of Np(IV) at the same concentration of HTTA but in the presence of TPPO. From (14) and (15) it can be shown that

$$K_{AB}/K_A = D_{AB}/D_A [\text{TPPO}] = (D - D_A)/D_A [\text{TPPO}] = \beta_{AB}, \quad (16)$$

where β_{AB} is the equilibrium constant for the organic phase reaction represented by (17)



In order to calculate the adduct formation constant (β_{AB}) using the relation expressed by (16), the distribution ratio data for Np(IV) were obtained by keeping the concentrations of HTTA and H^+ constant and varying TPPO concentration. The data obtained are given in table 4 along with the β_{AB} values calculated from these data. An average value of $\beta_{AB} = (1.78 \pm 0.15) \times 10^4$ was obtained.

4. Discussion

A comparison of the β_{AB} values obtained in the present work with those obtained earlier using solvent extraction methods, given in table 5, indicates excellent agreement between the two, thus supporting the view that adduct formation responsible for synergistic enhancement results in the organic phase. The solvent extraction methods, as illustrated in the present work with TPPO, are more commonly used to calculate the formation constants of the adducts formed in synergistic extraction. However, when the oxidation state of the metal ion is unstable, especially in contact with an organic extractant, as in the case of U(IV) (Irving and Edgington 1961) or when the neutral donor alone extracts the metal ion under the experimental conditions used, thereby leading to the formation of a number of species in the organic phase, as in the case of the extraction of tetravalent metal ions from nitric acid medium (Irving and Edgington 1961) the solvent extraction method is rather difficult to use for the evaluation of adduct formation constants. In such cases the spectrophotometric method becomes

Table 4. Variation of the distribution ratio of Np(IV) with TPPO concentration. (Aq. phase : 1.0 M HClO_4 ; Temp : 25° C)

[TPPO] M $\times 10^2$	[HTTA] = 0.02 M		[HTTA] = 0.025 M	
	D	$\beta_{AB} \times 10^{-4}$	D	$\beta_{AB} \times 10^{-4}$
0.0	0.0712	..	0.177	..
0.1	1.48	1.99	3.22	1.72
0.2	2.93	2.01	6.52	1.79
0.3	4.06	1.87	9.00	1.66
0.4	5.00	1.73	11.6	1.61
0.5	6.49	1.80	13.9	1.55

Table 5. Summary of the β_{AB} values for adducts between $\text{Np}(\text{TTA})_4$ and some neutral donors.

Neutral donor	Spectrophotometric method		Solvent extraction method	
	$\log \beta_{AB}$	Ref.	$\log \beta_{AB}$	Ref.
TOPO	5.67	Patil <i>et al</i> 1980b
TPPO	4.27	Present work	4.25	Present work
DBBP	3.67	Present work	3.66	Sajun <i>et al</i> 1981
DOSO	3.33	Present work	3.48	Patil <i>et al</i> 1981
TBP	2.75	Ramanujam <i>et al</i> 1979

distinctly advantageous provided the metal betadiketonate has suitable absorption spectrum and is influenced significantly by adduct formation with neutral donor. Fortunately all the tetravalent actinide betadiketonates, barring Th, do exhibit this and hence the adduct formation in their case can be conveniently studied by spectrophotometry.

From the data presented in table 5, it is seen that the adduct formation constants decrease in the order: **TOPO** > **TPPO** > **DBBP** > **DOSO** > **TBP**, and this order is the same as the order of the basicity of these neutral donors. Thus, it can be concluded that the strength of the adduct increases with the basicity of the neutral donor.

The absorption spectra of all the adducts, $\text{Np}(\text{TTA})_4\text{S}$, studied were identical to each other, whereas they differed very much from that of the 8-coordinated $\text{Np}(\text{TTA})_4$. Thus the spectral changes observed in the present study can be attributed to an increase in the coordination number of $\text{Np}(\text{IV})$ from 8 in $\text{Np}(\text{TTA})_4$ to 9 in the adduct, indicating that the neutral donor is directly attached to the metal. It may be reasonable to expect these adducts may be isostructural with similar adducts of $\text{Th}(\text{TTA})_4$ and $\text{U}(\text{TTA})_4$ with TOPO which are established to be 9-coordinated (Leipoldt 1975; Patil *et al* 1979c).

Acknowledgement

We are grateful to Dr M V Ramaniah, Radiological Group, for his interest in this work. One of us (MSS) is thankful to the Department of Atomic Energy for a fellowship under the Bombay University-BARC collaboration programme.

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