# Studies on the Extraction of Metal Complexes

## XXI. The Complex Formation of Thorium with Tropolone

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A study on chloroform extraction of the Y(III), La(III), Th(IV) and U(VI) tropolonates showed that Th and U may be separated very well from the trivalent ions.

Calculations on the distribution curve for Th gave a mean complexity constant of 8.14 for the formation of the Th tropolonate. This value is higher than for the acetylacetonate, but lower than for the oxinate.

Tropolone has a structure such that one might suppose that it would form extractable metal complexes. This supposition is supported by some statements by Cook and Loudon [1] and by Doering and Knox [2] concerning the solubility of the Cu(II) and Fe(III) tropolonates in chloroform. A study was therefore undertaken to discover if Th(IV), U(VI) and trivalent metals like Y(III) and La(III) could be separated by chloroform extraction using tropolone as the complexing agent.

Apart from the interest in solvent extraction separations, it is possible to determine from the data on Th the complex formation between $Th^{4+}$ and the tropolonate ion ($A^-$). Previously such investigations have been published by our group for the ligand ions acetylacetonate [3], oxinate [4] and cupferrate [4]. Studies on the complex formation of some bivalent metals with tropolone have been carried out by Bryant, Fernelius and Douglas [5].

## EXPERIMENTAL

The experimental technique has been described in several of the papers in this series (*cf. e. g.* Ref.[4]) and all experiments were again carried out at 25° C. The tropolone, which was supplied by Dr. Hans Fernholz, was dissolved in alcohol-free, water-saturated chloroform. The ionic strength in the aqueous phase was kept constant at 0.1 M using 0.1 M $HClO_4$, $NaClO_4$ and NaOH, and the initial volumes of the two phases were 15 ml. The distribution of Th, Y and La was measured radiometrically using $^{234}Th(UX_1)$, $^{140}La$ and $^{90}Y$ as tracers. The distribution of U, however, was determined by spectrophotometric

*Table 1. Distribution of U(VI) between chloroform and 0.1 M perchlorate solutions at 25° C as a function of the tropolonate ion concentration in the aqueous phase.* $[U]'_{aq}=10^{-4}\ M$.

| $[HA]'_{org}$ M | $A_{400}$ | log $q$ [a] | $-$log $[H^+]$ | $-$log $[A^-]$ |
|---|---|---|---|---|
| 0.05 | 0.452 | +0.33 | 1.03 | 8.68 |
| 0.05 | 0.488 | +0.45 | 1.15 | 8.56 |
| 0.05 | 0.561 | +0.74 | 1.24 | 8.47 |
| 0.05 | 0.607 | +1.04 | 1.53 | 8.18 |
| 0.05 | 0.655 | +1.91 | 2.00 | 7.71 |
| 0.05 | 0.659 | +2.21 | 2.31 | 7.40 |
| 0.025 | 0.112 | $-$0.69 | 1.02 | 8.99 |
| 0.025 | 0.171 | $-$0.46 | 1.12 | 8.89 |
| 0.02 | 0.132 | $-$0.60 | 1.00 | 9.11 |
| 0.02 | 0.189 | $-$0.40 | 1.24 | 8.87 |
| 0.02 | 0.342 | +0.03 | 1.52 | 8.59 |
| 0.02 | 0.649 | +1.67 | 2.09 | 8.02 |

[a]) $q=A_{400}/(0.663-A_{400})$

*Table 2. Distribution of Th-$^{234}$Th between chloroform and 0.1 M perchlorate solutions at 25° C as a function of the tropolonate ion concentration in the aqueous phase.*

| $[HA]'_{org}$ M | $-$log $[Th]'_{aq}$ | $I_{org}$ cpm | $I_{aq}$ cpm | log $q$ | $-$log $[H^+]$ | $-$ log $[A^-]$ |
|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 0.1 | 5.70 | 6 429 | 1 095 | +0.80 | 1.07 | 8.34 |
| 0.1 | 5.88 | 13 426 | 672 | +1.33 | 1.29 | 8.12 |
| 0.1 | 5.70 | 6 905 | 366 | +1.30 | 1.34 | 8.07 |
| 0.1 | 5.88 | 10 952 | 163.0 | +1.86 | 1.64 | 7.77 |
| 0.1 | 5.70 | 7 381 | 114.3 | +1.84 | 1.67 | 7.74 |
| 0.1 | 5.88 | 13 817 | 79.6 | +2.27 | 2.19 | 7.22 |
| 0.1 | 5.88 | 12 940 | 12.2 | +3.05 | 2.55 | 6.86 |
| 0.1 | 5.88 | 12 751 | 6.2 | +3.34 | 2.77 | 6.64 |
| 0.1 | 5.88 | 11 135 | 7.4 | +3.21 | 5.82 | 3.59 |
| 0.1 | 5.88 | 11 040 | 4.1 | +3.46 | 5.96 | 3.45 |
| 0.1 | 5.88 | 11 004 | 5.2 | +3.35 | 6.43 | 2.98 |
| 0.1 | 5.88 | 12 680 | 3.4 | +3.60 | 6.45 | 2.96 |
| 0.1 | 6.18 | 7 911 | $-$0.8 | $-$ | 6.86 | 2.56 |
| 0.1 | 5.70 | 7 487 | 7.1 | +3.05 | 6.98 | 2.45 |
| 0.1 | 5.70 | 7 317 | 33.2 | +2.37 | 7.73 | 1.76 |
| 0.1 | 5.88 | 12 582 | 412 | +1.51 | 8.74 | 1.17 |
| 0.05 | 5.70 | 6 152 | 7 275 | $-$0.05 | 1.05 | 8.66 |
| 0.05 | 5.70 | 9 577 | 3 373 | +0.48 | 1.38 | 8.33 |
| 0.05 | 5.70 | 11 726 | 1 105 | +1.05 | 1.61 | 8.10 |
| 0.05 | 5.70 | 12 533 | 359 | +1.57 | 1.89 | 7.82 |
| 0.05 | 5.88 | 9 510 | 115.6 | +1.94 | 2.07 | 7.64 |
| 0.05 | 5.70 | 12 573 | 53.2 | +2.40 | 2.16 | 7.55 |
| 0.05 | 5.88 | 9 649 | 105.8 | +1.99 | 2.20 | 7.51 |
| 0.05 | 5.88 | 9 757 | 85.9 | +2.08 | 2.23 | 7.48 |
| 0.05 | 5.88 | 9 492 | 6.8 | +3.17 | 3.52 | 6.19 |
| 0.05 | 5.88 | 7 915 | 8.6 | +2.99 | 4.47 | 5.24 |
| 0.05 | 5.88 | 8 058 | 3.8 | +3.36 | 4.79 | 4.92 |

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| 0.05 | 5.88 | 7 930 | 4.5 | +3.27 | 6.37 | 3.34 |
| 0.05 | 5.88 | 8 038 | 12.3 | +2.84 | 7.26 | 2.48 |
| 0.05 | 5.88 | 9 422 | 17.2 | +2.77 | 7.30 | 2.44 |
| 0.05 | 5.88 | 9 311 | 71.8 | +2.14 | 8.10 | 1.78 |
| 0.05 | 5.88 | 8 510 | 547 | +1.22 | 10.33 | 1.30 |
| 0.02 | 5.88 | 1 446 | 10 539 | −0.84 | 1.07 | 9.04 |
| 0.02 | 5.88 | 2 666 | 8 992 | −0.50 | 1.34 | 8.77 |
| 0.02 | 5.88 | 5 767 | 4 985 | +0.09 | 1.63 | 8.48 |
| 0.02 | 5.88 | 8 583 | 1 886 | +0.69 | 1.96 | 8.15 |
| 0.02 | 5.70 | 11 755 | 1 683 | +0.87 | 2.03 | 8.08 |
| 0.02 | 5.70 | 11 861 | 952 | +1.12 | 2.32 | 7.79 |
| 0.02 | 5.70 | 12 978 | 249 | +1.74 | 2.67 | 7.44 |
| 0.01 | 5.88 | 100.0 | 11 159 | −2.02 | 1.04 | 9.37 |
| 0.01 | 5.88 | 361 | 10 849 | −1.45 | 1.09 | 9.32 |
| 0.01 | 5.88 | 554 | 13 787 | −1.37 | 1.29 | 9.12 |
| 0.01 | 5.88 | 2 128 | 9 904 | −0.64 | 1.56 | 8.85 |
| 0.01 | 5.88 | 2 490 | 11 742 | −0.65 | 1.60 | 8.81 |
| 0.01 | 5.88 | 6 700 | 7 067 | +0.00 | 1.88 | 8.53 |
| 0.01 | 5.88 | 7 698 | 4 054 | +0.31 | 2.03 | 8.38 |
| 0.01 | 5.88 | 9 331 | 2 108 | +0.67 | 2.20 | 8.21 |
| 0.01 | 5.88 | 12 801 | 682 | +1.30 | 2.48 | 7.93 |
| 0.01 | 5.88 | 11 599 | 18.9 | +2.82 | 4.97 | 5.44 |
| 0.01 | 5.88 | 11 354 | 23.3 | +2.71 | 7.58 | 2.89 |
| 0.005 | 6.18 | 37.3 | 11 223 | −2.45 | 1.10 | 9.61 |
| 0.005 | 6.18 | 90.7 | 11 071 | −2.06 | 1.37 | 9.34 |
| 0.005 | 6.18 | 337 | 10 783 | −1.48 | 1.66 | 9.05 |
| 0.005 | 6.18 | 1 378 | 9 649 | −0.82 | 1.95 | 8.76 |
| 0.005 | 6.18 | 4 623 | 6 121 | −0.09 | 2.26 | 8.45 |
| 0.005 | 6.18 | 8 704 | 3 552 | +0.42 | 2.54 | 8.17 |
| 0.002 | 6.18 | 11.2 | 9 449 | −2.90 | 1.33 | 9.78 |
| 0.002 | 6.18 | 36.9 | 9 293 | −2.37 | 1.69 | 9.42 |
| 0.002 | 6.18 | 135.0 | 9 184 | −1.80 | 1.92 | 9.19 |
| 0.002 | 6.18 | 684 | 8 615 | −1.07 | 2.20 | 8.91 |
| 0.002 | 6.18 | 2 110 | 7 339 | −0.51 | 2.50 | 8.61 |
| 0.002 | 6.18 | 5 087 | 4 184 | +0.12 | 2.88 | 8.23 |
| 0.001 | 6.18 | 21.5 | 8 885 | −2.59 | 1.51 | 9.80 |
| 0.001 | 6.18 | 28.4 | 8 925 | −2.47 | 1.81 | 9.50 |
| 0.001 | 6.18 | 212 | 7 992 | −1.56 | 2.26 | 9.16 |
| 0.001 | 6.18 | 1 619 | 7 155 | −0.62 | 2.70 | 8.72 |
| 0.001 | 6.18 | 5 274 | 3 380 | +0.22 | 3.05 | 8.37 |

\* Standard deviation: $\sqrt{\overline{I}}/\sqrt{\overline{5}}$ cpm.

measurements of the chloroform phases at 400 m$\mu$ using a Beckman DU spectrophotometer with 1 cm cells. With Y and La only a few experiments were made, as the solubilities of these tropolonates in chloroform are only about $27 \cdot 10^{-6}$ M and $5 \cdot 10^{-6}$ M.

The hydrogen ion concentration, $-\log[H^+]$, was measured by means of a Radiometer pHM3i potentiometer equipped with glass and calomel electrodes, which were checked against 0.1 M buffers of known $-\log[H^+]$. The free ligand ion concentration in the aqueous phase, $-\log[A^-]$, was calculated using the stoichiometric dissociation constant $10^{-6.71}$ and the partition coefficient $10^{1.70}$ given in Part XVIII [6].

In the Tables, [HA]$'_{org}$ refers to the initial concentration of tropolone in the chloroform phase, and [U]$'_{aq}$ and [Th]$'_{aq}$ refer to the initial total concentrations of U and Th

in the aqueous phase. $I_{org}$ and $I_{aq}$ in Table 2 are the measured radioactivities of equal volumes of the phases and the distribution ratio $q$ is given by

$$q = \frac{I_{org}}{I_{aq}} \cdot (1.067 \pm 0.010)$$

The correction factor 1.067 is introduced because the ratio $I_{org}/I_{aq}$ does not quite correspond to the ratio of Th concentrations due to differences in absorption and scattering of beta particles. The correction factor was calculated from the data for the Th-tropolone system with the method described in Part VI [4].

The partition coefficient of ThA$_4$ was determined from 16 values on the plateau of the distribution curve (see Fig. 2)

$$\lambda_4 = \frac{I_{org}}{I_{aq}} = \frac{190\ 756}{140.2 \pm 5.3} \cdot (1.067 \pm 0.010) = 1\ 450 \pm 70$$

$$\log \lambda_4 = 3.16 \pm 0.02$$

## RESULTS

Fig. 1 shows that $UO^{2+}$ and $Th^{4+}$ may be separated very well from trivalent ions like $Y^{3+}$ and $La^{3+}$ by extraction with e. g. a 0.05 M chloroform solution of tropolone at pH 2. The sequence for $Th^{4+}$, $Y^{3+}$ and $La^{3+}$ is that expected from the ionic charges and radii (1.02, 0.92 and 1.14 Å). As with cupferron [7] the extraction of $La^{3+}$ is poor, the solubility of La tropolonate being even less in chloroform than in the aqueous phase ($\lambda_3 < 1$).

The data for U(VI) are given in Table 1. The range of log $q$ is too small for the calculation of complexity constants. However, if log $q$ is plotted against $-\log[A^-]$ a straight line is obtained with a slope equal to 2. The equation for this line is (eqn. 7 in Part V[8])

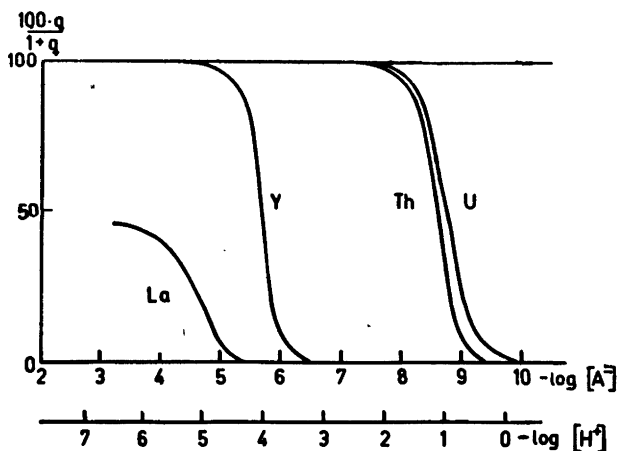$$\log q = \log \lambda_2 \varkappa_2 + 2 \log [A^-]$$



*Fig. 1. The distributition of Y(III), La(III), Th(IV) and U(VI) between chloroform and 0.1 M perchlorate solutions as a function of the tropolonate ion concentration. The corresponding values of $-\log[H^+]$ are given for the case when an aqueous solution is equilibrated with an equal volume of a 0.05 M solution of tropolone in chloroform.*
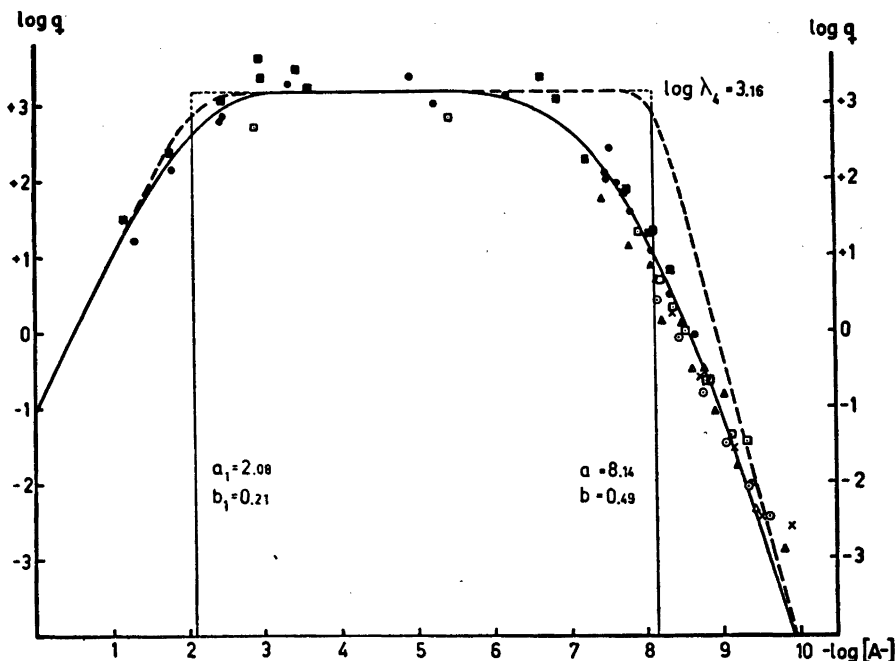
*Fig. 2. The distribution ratio of Th as a function of the tropolonate ion concentration in the aqueous phase. To the right positive complexes predominate in the aqueous phase and to the left negative complexes seem to be formed. In the intermediate range the uncharged complex* $ThA_4$ *predominates (case III in Part V[8]). Initial concentration of tropolone in the chloroform phase:* ■ *0.1 M;* ● *0.05 M;* ▲ *0.02 M;* □ *0.01 M;* ○ *0.005 M;* △ *0.002 M;* × *0.001 M.*

where

$$\log \lambda_2 \varkappa_2 = 17.48$$

The data for thorium are given in Table 2, and are plotted in Fig. 2. The full curve in this figure is calculated with the two-parameter method described in Part V [8] (case III) using the following parameters:

$$a = 8.14$$
$$b = 0.49$$
$$\log \lambda_4 = 3.16$$
$$a_1 = 2.08$$
$$b_1 = 0.21$$

The parameter $a$ expresses the mean complexity constant $10^a$ and the complexity product

$$\varkappa_4 = \frac{[ThA_4]}{[Th^{4+}][A^-]^4} = k_1 k_2 k_3 k_4 = 10^{4a} = 10^{32.56}$$

The parameter $b$ expresses the mean spreading factor of the complexity constants $k_n$

$$k_n / k_{n+1} = 10^{2b} = 10^{0.98}$$

The complexity constants are defined as

$$k_n = \frac{[ThA_n]}{[ThA_{n-1}][A]} = 10^{a+b(5-2n)}$$

and hence

$$k_1 = 10^{9.61} \qquad k_3 = 10^{7.65}$$
$$k_2 = 10^{8.63} \qquad k_4 = 10^{6.67}$$

The distribution constant of Th tropolonate is

$$\lambda_4 = \frac{[ThA_4]_{org}}{[ThA_4]_{aq}} = 10^{3.16}$$

Furthermore, the results at high tropolonate ion concentrations indicate that negative complexes, $ThA_5^-$ and $ThA_6^{2-}$, are also formed. These complexity constants are obtained from the parameters $a_1$ and $b_1$

$$k_5 = 10^{a_1+b_1} = 10^{2.29}$$
$$k_6 = 10^{a_1-b_1} = 10^{1.87}$$

The dashes represent the curve calculated assuming that the only Th complexes formed are $ThA_4$ and $ThA_6^{2-}$. Obviously this is not so.


## DISCUSSION

It has been shown by Bryant, Fernelius and Douglas [5] that the complex formation of Cu(II) with acetylacetone is weaker than with tropolone and this seems also to be the case for thorium.

Table 3 lists the results for thorium that have been published so far by our group. As new data on other reagents will be published shortly a general discussion of our results will be deferred. However, some properties, which seem to influence the complexity constants of $Th^{4+}$ may be indicated briefly.

From Table 3 it is obvious that no general statements such as "five-membered chelate rings are more stable than six-membered rings" or "acid strength correlates with chelate stability" are sufficient to explain the behavior of these different agents with $Th^{4+}$.

No such correlation as the latter should be expected as hydrogen (on the basis of infrared measurements [9] and theoretical calculations [10]) appears to form one short covalent bond and one long ionic hydrogen bond with the two donor atoms in the chelate ring, while thorium would very likely form only ionic bonds. It seems as if there is a marked correlation between the infrared vibration frequency of the OH-bond and the calculated length of the H-bond except for cupferron. This may indicate that the chelate ring in cupferron is not planar due to a O—O repulsion. The distance in acetylacetone is especially

*Table 3. Summary of data on some chelating agents.*



| Structure | Acetylacetone | Cupferron | Tropolone | Oxine |
|---|---|---|---|---|
| No. of atoms in chelate ring | 6 | 5 | 5 | 5 |
| O—O(N)distance (Å) in chelate ligand [a] | 2.40 | 2.15 | 2.50 | 2.80 |
| OH—O(N)distance [a] (Å) | 1.40 | 1.45 | 1.90 | 2.25 |
| Frequency (cm$^{-1}$) of infrared abs. max. for OH-band | 2 650 | 3 360 | 3 100 | 3 430 |
| Length (Å) of OH-bond from infrared data [b] | 1.12 | 1.00 | 1.04 | 0.99 |
| Dissociation constant of of HA, p$k_a$ | 8.81 [c] | 4.16 | 6.71 | 9.66 |
| Mean complexity constant of ThA$_4$, $\frac{1}{4}$log $\varkappa_4$ ($= a$) | 6.70 [d] | 6.75 | 8.14 | 9.70 |
| Mean spreading factor, log $k_n$ $-$log $k_{n+1}$ ($= 2\ b$) | 0.90 [d] | 0.40 | 0.98 | 0.50 |
| Partition coefficient of HA between chloroform and water, log $k_d$ | 1.37 [e] | 2.18 | 1.71 | 2.66 |
| Partition coefficient of ThA$_4$ between chloroform and water, log $\lambda_4$ | 2.57 [d] | 2.79 | 3.16 | 2.39 |

[a] Calculated for planar chelate rings from covalent bond radii and approximate bond angles.

[b] Calculated from Badger's [11] rule $\omega^2\ (r\text{—}0.335)^3 =$ k, using $\omega = 3\ 620\ \text{cm}^{-1}$ and $r = 0.97$ Å for naphthol and phenol.

[c] Reported by Rydberg [12]. The value for the pure enol form (calculated from the keto-enol equilibrium constant of 0.205 reported by Eidinoff [13]) is 8.05.

[d] Calculated by the two-parameter method [8] from data given by Rydberg [3].

[e] Reported in Part IX [12]. The value for the pure enol form (calculated from data by Eidinoff [13] and Meyer [14]) is 2.03.

favorable for a strong chelate binding of hydrogen. In the case of thorium it seems as if the long O—N distance in the oxinate ligand is more favorable for complex formation than the somewhat shorter O—O distance in tropolone. The much lower complexity constants for the acetylacetonate and cupferrate ligands may very well be explained by the fact that these ligands are not stabilized in one plane by an aromatic ring, but may rotate around a bond in the part of the ligand ion, which forms the chelate ring.

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