Potentiometric and UV-Visible Spectrophotometric Studies of the Stability of Thorium(IV) Complexes with (o-Hydroxyphenyl) Mono- and Di-Methylenephosphonic Acids

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ORIGINAL PAPER

Potentiometric and UV-Visible Spectrophotometric Studies of the Stability of Thorium(IV) Complexes with (*o*-Hydroxyphenyl) Mono- and Di-Methylenephosphonic Acids

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Abstract Protometric studies were performed in aqueous solutions at 25 °C and 0.1 mol·dm^{-3} ionic strength ($NaClO_4$) to determine the complexing abilities of eight (*o*-hydroxy-phenyl) mono- and di-methylenephosphonic acids (differently substituted by chromophoric or auxochromic groups) towards thorium(IV). The number, the nature of the species present in solution, their overall stability constants over a broad acidity range and their individual electronic spectra, as resolved by computation, have been determined by potentiometry and UV-visible spectrophotometry.

The formation of 1:1 species, partially protonated MLH_x and totally deprotonated [ML], as well as hydroxo species – mononuclear $ML(OH)_x$ and dinuclear $M_2L(OH)_x$ is reported with thorium(IV). The results show that the complexing power, which is not very different in the lanthanide series, is much higher for thorium(IV). The ratio Th^{4+}/Eu^{3+} reaches eight $\log_{10}$ units with some of the ligands.

Keywords Thorium(IV) complexes · *o*-Hydroxyphenyl · Mono- and di-methylenephosphonic acids · Stability constants · Potentiometry · UV-visible spectrophotometry

1. Introduction

Thorium(IV) as the central metal ion in complexes has been studied as a representative model of the actinides. Kabachnik *et al.* [1] studied potentiometrically the complexation of the Th^{4+} ion at 25 °C (KCl 0.1 mol·dm^{-3}). They reported a constant $\log_{10}\beta_{110} = 23.9$ with methylenediphosphonic acid, but with 1-hydroxyethane-1,1-diphophonic acid reported the

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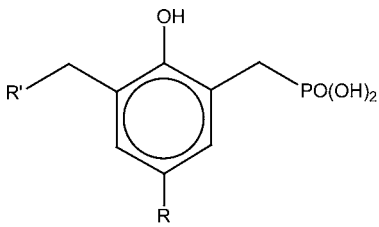
presence of two equilibria:

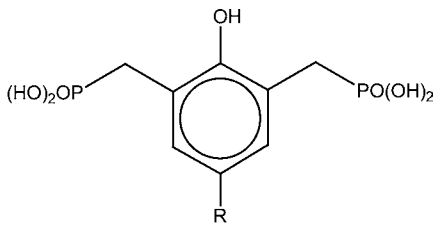
$$Th^{4+} + H_{-1}L^{5-} \rightleftharpoons Th(H_{-1}L)^{-} \quad \log_{10}\beta_{110} = 27.8$$
$$Th^{4+} + 2H_{-1}L^{5-} \rightleftharpoons Th(H_{-1}L)_2^{6-} \quad \log_{10}\beta_{120} = 39.9$$

New techniques of separation and concentration of actinides based on polymeric agents were used by Novikov *et al*. [2] for the interaction of poly (ethyleneimine-methylphosphonic) acids with actinide ions in a homogenous phase. Sabharwal *et al*. [3] reported that the extraction of thorium(IV) from bifunctional resins of phosphonic acids is a function of the nitric acid concentration. Actinide complexation with phosphonate molecules in aqueous solution was studied by Nash [4]. This thermodynamic and kinetic study showed that ligands with a doubly ionizable phosphonate group (-PO_3H_2), such as 1,1- and 1,2- diphosphonics, are very efficient in the processes of separation and in the treatment of nuclear wastes. A liquid–liquid extraction method was developed by Tao *et al*. [5] who studied the extraction of thorium nitrate with tri-*N*-butylphosphate (TBP). For Karayannis and co-workers [6], thorium tetrachloride with neutral phosphate and phosphonate esters gave complexes with polymeric configurations involving 8-coordinated metal ions. This fact has been widely reported and comparison can be made in the case of thorium tetraacetate complexes with EDTA and CDTA, which are highly stable ($\log_{10}\beta_{110} \sim 24$) [7] as compared to those formed with the triacetates NTA and HEDTA which have fewer coordinating atoms [8]. On the other hand, 8-coordination, assured by the eight donor atoms of the pentaacetate (DTPA), gives greater stability when complexed with thorium ($\log_{10}\beta_{110} > 27$). When this coordination is not assured, the formation of ThL complexes at acidic pH is followed by the formation of hydroxy and eventually polymerized species. However, even though DTPA shows 8-coordination of Th^{4+}, hydrolysis occurs at high pH with the formation of a monohydroxo complex [1]. TTHA (triethylene-tetraamine-hexaacetic acid), which has a very high potential for coordination, forms a very stable complex ($\log_{10}\beta_{110} \gg 27$) [9]. The complexing power of some phosphonic ligands with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) has been recently reported by Benghanem *et al*. [10].

The study of thorium complexes has undergone renewed interest with their implication in environmental chemistry and more so in the biological and medical sciences as in anti-viral drugs [11], hypothalamus metabolism [12] and in William's disease [13]. This is, therefore, a detailed potentiometric and spectrophotometric study concerning the complexation of the thorium cation with eight *o*-hydroxyphenyl ligands: 5 mono-methylene (triacids, H_3L,



Triacids (H_3L)



Pentaacids (H_5L)

1a : R = H and R' = H
1b : $PO(OH)_2$ in *para*, R and R' in *ortho* = H
1c : R = NO_2 and R' = H
1d : R = CH_3 and R' = NO_2
1e : R = NO_2 and R' = CH_3

2a : R = CH_3
2b : R = NO_2
2c : R = Cl

compounds **1a**–**1e**) and 3 di-methylene (pentaacids, H_5L, compounds **2a**–**2c**). The study of the complexing power of these molecules has possible applications in the treatment of radioactive liquid waste, because thorium may be considered to be a model tetravalent actinide. Eventually, a comparison is made with complexation of lanthanides, as well as a comparison of the complexing power with different ligands.

2. Experimental

2.1. Reagents

All of the compounds were prepared according to the method previously described [14] and their purity was further monitored by microanalysis:

Anal. Calc. for **1a**: C: 44.70; H: 4.82	Found C: 44.80; H: 4.80
Anal. Calc. for **1b**: C: 45.68; H: 4.82	Found C: 45.83; H: 4.70
Anal. Calc. for **1c**: C: 37.15; H: 3.76	Found C: 37.04; H: 3.53
Anal. Calc. for **1d**: C: 38.90; H: 4.08	Found C: 39.40; H: 4.01
Anal. Calc. for **1e**: C: 40.18; H: 4.32	Found C: 39.93; H: 4.11
Anal. Calc. for **2a**: C: 34.12; H: 5.82	Found C: 34.37; H: 5.58
Anal. Calc. for **2b**: C: 29.40; H: 3.39; N: 4.28	Found C: 28.50; H: 3.73; N: 3.99
Anal. Calc. for **2c**: C: 28.91; H: 4.69	Found C: 29.08; H: 4.40

They were used as free acids and their solutions were made by dissolution of a weighed quantity in bi-distilled water. Solutions of $1\,mol{\cdot}dm^{-3}$ $NaClO_4{\cdot}6H_2O$ (Fluka p.a.) and $1\,mol{\cdot}dm^{-3}$ NaOH and HCl (Merck) were prepared with doubly distilled and boiled water. The pH values of the solutions were adjusted by simple addition of acid ($HClO_4$) or of base (NaOH), and monitored with a precision pH-meter. The solution of $NaClO_4$ was added to the medium so that the ionic strength, I, remains constant and equal to $0.1\,mol{\cdot}dm^{-3}$. The base titrant used was sodium hydroxide prepared from an aqueous dilution of the commercial solution and its concentration was determined using a potassium hydrogen phthalate standard solution.

The metallic salt was the commercial p.a. thorium nitrate $Th(NO_3)_4{\cdot}5H_2O$. This salt was dried at room temperature under vacuum before use. Its stock aqueous solution $10^{-2}\,mol{\cdot}dm^{-3}$ was titrated by complexometry with EDTA at pH-6 (sodium acetate), using xylenol orange as indicator [15].

Ligand solutions were kept away from light in order to avoid degradation and were prepared in the concentration range 10^{-2} or $10^{-3}\,mol{\cdot}dm^{-3}$. A given amount of perchloric acid was initially added to all ligand solutions in order to completely protonate the ligand. The solution was then neutralized by NaOH solution 0.1 or $1\,mol{\cdot}dm^{-3}$ until $-\log_{10}[H^+] = 12$. In the following discussion, $-\log_{10}[H^+]$ will be abbreviated as pH.

The final analytical concentration of metal was 10^{-3} or $10^{-4}\,mol{\cdot}dm^{-3}$ for the potentiometric study and $10^{-4}\,mol{\cdot}dm^{-3}$ for measurements by spectrophotometry. $NaClO_4$, $0.1\,mol{\cdot}dm^{-3}$, was used as the reference solution. The final solutions of metal and ligand were prepared just before the measurements.

2.2. Potentiometric measurements

The potentiometric investigations of acid-base and metal-binding equilibria were carried out at 25.0 ± 0.1°C under an argon stream and at an ionic strength of $0.1\,mol{\cdot}dm^{-3}$ ($NaClO_4$).

The complexation was studied in aqueous solution with equal analytical concentrations of the ligand C_L and the cation C_M (10^{-3} mol·dm^{-3} with **1b**, **1d**, **2c** and 10^{-4} mol·dm^{-3} with **1a**, **1c**, **1e**, **2a**, **2b**). The titrating agent, (0.1 or 0.01 mol·dm^{-3}) NaOH, used was stored in a polyethylene container equipped with a CO_2 trap. All experiments were performed in a thermoregulated double-wall glass cell (25 cm^3) at 25.0 ± 0.1 °C according to the method previously described [16].

The stepwise addition of base was carried out with a microburette (Dosimat E 635, 1 cm^3) driven by an automatic titrator (Titroprocessor 636 Metrohm) able to deliver amounts of solution as small as 10^{-3} cm^3. The dynamic mode (variable addition of titrant, smaller in the steep equivalence regions) was used to establish the titration curve and its first derivative, and to collect the numerical data. The logarithm of the concentration of H^+ was measured with a combined glass electrode (Ingold) in which the reference liquid was replaced by a NaCl (0.01 mol·dm^{-3})-$NaClO_4$ (0.09 mol·dm^{-3}) solution of the same ionic strength as the solution to be measured. The electrode was calibrated in concentration units, using the experimental relation given below, with a and b being constants experimentally determined with calibration solutions of 10^{-2} and 10^{-3} mol·dm^{-3} HCl in 0.1 mol·dm^{-3} $NaClO_4$:

$$-\log_{10}[H^+]_{true} = -\log_{10}[H^+]_{read} + a + b\ \log_{10}[H^+]_{read}$$

The quantities within square brackets are the concentrations of the species.

2.3. Spectrophotometric measurements

The UV-visible spectra between 200 and 550 nm were recorded using a Shimadzu UV 2101 PC spectrophotometer equipped with a thermostat and matched 10 mm quartz cells. The absorption variations of acid-base and metal-binding equilibria were carried out at 25.0 ± 0.1 °C and the ionic strength, I, of solutions was maintained constant at 0.1 mol·dm^{-3} with the help of the supporting electrolyte, $NaClO_4$. The concentration of the ligands should not exceed 10^{-3} mol·dm^{-3} to guarantee accurate and confident absorbance values between 0.2 and 2.0. All investigations in the presence of metal ions were carried out at a 1:1 mole ratio of metal ion to ligand. No determination could be made with higher mole ratios due to precipitation phenomena. Therefore, the analytical concentration of the metal and ligand was fixed at 10^{-4} mol·dm^{-3}. Under such experimental conditions, only mononuclear and dinuclear complexes were envisaged. The spectra were recorded immediately after mixing the reagents and it took less than one minute to obtain the absorption curve in the studied range from 200 to 550 nm.

The 'flask' method was used which consists of preparing solutions separately in 20 mL measuring flasks, each containing the same quantities of ligand-metal, to which NaOH was added progressively to encompass the pH range from 1–12. This study permits calculation of the formation constants of the complexes as well as their molar extinction coefficients, which were then used to draw the individual electronic spectra of the species present in solution. The quantitative interpretation was carried out with two types of molecules (triacids: **1c**, **1d**, **1e**; and pentaacid: **2b**) containing the chromophore group NO_2 on the aromatic nucleus. Other molecules were not studied because of their feeble and insignificant spectral variations.

2.4. Computations

All of the equilibrium constants and their equations corresponding to the different equilibria involved in this study are described in our earlier publication [16].

2.4.1. Potentiometric data

Approximate values of the stepwise protonation constants, K_i, the overall protonation constants, β_{01z}, of the ligands [16, 17] and the hydrolysis constants, $\beta_{10\text{-}z}$, of thorium(IV) [18] were determined earlier and have been reported in the literature. The overall stability constants, $\beta_{x,y,z}$, of the complexes are computed. Treatment of the potentiometric data was done using several titrations, each including not less than 150 points, with the help of the SIRKO program [19]. The values reported in the tables are the mean values of the results of N independent runs, given with their 95% confidence interval $\pm 2\sigma_{N-1}$ where σ is the standard deviation. The R-factor (R_f) is the result of a statistical test related to the fit between the experimental and the calculated curves.

2.4.2. Spectrophotometric data

The whole set of spectrophotometric data (23 solutions and 32 wavelengths) obtained for different pH values was analyzed using the multiwavelength program Letagrop-Spefo [20], which refines the overall stability constants $\beta_{x,y,z}$ of the complexes. The protonation constants, $\beta_{0,1,z}$, of the deprotonated forms of the ligands were constant during the refinement procedure, as were the formation constants, $\beta_{1,0,z}$, of the hydroxo species for which z are negative. The calculated values are presented with a 99% confidence interval ($\pm 3\sigma$). The overall stability constants, $\beta_{x,y,z}$, of the complexes correspond to the following equilibrium:

$$x\mathrm{M}^{m+} + y\mathrm{L}^{n-} + z\mathrm{H}^{+} \rightleftharpoons \mathrm{M}_x\mathrm{L}_y\mathrm{H}_z^{(xm-yn+z)+}$$

$$\beta_{x,y,z} = \left[\mathrm{M}_x\mathrm{L}_y\mathrm{H}_z^{(xm-yn+z)+}\right]/[\mathrm{M}^{m+}]^x[\mathrm{L}^{n-}]^y[\mathrm{H}^{+}]^z$$

where x pertains to the metal (M), y is for the ligand (L) and z for the proton (H). In the case of hydroxo species, z is negative.

Using these data, the individual electronic spectra for each species could be constructed. For a given model, the quality of the fit is judged from the value of U, the sum of the squares of the differences between the experimental and calculated absorptions for N solutions at L wavelengths. If the value of U is smaller than 0.02 for (N, L), it is considered a good fit for such rather complicated multiparameter systems.

3. Results

A detailed quantitative interpretation of the potentiometric and spectrophotometric data was carried out and is presented below. The complete experimental data used for this interpretation are given as supplementary material in the Addenda.

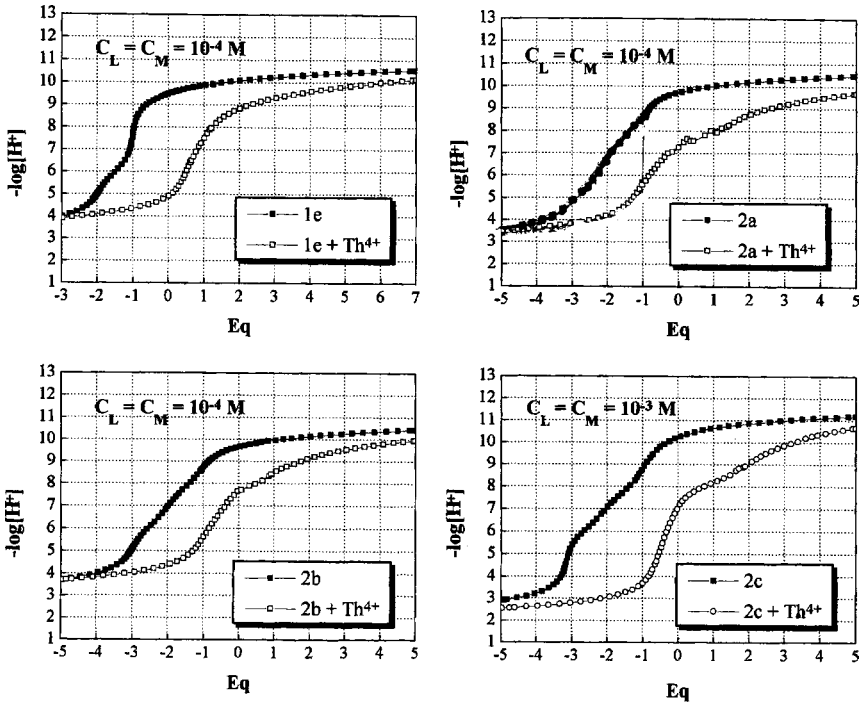


Fig. 1 Titration curves for the ligands and Th(IV)-ligand complexes in aqueous solution. ($C_L = C_M = 10^{-3}$ mol·dm^{-3}, 25 °C, $I = 0.1$ mol·dm^{-3} $NaClO_4$)

3.1. Potentiometric determinations

For the sake of clarity the interpretation of the experimental data is separated from that of the calculated parameters.

3.2.1. pH titrations

The titration curves of the ligand in the presence of Th^{4+} are shown in Fig. 1. They are all characterized by an important decrease in the overall pH suggesting the formation of very stable complexes. However, the complexation with Th^{4+} appears to vary from one ligand to the other, much more than was the case with the lanthanides [17].

(a) Triacids

- Ligand **1a**. The titration curve of **1a** in the presence of Th^{4+} is characterized by a very significant pH decrease around seven base equivalents. An inflexion at four equivalents corresponds to the formation of ThL^{+} and this is followed by a steep increase in pH between four and six equivalents with an inflexion at five equivalents corresponding to the formation of ThL(OH). This curve continues to increase indicating the probable formation of other species, which were identified later with theoretical calculations.
- Ligand **1b**. The addition of Th^{4+} to a solution of ligand **1b** and its titration by NaOH result in an inflexion at three equivalents which corresponds to ThL^{+}, followed by three clear inflexions corresponding: at four equivalents to ThL(OH), at five to $ThL(OH)_2^-$

and at six to $ThL(OH)_4^{3-}$. There is another inflexion marked by a strong pH increase at 4.5 equivalents corresponding to the formation of the binuclear species, $Th_2L(OH)_6^-$. This model was found, after the testing of different models during calculations, to be the most suitable.

– Ligand **1c**. The experimental curve of this ligand with Th^{4+} shows a feeble decrease in pH indicating weak complexation with this ligand. A jump in pH between one and three base equivalents is due to the neutralization of the protons of the ligand and the formation of ThL^+ at three equivalents. This is followed by a large buffer zone within the limits of three and eight equivalents corresponding to different hydroxide species that are difficult to identify directly from the experimental curves. *A posteriori* calculations propose that the best model observed between pH 3.71 and 10.02 is: ThL^+, ThL(OH), $ThL(OH)_2^-$ and $ThL(OH)_3^{2-}$.
– Ligand **1d**. When Th^{4+} is added to a solution of **1d**, the titration curve indicates a significant lowering of pH even beyond six equivalents of base and this is not solely because of the hydrolysis of the cation. This curve is characterized principally by a very clear inflexion at 4.5 equivalents that corresponds to the formation of the binuclear species, $Th_2L(OH)_6^-$. Evidently, there are other species present but they cannot be identified only from the experimental form of the curve. Interpretation of the data to pH-10.8 leads to a good set of parameters for the system composed of: ThL^+, ThL(OH), $ThL(OH)_2^-$, $ThL(OH)_4^{3-}$ and $Th_2L(OH)_6^-$.
– Ligand **1e**. The addition of Th^{4+} to this ligand results in the decrease of the pH curve until seven base equivalents have been added. A first zone, characterized between one and three equivalents, corresponds to deprotonation of the ligand. This is followed by a second zone characterized by different inflexions at three equivalents, ThL^+, and four equivalents, ThL(OH). The numerical interpretation gives the best result for the model: ThL^+, ThL(OH), $ThL(OH)_2^-$, $ThL(OH)_3^{2-}$ and $ThL(OH)_4^{3-}$.

(b) Pentaacids

In regards to the pentaacids **2a** and **2b**, a steep decrease of pH is observed, limited by an inflexion around four equivalents which corresponds without doubt to the species ThLH. A second zone with a high increase of pH is defined between four and nine equivalents that is certainly due to the presence of other species which can not be directly identified here, but can be by testing different models. On the other hand, for **2c** the curve shows, as for all previous ligands, an inflexion at four equivalents, ThLH, and a zone between four and nine equivalents showing clearly inflexions at five equivalents, ThL^-, at six equivalents, $ThL(OH)^{2-}$, and at seven equivalents, $ThL(OH)_2^{3-}$. A certain increase of pH beyond this range suggests the possible presence of another species.

3.1.2. Numerical interpretation

The interpretation of the experimental data and testing of different models were carried out with the help of the Sirko_P program [19], in which the values of the protonation constants of the ligands [16, 17] and the hydrolysis constants of the Th^{4+} cation [18] used were determined earlier. This treatment allowed the determination of the logarithms of the overall stability constants, $\log_{10}\beta_{x,y,z}$, and the standard deviation σ_{N-1} for the different complexes. These results are grouped in Table 1.

The models that were postulated during the interpretation of the titration curves were confirmed by these calculations with determination of the stoichiometry, number and nature of species in each case.

Table 1 Values of $\log_{10}\beta_{11z} \pm \sigma_{N-1}$ ($N = 8$) determined by the Sirko_P program for the complexes formed with Th^{4+} in aqueous solution from potentiometric data (25 °C, $I = 0.1$ mol·dm^{-3} $NaClO_4$)

Ligand	*xyz*	Species	$\log_{10}\beta_{xyz} \pm \sigma_{n-1}$	pH range	R_f (%)
1a with $C_M = C_L = 10^{-4}$ M[a]	110	ThL^{+}	14.55 ± 0.10	3.69 to 9.91	1.10
	11-1	ThL(OH)	9.35 ± 0.13		
	11-2	$Th(OH)_2^{-}$	1.85 ± 0.22		
	11-3	$ThL(OH)_3^{2-}$	-6.98 ± 0.23		
1b with $C_M = C_L = 10^{-3}$ M[a]	110	ThL^{+}	15.50 ± 0.18		
	11-1	ThL(OH)	11.16 ± 0.23	2.63 to 10.80	3.50
	11-2	$ThL(OH)_2^{-}$	5.05 ± 0.28		
	11-4	$ThL(OH)_4^{3-}$	-12.59 ± 0.25		
	21-6	$Th_2L(OH)_6^{-}$	-8.61 ± 0.57		
1c with $C_M = C_L = 10^{-4}$ M[a]	110	ThL^{+}	12.40 ± 0.01		
	11-1	ThL(OH)	6.29 ± 0.03	3.71 to 10.02	2.10
	11-2	$ThL(OH)_2^{-}$	-2.73 ± 0.04		
	11-3	$ThL(OH)_3^{2-}$	-11.22 ± 0.01		
1d with $C_M = C_L = 10^{-3}$ M[a]	110	ThL^{+}	13.80 ± 0.70		
	11-1	ThL(OH)	11.55 ± 0.62	2.76 to 10.82	3.40
	11-2	$ThL(OH)_2^{-}$	6.10 ± 0.69		
	11-4	$ThL(OH)_4^{3-}$	-11.63 ± 0.94		
	21-6	$Th_2L(OH)_6^{-}$	-6.82 ± 0.71		
1e with $C_M = C_L = 10^{-4}$ M[a]	110	ThL^{+}	11.97 ± 0.04		
	11-1	ThL(OH)	5.95 ± 0.01	3.88 to 10.16	2.10
	11-2	$ThL(OH)_2^{-}$	-2.80 ± 0.05		
	11-3	$ThL(OH)_3^{2-}$	-11.82 ± 0.08		
	11-4	$ThL(OH)_4^{3-}$	-22.43 ± 0.30		
2a with $C_M = C_L = 10^{-4}$ M[a]	110	ThL^{-}	16.42 ± 0.29		
	111	ThLH	23.15 ± 0.35		
	11-1	$ThL(OH)^{2-}$	8.36 ± 0.25	3.47 to 9.68	1.30
	11-2	$ThL(OH)_2^{3-}$	0.02 ± 0.01		
	11-4	$ThL(OH)_4^{5-}$	-18.16 ± 0.27		
2b with $C_M = C_L = 10^{-4}$ M[a]	110	ThL^{-}	13.37 ± 0.04		
	111	ThLH	20.12 ± 0.03	3.67 to 9.98	0.75
	11-1	$ThL(OH)^{2-}$	4.68 ± 0.30		
	11-2	$ThL(OH)_2^{3-}$	-4.02 ± 0.47		
	11-4	$ThL(OH)_4^{5-}$	-23.63 ± 0.50		
2c with $C_M = C_L = 10^{-3}$ M[a]	110	ThL^{-}	19.48 ± 0.38		
	111	ThLH	24.63 ± 0.40		
	11-1	$ThL(OH)^{2-}$	11.06 ± 0.37	2.49 to 10.65	3.70
	11-2	$ThL(OH)_2^{3-}$	3.17 ± 0.38		
	11-3	$ThL(OH)_3^{4-}$	-6.74 ± 0.57		
	11-4	$ThL(OH)_4^{5-}$	-16.56 ± 0.29		

[a] M denotes the concentration in units of mol · L^{-1}

3.2. Spectrophotometric determinations

Under this sub-heading, only ligand **1c**, **1d**, **1e** and **2b** will be studied as only they contain the chromophore group NO_2, and hence undergo significant spectral variations that can be exploited relatively easily.

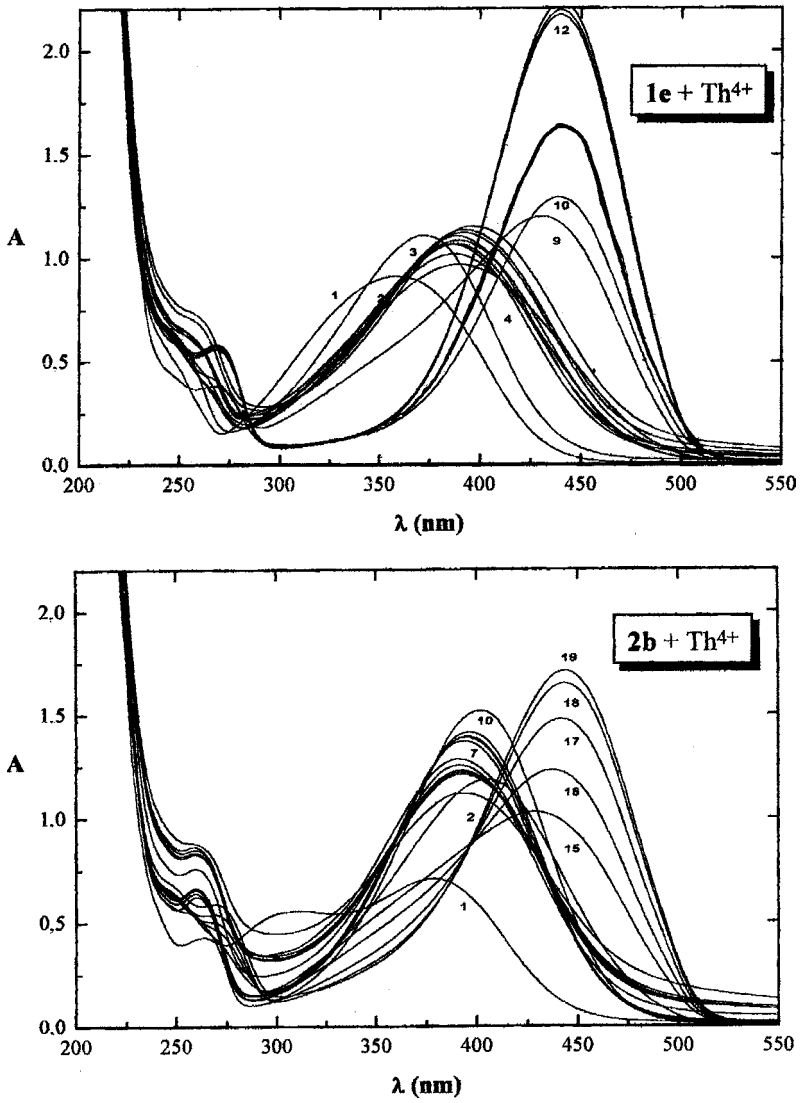


Fig. 2 Experimental UV-visible spectra of the complexes of ligand X with Th^{4+}

3.2.1. UV-visible experimental spectra

The spectral variations with respect to the pH of different solutions corresponding to the four ligands and the thorium(IV) cation in the ratio $[L]_0/[M]_0 = 1$ are presented in Fig. 2.

(a) Ligands **1c**, **1e** and **2b**

It is remarked that the spectra of these three ligands are characterized by their nearly identical evolution with respect to pH. The principal absorption band, which corresponds to the totally protonated molecule, appears at 320 nm ($\varepsilon = 9270\,L{\cdot}mol^{-1}{\cdot}cm^{-1}$) for **1c**, at 325 nm ($\varepsilon = 9020\,L{\cdot}mol^{-1}{\cdot}cm^{-1}$) for **1e**, and at 328 nm ($\varepsilon = 8070\,L{\cdot}mol^{-1}{\cdot}cm^{-1}$) for **2b**, disappears and

leaves a new band at 332, 360 and 375 nm, respectively. This indicates the total disappearance of the protonated species and suggests instant complexation even at low pH.

Increasing the pH to eight produces a regular bathochromic shift with significant absorption variations. For pH > 8, an intense maximum is observed at 415 nm for **1c** and at 440 nm for **1e** and **2b**, corresponding to the totally deprotonated complex.

In highly alkaline media (pH > 10), the successive spectra are superposed, indicating that the totally deprotonated species are preserved. This is supported by the presence of only a single intense band for the trianion (or the totally deprotonated ligand), at 422 nm for **1c** and at 437 nm for **1e**. In case of **2b**, this band which corresponds to the pentaanion (or the totally deprotonated ligand) is situated at 446 nm, which means there is still some free deprotonated ligand here.

(b) Ligand **1d**

Three absorption maxima with bathochromic shifts are observed. However, the accompanying spectral variations are quite low. It may also be recalled here that for all the ligands, the ligand-thorium(IV) spectra present isosbestic points, clearly indicating the presence of two species in equilibrium.

3.2.2. Stability constants

The logarithm of the apparent overall stability constants for the equilibria under study were calculated using the Letagrop program [20] and are presented in Table 2. This also gives the stoichiometry of the different identified species in the pH range of 1.49 to 11.44. The protonation constants of the ligand and those of the hydrolysis of the metal were determined beforehand and were fixed for the calculation of these stability constants.

The β_{01z} values were obtained by titration, which led simultaneously to two sets of optimized parameters: the overall stability constants and the extinction coefficients ε of all species involved in the complexation reactions. Using these data, the calculated values, or β_{xyz} values, are indicated here with the usual 99% confidence interval ($\pm 3\sigma$).

3.2.3. Individual electronic spectra

With the help of the calculated stability constants and the specific extinction coefficients, the individual electronic spectra of the ligand-thorium(IV) complexes were calculated. The spectra of all the identified species are given in Fig. 3.

4. Discussion

4.1. Nature of the complexes formed

For simplicity, the charges of the complexes will be omitted in the following discussion.

4.1.1. Triacids

In the pH range of 4 and 9, the potentiometric and spectrophotometric studies show the presence of the identical species types: ML, MLOH and $ML(OH)_2$. No protonated species were identified by the technique of potentiometry, whereas spectrophotometry helped in the

Table 2 Values of $\log_{10}\beta_{11z}$ determined by the Letagrop program for the complexes formed with Th^{4+} in aqueous solution from spectrophotometric data (25 °C, I = 0.1 mol·dm^{-3} $NaClO_4$)

Ligand	$\log_{10}\beta_{112}$	$\log_{10}\beta_{111}$	$\log_{10}\beta_{110}$	$\log_{10}\beta_{11-1}$	$\log_{10}\beta_{11-2}$	$\log_{10}\beta_{11-3}$	$\log_{10}\beta_{11-4}$	$\log_{10}\beta_{21-6}$
1c	19.24 ± 0.13	16.50 ± 0.11	10.65 ± 0.08	5.50 ± 0.12	−2.87 ± 0.21	–	–	–
1d	–	–	12.39 ± 0.07	10.80 ± 0.10	5.16 ± 0.18		−10.98 ± 0.21	−5.43 ± 0.19
1e	–	13.73 ± 0.13	10.61 ± 0.10	6.57 ± 0.08	−2.95 ± 0.17	−11.29 ± 0.19	–	–
2b	26.53 ± 0.17	21.15 ± 0.16	13.17 ± 0.09	4.72 ± 0.07	−5.10 ± 0.22	–	−27.05 ± 0.18	–

Note. Range of pH:1.49 to 11.44.

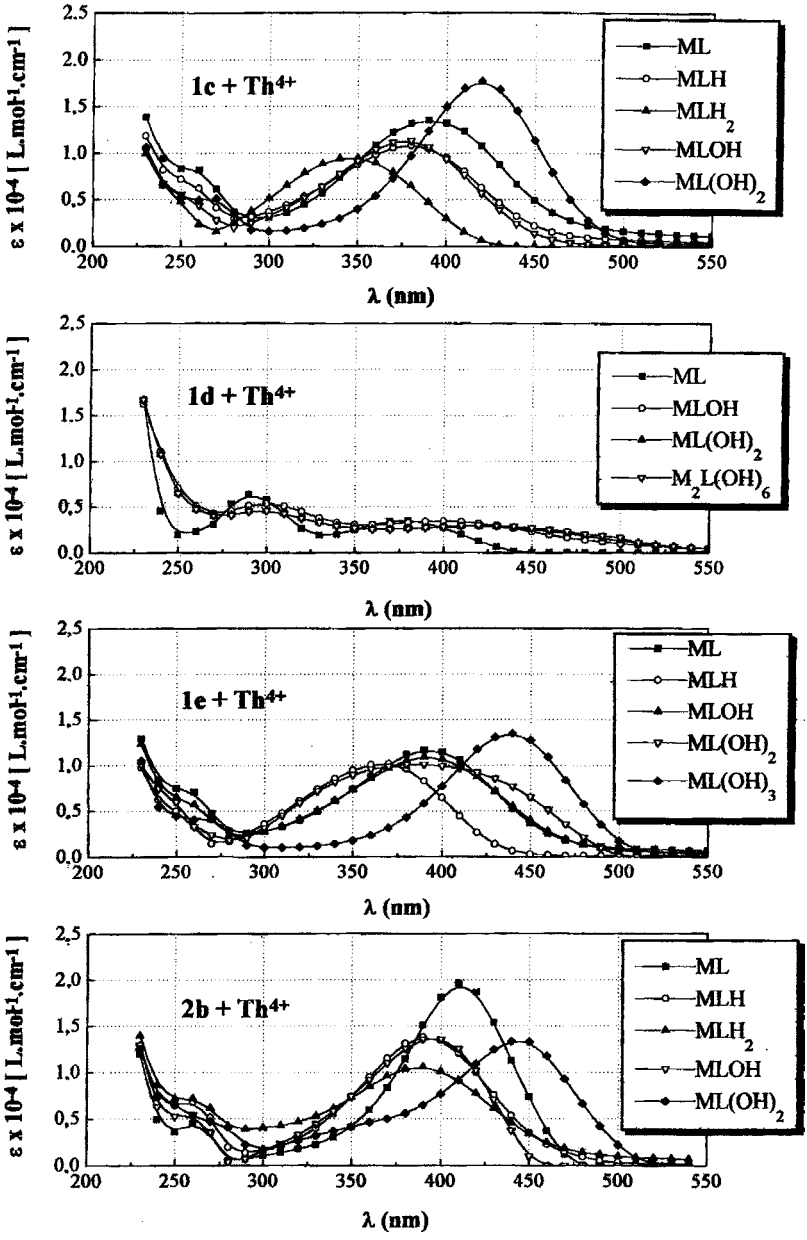


Fig. 3 Calculated electronic spectra of the complexes of ligand X with Th^{4+}

detection of MLH for **1c** and **1e**, but not for **1d**, most probably because of the restricted range of pH interpreted. In the case of **1c**, MLH_2 was identified.

In the alkaline zone, potentiometric measurements showed either $ML(OH)_3$ for **1a** and **1c** and $ML(OH)_4$ for **1b** and **1d**, or both of them in the case of **1e**. The presence of the

Table 3 Mean values of the logarithm of the stability constants of thorium(IV)

Ligand	MLH_2	MLH	ML	MLOH	$ML(OH)_2$	$ML(OH)_3$	$ML(OH)_4$	$M_2L(OH)_6$
1c	–	–	12.40^{p}	6.29^{p}	-2.73^{p}	-11.22^{p}	–	–
	19.24^{s}	16.50^{s}	10.65^{s}	5.50^{s}	-2.87^{s}	–	–	–
1d	–	–	13.80^{p}	11.55^{p}	6.10^{p}	–	-11.63^{p}	-6.82^{p}
	–	–	12.39^{s}	10.80^{s}	5.16^{s}	–	-10.98^{s}	-5.43^{s}
1e	–	–	11.97^{p}	5.95^{p}	-2.80^{p}	-11.82^{p}	-22.43^{p}	–
	–	13.73^{s}	10.61^{s}	6.57^{s}	-2.95^{s}	-11.29^{s}	–	–
2b	–	20.12^{p}	13.37^{p}	4.68^{p}	-4.02^{p}	–	-26.63^{p}	–
	26.53^{s}	21.15^{s}	13.17^{s}	4.72^{s}	-5.10^{s}	–	-27.05^{s}	–

mono- and binuclear species, $ML(OH)_4$ and $M_2L(OH)_6$, identified potentiometrically, was confirmed spectrophotometrically for **1d**.

4.1.2. Pentaacids

With all the ligands, potentiometric data indicated the presence of MLH, ML, MLOH, $ML(OH)_2$ and $ML(OH)_4$. However, in case of ligand **2c**, in addition to these five species, $ML(OH)_3$ was identified. Spectrophotometric measurements confirmed in the case of **2b** the presence of MLH, ML, MLOH and $ML(OH)_2$ with the added presence of MLH_2. No binuclear species were found with the pentaacids, in keeping with the absence of an inflexion corresponding to the addition of 4.5 equivalents of base after neutralization.

4.2. Comparison of the constants

An examination of Table 3 shows good agreement between the values of the stability constants calculated on the basis of the two experimental methods. The values with the superscript (*p*) result from potentiometric measurements whereas those marked by (*s*), are spectrophotometric values.

The values of β_{110} are much more different from each other than in case of lanthanides [16, 17]. For the triacids, values of $\log_{10} \beta_{110}$ vary between 12 and 15.5, whereas in the case of the pentaacids the variation is between 13 and 19.5. For thorium, the ligand **1b** is not the weakest complexing agent as it is in the case with lanthanides. On the contrary, it is the strongest complexing ligand in the triacid series; **2c** being the same in the case of pentaacids.

4.3. Distribution curves of the complexes: speciation

The values of the stability constants were used along with the Haltafall program [21] to calculate the percentage formation of the different species resulting from ligand-Th^{4+} complexation. The distribution curves of all of these species are shown in Fig. 4. The concentrations of the different species were calculated as a function of $-\log_{10}[H^+]$ at $C_L = C_{Th^{4+}} = 10^{-4}$ mol·dm^{-3} for **1a**, **1c**, **1e**, **2a** and **2b**, and at $C_L = C_{Th^{4+}} = 10^{-3}$ mol·dm^{-3} for **1b**, **1d** and **2c**.

4.3.1. Triacids

The curves obtained for the triacids **1a**, **1b**, **1c**, **1d** and **1e** clearly indicate a high complexing ability of these ligands. Indeed, it can be observed that the most stable hydroxide of the

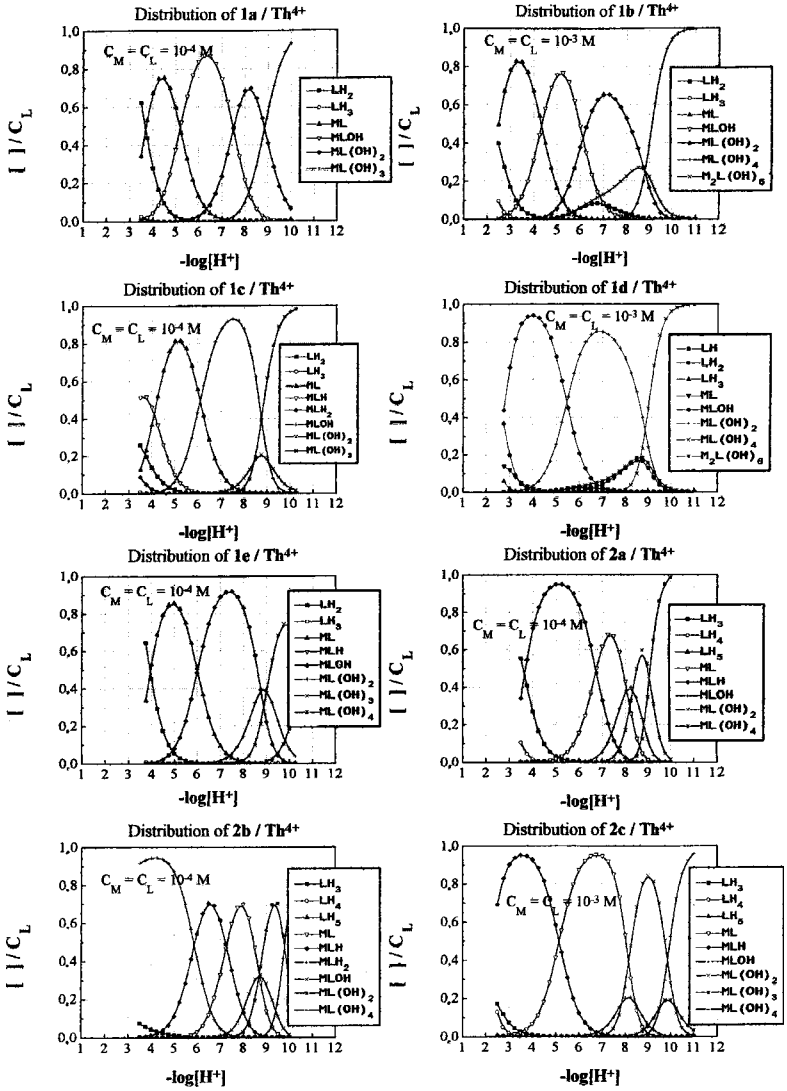


Fig. 4 Distribution curves of the complexes of ligand X with Th^{4+}

metal, $Th(OH)^{3+}$, does not exist in the whole range of pH, which is indicative of the fact that all the metal has been complexed by the ligand. The preponderant complex in the range of pH 4 to 9 is ThL(OH): 85% with **1a**, 78% with **1b**, and 92% with **1c**, **1d** and **1e**. There is a significant coexistence with the species ThL^{+}, around 80%, with all the ligands except for **1d**. Eventually, it may be remarked that the species $M_2L(OH)_6$ is formed only with **1b** and **1d** and attains, at best, 20%.

4.3.2. Pentaacids

As regards pentaacids, the presence of the protonated species LH_4 and LH_3 is observed. In acidic medium, pH-4 to 6, the predominant species is ThLH and is formed at around 95%

Table 4 Complexing selectivity, S, for the ligands studied: $S(M/M') = \beta_{110}(M)/\beta_{110}(M')$

	Ligand							
Cation	**1a**	**1b**	**1c**	**1d**	**1e**	**2a**	**2b**	**2c**
Th^{4+}	14.5	15.5	12.4	13.8	12.0	16.4	13.4	19.5
Eu^{3+}	10.6	7.5	9.1	10.3	10.1	12.0	11.9	12.2
Reference	[16]	[16]	[16]	[16]	[16]	[17]	[17]	[17]
$S(Th^{4+}/Eu^{3+})$	3.9	8.0	3.3	3.5	1.9	4.4	1.5	8.3

with ligands **2a** and **2c** around 80% with **2b**. Within the pH limits of 6 to 8, it is ThL^- that is formed significantly: 68% with **2a** and **2b**, and up to 95% with **2c**.

4.4. Comparison between lanthanides(III) and thorium(IV)

Strictly speaking, actinides(III) should be compared to lanthanides(III); however, the former are very similar to the latter. Hence, here thorium(IV) has been compared to the lanthanides(III) in order to observe the influence of charge on the complexing power of the ion. As could be predicted, the complexes of thorium are much stronger than those of the lanthanides. Table 4 shows that the selectivity for Th^{4+}/Eu^{3+} reaches eight $\log_{10}$ units for **1b** and **2c**, whereas it is about 2–4 $\log_{10}$ units for the other ligands.

4.5. Comparison with other ligands

Table 5 indicates that none of the ligands studied is as strong as DTPA or TTHA, or even EDTA or HEDTA. However, they are all either comparable, or slightly superior, to NTA in their complexing ability. Ligand **2c** is an exception as its complexing power exceeds that of HEDTA.

Figure 5 represents the percentage of free Th^{4+}, calculated as a function of $-\log_{10}[H^+]$ for the different ligands, all at $C_L = C_M = 10^{-4}$ mol·dm^{-3}.

5. Conclusion

This study of the complexation of Th^{4+} with different phenol-methylenephosphonic acids shows the presence of up to six different species in solution, depending upon the pH. The potentiometric and spectrophotometric data used with different computer programs (Sirko_P and Letagrop_Spefo) give convergent results. The calculated stability constants are quite high but remain inferior to those with TTHA and DTPA, and even to EDTA and HEDTA. The complexing power of thorium(IV) is compared with and found to be superior to those of

Table 5 Logarithms of stability constants of the 1:1:0 complexes formed from different complexing agents with Th^{4+} in aqueous solution

Ligand	$\log_{10}\beta_{110}$	Ref.
EDTA	23.2	[7]
DTPA	>27	[7]
NTA	12.4	[8]
HEDTA	18.5	[8]
TTHA	≫27	[9]

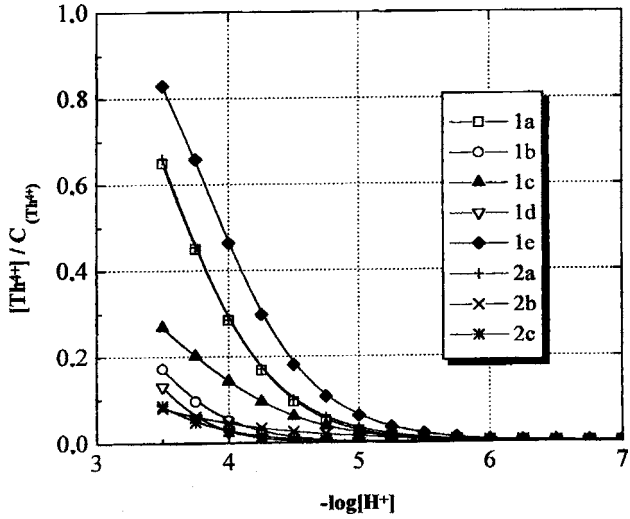


Fig. 5 Fraction of calculated free Th^{4+} concentration *vs.* $-\log_{10}[H^+]$ for the eight ligands

the lanthanides(III). This is quite logical as generally the complexing ability increases with increasing cationic charge.

Addenda

Experimental potentiometric data for the ligand-thorium(IV) complexation studies used for testing of models and for the calculation of stability constants (V = volume of NaOH added to solution).

Ligand **1a**-Thorium(IV)

V (mL)	pH	V (mL)	pH	V (mL)	pH	V (mL)	pH
0.000	3.711	0.301	4.698	0.439	7.247	0.621	9.048
0.001	3.702	0.321	4.871	0.449	7.401	0.643	9.132
0.002	3.701	0.331	5.002	0.461	7.586	0.666	9.212
0.003	3.699	0.340	5.111	0.471	7.826	0.690	9.290
0.029	3.751	0.352	5.351	0.476	7.817	0.715	9.361
0.058	3.819	0.357	5.479	0.477	7.843	0.741	9.422
0.085	3.878	0.361	5.594	0.488	8.052	0.768	9.498
0.113	3.942	0.367	5.790	0.498	8.196	0.794	9.562
0.140	4.013	0.374	5.976	0.505	8.279	0.820	9.621
0.166	4.091	0.380	6.171	0.515	8.360	0.848	9.675
0.191	4.176	0.388	6.335	0.531	8.514	0.877	9.731
0.216	4.269	0.396	6.522	0.546	8.635	0.905	9.771
0.238	4.367	0.405	6.705	0.563	8.745	0.936	9.820
0.260	4.475	0.414	6.892	0.581	8.850	0.966	9.861
0.281	4.582	0.424	6.977	0.601	8.950	0.996	9.903
						1.000	9.913

Ligand **1b**-Thorium(IV)

V (mL)	pH	*V* (mL)	pH	*V* (mL)	pH	*V* (mL)	pH
0.000	2.700	0.311	4.130	0.473	6.980	0.670	9.611
0.001	2.691	0.320	4.299	0.476	7.095	0.687	9.736
0.002	2.686	0.330	4.409	0.482	7.278	0.704	9.846
0.003	2.685	0.343	4.505	0.489	7.452	0.723	9.968
0.016	2.698	0.361	4.538	0.497	7.616	0.741	10.059
0.048	2.741	0.390	4.674	0.506	7.773	0.762	10.147
0.079	2.790	0.411	4.833	0.517	7.932	0.785	10.238
0.109	2.844	0.428	5.067	0.528	8.074	0.807	10.321
0.138	2.908	0.434	5.229	0.541	8.209	0.831	10.407
0.165	2.976	0.436	5.281	0.555	8.375	0.855	10.481
0.192	3.057	0.443	5.582	0.569	8.517	0.88	10.547
0.217	3.153	0.445	5.691	0.583	8.652	0.906	10.613
0.238	3.261	0.447	5.809	0.598	8.840	0.933	10.674
0.258	3.391	0.452	5.981	0.611	9.039	0.960	10.727
0.273	3.528	0.454	6.074	0.620	9.134	0.989	10.776
0.286	3.679	0.461	6.358	0.627	9.229	1.000	10.803
0.296	3.838	0.466	6.676	0.640	9.347		
0.304	3.971	0.468	6.781	0.655	9.482		

Ligand **1c**-Thorium(IV)

V (mL)	pH	*V* (mL)	pH	*V* (mL)	pH	*V* (mL)	pH
0.000	3.713	0.292	4.744	0.389	7.359	0.617	9.232
0.001	3.706	0.302	4.881	0.396	7.540	0.642	9.307
0.002	3.706	0.311	5.028	0.404	7.697	0.667	9.378
0.003	3.708	0.319	5.188	0.413	7.866	0.693	9.443
0.024	3.755	0.325	5.347	0.423	8.020	0.719	9.504
0.052	3.826	0.331	5.540	0.434	8.176	0.747	9.567
0.078	3.885	0.335	5.684	0.446	8.316	0.774	9.628
0.105	3.942	0.339	5.848	0.459	8.441	0.802	9.689
0.133	4.010	0.344	6.042	0.475	8.569	0.829	9.746
0.161	4.081	0.349	6.189	0.491	8.678	0.858	9.795
0.187	4.159	0.356	6.358	0.509	8.786	0.887	9.844
0.212	4.248	0.365	6.553	0.528	8.884	0.916	9.888
0.235	4.345	0.373	6.810	0.549	8.979	0.947	9.932
0.257	4.458	0.380	7.068	0.571	9.068	0.977	9.979
0.277	4.592	0.384	7.195	0.594	9.153	1.000	10.010

Ligand **1d**-Thorium(IV)

V (mL)	pH	*V* (mL)	pH	*V* (mL)	pH	*V* (mL)	pH
0.000	2.732	0.380	3.799	0.483	6.859	0.674	9.582
0.001	2.719	0.398	3.902	0.487	7.045	0.691	9.748
0.002	2.717	0.418	4.128	0.492	7.254	0.706	9.851
0.003	2.710	0.424	4.226	0.498	7.428	0.724	9.964
0.010	2.715	0.430	4.328	0.505	7.614	0.742	10.067
0.044	2.759	0.440	4.651	0.512	7.777	0.763	10.152

Ligand **1d**-Thorium(IV)

V (mL)	pH	*V* (mL)	pH	*V* (mL)	pH	*V* (mL)	pH
0.075	2.805	0.442	4.742	0.521	7.930	0.785	10.252
0.105	2.859	0.445	4.849	0.532	8.084	0.807	10.317
0.134	2.915	0.450	5.209	0.544	8.252	0.832	10.382
0.163	2.979	0.451	5.190	0.555	8.402	0.859	10.485
0.190	3.047	0.452	5.256	0.568	8.546	0.882	10.542
0.217	3.119	0.456	5.508	0.582	8.684	0.909	10.608
0.243	3.200	0.461	5.672	0.596	8.820	0.936	10.662
0.267	3.287	0.462	5.753	0.612	8.975	0.964	10.706
0.291	3.376	0.467	5.968	0.626	9.119	0.994	10.754
0.314	3.474	0.472	6.230	0.641	9.293	1.000	10.771
0.337	3.571	0.476	6.483	0.653	9.378		
0.359	3.677	0.478	6.620	0.661	9.477		

Ligand **1e**-Thorium(IV)

V (mL)	pH	*V* (mL)	pH	*V* (mL)	pH	*V* (mL)	pH
0.000	3.905	0.302	4.911	0.401	7.516	0.628	9.398
0.001	3.899	0.313	5.058	0.409	7.741	0.653	9.476
0.002	3.897	0.322	5.205	0.416	7.910	0.678	9.542
0.003	3.895	0.330	5.354	0.421	7.971	0.704	9.609
0.029	3.944	0.337	5.533	0.435	8.201	0.731	9.670
0.058	4.010	0.343	5.706	0.445	8.341	0.758	9.731
0.086	4.068	0.347	5.834	0.457	8.483	0.786	9.782
0.114	4.123	0.352	6.056	0.471	8.610	0.815	9.836
0.142	4.188	0.357	6.238	0.486	8.739	0.844	9.897
0.170	4.257	0.362	6.404	0.502	8.855	0.872	9.951
0.196	4.338	0.365	6.499	0.519	8.958	0.900	10.001
0.221	4.424	0.371	6.681	0.539	9.058	0.929	10.042
0.244	4.522	0.378	6.898	0.560	9.154	0.960	10.091
0.266	4.634	0.386	7.148	0.581	9.242	0.990	10.133
0.286	4.766	0.392	7.280	0.604	9.323	1.000	10.155

Ligand **2a**-Thorium(IV)

V (mL)	pH	*V* (mL)	pH	*V* (mL)	pH	*V* (mL)	pH
0.000	3.494	0.315	4.292	0.462	6.828	0.658	8.412
0.001	3.488	0.334	4.446	0.472	7.004	0.673	8.537
0.002	3.484	0.346	4.571	0.483	7.073	0.687	8.646
0.003	3.484	0.359	4.735	0.501	7.264	0.705	8.761
0.018	3.505	0.368	4.903	0.516	7.506	0.723	8.865
0.048	3.555	0.375	5.033	0.526	7.652	0.743	8.957
0.078	3.601	0.384	5.219	0.535	7.567	0.765	9.053
0.108	3.648	0.391	5.293	0.543	7.560	0.787	9.137
0.138	3.701	0.399	5.577	0.576	7.822	0.810	9.215
0.167	3.757	0.408	5.758	0.593	7.832	0.834	9.295
0.196	3.822	0.416	5.966	0.606	7.996	0.859	9.367

0.223	3.893	0.425	6.144	0.609	7.959	0.884	9.433
0.249	3.973	0.433	6.301	0.623	8.127	0.911	9.491
0.274	4.071	0.442	6.472	0.637	8.204	0.939	9.553
0.295	4.177	0.452	6.657	0.643	8.269	0.966	9.606
						1.000	9.675

Ligand **2b**-Thorium(IV)

V (mL)	pH	*V* (mL)	pH	*V* (mL)	pH	*V* (mL)	pH
0.000	3.704	0.307	4.411	0.460	6.936	0.676	9.011
0.001	3.701	0.327	4.526	0.469	7.139	0.695	9.117
0.002	3.694	0.345	4.673	0.478	7.308	0.714	9.210
0.003	3.691	0.358	4.811	0.488	7.484	0.736	9.305
0.015	3.706	0.370	4.970	0.498	7.667	0.758	9.386
0.031	3.733	0.379	5.117	0.508	7.707	0.782	9.464
0.060	3.785	0.387	5.275	0.531	7.910	0.806	9.545
0.090	3.829	0.394	5.452	0.547	7.985	0.831	9.614
0.120	3.877	0.401	5.628	0.568	8.135	0.857	9.685
0.150	3.927	0.409	5.805	0.586	8.343	0.883	9.744
0.179	3.986	0.417	6.010	0.593	8.422	0.910	9.798
0.207	4.049	0.425	6.198	0.607	8.559	0.939	9.859
0.235	4.122	0.433	6.380	0.621	8.671	0.966	9.907
0.261	4.206	0.441	6.548	0.637	8.764	0.996	9.957
0.285	4.299	0.451	6.762	0.657	8.897	1.000	9.968

Ligand **2c**-Thorium(IV)

V (mL)	pH	*V* (mL)	pH	*V* (mL)	pH	*V* (mL)	pH
0.003	2.556	0.41	3.846	0.505	7.217	0.734	9.381
0.025	2.573	0.418	4.012	0.512	7.359	0.748	9.499
0.039	2.585	0.424	4.169	0.521	7.496	0.764	9.619
0.072	2.622	0.429	4.306	0.533	7.652	0.781	9.734
0.104	2.658	0.436	4.549	0.545	7.783	0.799	9.853
0.135	2.697	0.439	4.674	0.559	7.902	0.818	9.954
0.167	2.744	0.444	4.916	0.575	8.022	0.838	10.047
0.197	2.793	0.448	5.094	0.593	8.137	0.86	10.203
0.226	2.85	0.453	5.292	0.611	8.257	0.877	10.289
0.255	2.915	0.457	5.481	0.63	8.387	0.893	10.348
0.282	2.987	0.462	5.731	0.647	8.526	0.916	10.422
0.308	3.072	0.467	5.964	0.664	8.723	0.941	10.512
0.332	3.17	0.473	6.174	0.672	8.815	0.965	10.568
0.353	3.281	0.478	6.373	0.685	8.877	0.992	10.652
0.372	3.407	0.485	6.6	0.69	8.914	1.000	10.676
0.389	3.557	0.491	6.801	0.708	9.126		
0.401	3.702	0.498	7.002	0.721	9.264		

Experimental spectrophotometric absorbance data for ligand-thorium(IV) mixtures at different pH ranging from 1.5 to 11.5. These values, recorded between 200 and 550 nm, were used for the testing of models and the calculation of stability constants.

Ligand **1c**-Thorium(IV)

λ/pH	1.542	1.664	2.183	3.618	3.653	3.828	4.135	4.852	6.923	7.482	7.643	8.370	8.908	9.798	9.826	10.537
550	0.0107	0.0099	0.0200	0.0485	0.0455	0.0514	0.0551	0.0794	0.0160	0.0215	0.0228	0.0194	0.0213	0.0278	0.0331	0.0302
540	0.0109	0.0098	0.0204	0.0513	0.0482	0.0547	0.0591	0.0849	0.0164	0.0224	0.0238	0.0202	0.0224	0.0287	0.0338	0.031
530	0.0111	0.0097	0.0209	0.0548	0.0515	0.0589	0.0639	0.0912	0.0172	0.0235	0.0250	0.0212	0.0237	0.0303	0.0354	0.0324
520	0.0112	0.0098	0.0216	0.0588	0.0553	0.0638	0.0692	0.0985	0.0182	0.025	0.0267	0.0229	0.0261	0.0333	0.0382	0.0349
510	0.0114	0.0098	0.0223	0.0635	0.0599	0.0693	0.0756	0.1072	0.0197	0.0273	0.0296	0.0266	0.0323	0.0403	0.0458	0.0424
500	0.0116	0.0097	0.0232	0.0694	0.0656	0.0763	0.0838	0.1183	0.0218	0.0316	0.0366	0.0376	0.0535	0.0616	0.0709	0.0681
490	0.0117	0.0096	0.0242	0.0773	0.0735	0.0861	0.0949	0.1339	0.0264	0.0417	0.0545	0.0692	0.1169	0.1238	0.1445	0.1447
480	0.0120	0.0098	0.0262	0.0892	0.0860	0.1011	0.1127	0.1577	0.0378	0.0625	0.0903	0.1319	0.2402	0.2430	0.2851	0.2918
470	0.0123	0.0103	0.0296	0.1090	0.1069	0.1262	0.1423	0.1966	0.0620	0.1001	0.1513	0.2337	0.4331	0.4286	0.5044	0.5217
460	0.0127	0.0112	0.0356	0.1421	0.1426	0.1680	0.1919	0.2586	0.1070	0.1616	0.2421	0.3749	0.6937	0.6786	0.7961	0.8275
450	0.0145	0.0145	0.0476	0.1982	0.2033	0.2370	0.2722	0.3547	0.1851	0.2540	0.3645	0.5551	0.9995	0.972	1.1325	1.1784
440	0.0201	0.0240	0.0714	0.2841	0.2957	0.3390	0.3897	0.4919	0.3017	0.3770	0.5142	0.7465	1.2914	1.2526	1.4452	1.5020
430	0.0335	0.0473	0.1163	0.4041	0.4247	0.4795	0.5472	0.6608	0.4609	0.5314	0.6761	0.9275	1.5160	1.4708	1.6701	1.7319
420	0.0621	0.0967	0.1949	0.5522	0.5824	0.6429	0.7243	0.8419	0.6485	0.6979	0.8337	1.0692	1.6226	1.5772	1.7574	1.8148
410	0.1164	0.1876	0.3185	0.7097	0.7489	0.8128	0.8999	1.0037	0.8465	0.863	0.9644	1.1521	1.5894	1.5532	1.6826	1.7241
400	0.2013	0.3188	0.4814	0.8486	0.8912	0.9505	1.0356	1.1169	1.0104	0.9925	1.0515	1.1686	1.4429	1.4216	1.4846	1.504
390	0.3087	0.4733	0.6530	0.9501	0.9932	1.0469	1.1245	1.1787	1.1307	1.0820	1.0946	1.1357	1.2357	1.2296	1.2289	1.2275
380	0.4364	0.6310	0.8108	1.0037	1.0425	1.0863	1.1511	1.1807	1.1812	1.1135	1.0869	1.0586	1.0100	1.0157	9658	0.9480
370	0.5707	0.7638	0.9152	1.0002	1.0318	1.0626	1.1117	1.1246	1.1516	1.0797	1.0258	0.9476	0.7966	0.8094	0.7298	0.7025
360	0.7004	0.8634	0.9621	0.9526	0.9755	0.9904	1.0214	1.0233	1.0565	0.9943	0.9288	0.8228	0.6172	0.6318	0.5439	0.5146
350	0.8163	0.9200	0.9532	0.8750	0.8878	0.8885	0.8973	0.8909	0.9153	0.8733	0.8089	0.6919	0.4749	0.4861	0.4009	0.3737
340	0.8914	0.9281	0.8970	0.7784	0.7822	0.7691	0.7574	0.7484	0.7591	0.7411	0.6848	0.5744	0.3710	0.3786	0.3046	0.2826
330	0.9089	0.8887	0.8060	0.6760	0.6707	0.6469	0.6207	0.6129	0.6083	0.6114	0.5689	0.4698	0.2968	0.3005	0.2400	0.2221
320	0.8585	0.7980	0.6930	0.5773	0.5670	0.5383	0.5059	0.5022	0.4812	0.4993	0.4687	0.3843	0.2451	0.2470	0.1976	0.1841
310	0.7433	0.6661	0.5686	0.4833	0.4690	0.4408	0.4098	0.4121	0.3732	0.4006	0.3838	0.3133	0.2065	0.2074	0.1695	0.1590
300	0.5971	0.5249	0.4477	0.4036	0.3871	0.3627	0.3392	0.3504	0.2895	0.3194	0.3172	0.2581	0.1835	0.1846	0.1578	0.1498
290	0.4473	0.3876	0.3354	0.3367	0.3214	0.3074	0.2959	0.3175	0.2215	0.2532	0.2598	0.2201	0.1875	0.1880	0.1749	0.1698

280	0.3089	0.2672	0.2445	0.3064	0.2937	0.2945	0.2990	0.3372	0.1890	0.2275	0.2552	0.2617	0.3282	0.3234	0.3427	0.3471
270	0.1976	0.1777	0.2076	0.3923	0.3885	0.4107	0.4461	0.5142	0.2891	0.3214	0.3562	0.3789	0.4811	0.4777	0.5030	0.5067
260	0.2045	0.2412	0.3511	0.5811	0.5835	0.6068	0.6512	0.7182	0.4630	0.4650	0.4774	0.4646	0.4941	0.4933	0.4903	0.4849
250	0.4350	0.4651	0.5679	0.7032	0.6981	0.7032	0.7280	0.7843	0.5507	0.5783	0.5888	0.5507	0.5437	0.5383	0.5238	0.5183
240	0.6647	0.6587	0.6959	0.8129	0.8082	0.8077	0.8306	0.8910	0.6513	0.6995	0.7180	0.6764	0.6774	0.6690	0.6544	0.6498
230	1.0405	1.0173	1.0210	1.1759	1.1778	1.1811	1.2187	1.2968	1.0190	1.0688	1.0892	1.0552	1.0506	1.0683	1.0572	1.0496
220	2.1140	2.1346	2.2084	2.4225	2.4410	2.4363	2.4857	2.5694	2.2987	2.3541	2.3682	2.3234	2.3330	2.3135	2.2959	2.2771
210	2.6983	2.7003	2.7343	2.8542	2.8546	2.8626	2.8787	2.9196	2.7506	2.7790	2.7972	2.7632	2.7744	2.7594	2.7467	2.7424
200	2.3536	2.3707	2.3936	2.5139	2.5007	2.4979	2.5224	2.5527	2.4079	2.4221	2.4263	2.4130	2.3994	2.4177	2.3962	2.3925

Ligand **1d**-Thorium(IV)

λ/pH	1.512	1.690	2.235	3.544	3.729	3.959	4.274	5.225	6.578	7.131	7.954	8.764	9.425	10.319	10.710	11.083	11.479
550	0.0092	0.0553	0.0641	0.0373	0.0364	0.0398	0.0533	0.0725	0.0583	0.0309	0.0283	0.0384	0.0691	0.0954	0.0993	0.1030	0.1037
540	0.0083	0.0581	0.0684	0.0417	0.0406	0.0452	0.0612	0.0822	0.0665	0.0375	0.0355	0.0500	0.0899	0.1252	0.1328	0.1370	0.1377
530	0.0084	0.0608	0.0734	0.0474	0.0467	0.0534	0.0716	0.0941	0.0772	0.0457	0.045	0.0656	0.1172	0.1648	0.1752	0.1817	0.1820
520	0.0089	0.0635	0.0794	0.0550	0.0551	0.0633	0.0842	0.1083	0.0902	0.0565	0.0571	0.0848	0.1503	0.2110	0.2255	0.2343	0.2359
510	0.0097	0.0687	0.0871	0.0652	0.0661	0.0759	0.1001	0.1260	0.1065	0.0702	0.0721	0.1078	0.1889	0.2635	0.2800	0.2930	0.2958
500	0.0112	0.0743	0.0963	0.0777	0.0794	0.0909	0.1186	0.1464	0.1254	0.0864	0.0896	0.1326	0.2271	0.3159	0.3355	0.3508	0.3543
490	0.0138	0.0818	0.1080	0.0933	0.0963	0.1098	0.1408	0.1705	0.1484	0.1060	0.1099	0.1592	0.2657	0.3674	0.3893	0.4082	0.4115
480	0.0182	0.0921	0.1233	0.1125	0.1168	0.1324	0.1662	0.1978	0.1741	0.1290	0.1324	0.1852	0.3012	0.4121	0.4351	0.4556	0.4589
470	0.0260	0.1069	0.1432	0.1361	0.1410	0.1583	0.1943	0.2274	0.2023	0.1541	0.1562	0.2091	0.3294	0.4445	0.4676	0.4882	0.4913
460	0.0395	0.1279	0.1691	0.1640	0.1689	0.1872	0.2245	0.2586	0.2322	0.1811	0.1805	0.2295	0.3485	0.4602	0.4817	0.5014	0.5038
450	0.0604	0.1556	0.2012	0.1960	0.2003	0.2183	0.2555	0.2896	0.2626	0.2086	0.2037	0.2450	0.3564	0.4569	0.4754	0.4927	0.4945
440	0.0905	0.1911	0.2391	0.2306	0.2336	0.2498	0.2848	0.3181	0.2910	0.2346	0.2246	0.2547	0.3526	0.4359	0.4511	0.4640	0.4646
430	0.1302	0.2314	0.2796	0.2646	0.2657	0.2784	0.3101	0.3419	0.3151	0.2567	0.2414	0.2588	0.3374	0.3992	0.4093	0.4183	0.4172
420	0.1771	0.2729	0.3182	0.2949	0.2931	0.3020	0.3285	0.3586	0.3334	0.2732	0.2532	0.2579	0.3145	0.3529	0.3572	0.3627	0.3602
410	0.2261	0.3113	0.3506	0.3176	0.3132	0.3171	0.3378	0.3661	0.3431	0.2827	0.2597	0.2532	0.2865	0.3023	0.3028	0.3033	0.2993
400	0.2690	0.3405	0.3719	0.3297	0.3225	0.3217	0.3373	0.3638	0.3441	0.2851	0.2616	0.2464	0.2582	0.2544	0.2516	0.2481	0.2431
390	0.2987	0.3562	0.3793	0.3298	0.3204	0.3159	0.3284	0.3539	0.3378	0.2812	0.2593	0.2383	0.2321	0.2128	0.2068	0.2003	0.1945
380	0.3094	0.3570	0.3743	0.3195	0.3091	0.3031	0.3151	0.3413	0.3282	0.2739	0.2554	0.2312	0.2133	0.1829	0.1747	0.1667	0.1601
370	0.2995	0.3443	0.3596	0.3029	0.2928	0.2878	0.3029	0.3311	0.3194	0.2667	0.2506	0.2254	0.2035	0.1670	0.1577	0.1490	0.1422
360	0.2739	0.3244	0.3447	0.2880	0.2788	0.2771	0.2985	0.3299	0.3185	0.2632	0.2489	0.2251	0.2076	0.1723	0.1636	0.1550	0.1481
350	0.2400	0.3081	0.3390	0.2829	0.2747	0.2777	0.3077	0.3435	0.3298	0.2682	0.2539	0.2341	0.2321	0.2076	0.2000	0.1927	0.1869
340	0.2143	0.3060	0.3551	0.2975	0.2905	0.2967	0.3346	0.3759	0.3568	0.2850	0.2687	0.2554	0.2724	0.2636	0.2592	0.2541	0.2490
330	0.2239	0.3338	0.4037	0.3433	0.3353	0.3420	0.3849	0.4302	0.4071	0.3198	0.2977	0.2893	0.3217	0.3252	0.3237	0.3216	0.3167
320	0.2995	0.4011	0.4754	0.4162	0.4060	0.4072	0.4502	0.4967	0.4732	0.3697	0.3396	0.3315	0.3707	0.3800	0.3801	0.3790	0.3748
310	0.4413	0.4900	0.5407	0.4909	0.4771	0.4724	0.5087	0.5529	0.5367	0.4247	0.3894	0.3798	0.4135	0.4219	0.4214	0.4213	0.4163
300	0.5623	0.5503	0.5666	0.5263	0.5116	0.5020	0.5325	0.5756	0.5663	0.4574	0.4222	0.4081	0.4276	0.4256	0.4226	0.4207	0.4159
290	0.5915	0.5508	0.5468	0.5093	0.4955	0.4855	0.5137	0.5584	0.5546	0.4535	0.4236	0.4037	0.4041	0.3844	0.3784	0.3731	0.3679
280	0.5062	0.4847	0.4847	0.4443	0.4322	0.4273	0.4625	0.5147	0.5100	0.4122	0.3897	0.3683	0.3655	0.3393	0.3331	0.3253	0.3212
270	0.3474	0.3897	0.4232	0.3905	0.3820	0.3926	0.4517	0.5208	0.5056	0.3886	0.3647	0.3500	0.3825	0.3737	0.3717	0.3666	0.3644

260	0.2286	0.3581	0.4475	0.4364	0.4356	0.4679	0.5626	0.6452	0.6125	0.4590	0.4133	0.3914	0.4724	0.4768	0.4758	0.4745	0.4729
250	0.2536	0.4495	0.5969	0.6053	0.6059	0.6510	0.7778	0.8749	0.8269	0.6281	0.5545	0.5279	0.6594	0.6868	0.6880	0.6945	0.6930
240	0.4316	0.6564	0.8617	0.9831	1.0013	1.0687	1.2280	1.3045	1.2610	1.0809	0.9665	0.9188	1.1166	1.1662	1.1689	1.1854	1.1825
230	1.0396	1.2299	1.4288	1.5452	1.5570	1.6043	1.7027	1.7098	1.7187	1.6884	1.6384	1.5954	1.6885	1.6974	1.6904	1.7024	1.6913
220	2.3215	2.3071	2.3581	2.4444	2.4321	2.4426	2.5079	2.5210	2.5576	2.4994	2.4733	2.4365	2.4595	2.4597	2.4501	2.4543	2.4579
210	2.3299	2.4475	2.5273	2.4978	2.4933	2.5273	2.5865	2.6578	2.6192	2.5000	2.4645	2.4491	2.5185	2.5215	2.5021	2.5012	2.5080
200	1.9309	2.0349	2.1178	2.0951	2.0896	2.1099	2.1567	2.1882	2.1795	2.0647	2.0477	2.0351	2.0845	2.0965	2.0991	2.0845	2.0930

Ligand 1e-Thorium(IV)

λ/pH	1.493	1.672	2.203	3.508	3.665	3.912	4.247	5.949	6.975	7.258	7.696	8.326	9.427	11.447	11.512	11.571	11.602
550	0.0092	0.0090	0.0186	0.0425	0.0502	0.0386	0.0631	0.0816	0.0368	0.0195	0.0157	0.0174	0.0149	0.0358	0.0222	0.0188	0.0187
540	0.0089	0.0090	0.0194	0.0453	0.0524	0.0420	0.0681	0.0877	0.0392	0.0208	0.0168	0.0183	0.0159	0.0372	0.0230	0.0199	0.0199
530	0.0094	0.0090	0.0202	0.0484	0.0572	0.0449	0.0738	0.0949	0.0424	0.0228	0.0179	0.0197	0.0177	0.0406	0.0254	0.0234	0.0226
520	0.0094	0.0091	0.0217	0.0522	0.0624	0.0483	0.0810	0.1040	0.0470	0.0252	0.0203	0.0228	0.0236	0.0490	0.0370	0.0346	0.0333
510	0.0095	0.0089	0.0228	0.0567	0.0685	0.0526	0.0905	0.1159	0.0532	0.0284	0.0244	0.0298	0.0434	0.0740	0.0800	0.0772	0.0749
500	0.0100	0.0091	0.0242	0.0635	0.0773	0.0598	0.1049	0.1340	0.0650	0.0375	0.0352	0.0498	0.1107	0.1587	0.2321	0.2290	0.2234
490	0.0103	0.0094	0.0264	0.0751	0.0914	0.0732	0.1278	0.1629	0.0870	0.0564	0.0581	0.0915	0.2540	0.3342	0.5522	0.5490	0.5365
480	0.0108	0.0099	0.0300	0.0944	0.1144	0.0968	0.1644	0.2090	0.1246	0.0901	0.0960	0.1515	0.4351	0.5538	0.9469	0.9439	0.9237
470	0.0122	0.0117	0.0372	0.1290	0.1548	0.1391	0.2243	0.2817	0.1882	0.1478	0.1554	0.2343	0.6514	0.8056	1.3998	1.3972	1.3687
460	0.0171	0.0182	0.0516	0.1872	0.2207	0.2084	0.3135	0.3864	0.2827	0.2352	0.2719	0.3362	0.8730	1.0465	1.8294	1.8266	1.7922
450	0.0307	0.0359	0.0817	0.2787	0.3194	0.3131	0.4402	0.5284	0.4133	0.3552	0.3533	0.4554	1.0552	1.2227	2.1302	2.1281	2.0898
440	0.0612	0.0758	0.1379	0.4046	0.4520	0.4541	0.5950	0.6897	0.5712	0.5040	0.4867	0.5791	1.1664	1.2918	2.2295	2.2268	2.1914
430	0.1220	0.01566	0.2364	0.5647	0.6113	0.6238	0.7644	0.8578	0.7414	0.668	0.6315	0.7005	1.2001	1.2495	2.1269	2.1247	2.0944
420	0.2242	0.20909	0.3851	0.7350	0.7772	0.8011	0.9229	1.0015	0.9010	0.8293	0.7728	0.8096	1.1654	1.1155	1.8628	1.8577	1.8361
410	0.3706	0.4842	0.5875	0.8938	0.9237	0.9566	1.0479	1.1041	1.0275	0.9627	0.8936	0.8953	1.0796	0.9221	1.4947	1.4877	1.4752
400	0.5385	0.6958	0.7986	1.0035	1.0212	1.0593	1.1172	1.1479	1.1002	1.0484	0.9754	0.9476	0.9733	0.7235	1.1243	1.1169	1.1123
390	0.694	0.8846	0.9752	1.0611	1.0672	1.1047	1.1335	1.1405	1.1208	1.0841	1.0164	0.9689	0.8679	0.5455	0.8012	0.7923	0.7941
380	0.8166	1.0126	1.0863	1.0530	1.0478	1.0796	1.0857	1.0749	1.0786	1.0571	1.0058	0.9507	0.7671	0.4009	0.5523	0.5434	0.5482
370	0.8870	1.0585	1.1072	0.9904	0.9767	0.9983	0.9891	0.9678	0.9883	0.9800	0.9508	0.8995	0.6762	0.2947	0.3758	0.3672	0.3724
360	0.9103	1.0342	1.0536	0.8951	0.8755	0.8853	0.8676	0.8407	0.8725	0.8742	0.8687	0.8264	0.5993	0.2211	0.2644	0.2555	0.2603
350	0.8970	0.9583	0.9500	0.7811	0.7578	0.7564	0.7327	0.7045	0.7440	0.7530	0.7679	0.7383	0.5280	0.1713	0.1933	0.1849	0.1888
340	0.8488	0.8484	0.8171	0.6689	0.6416	0.6308	0.6082	0.5848	0.6230	0.6343	0.6616	0.6452	0.4623	0.1403	0.1523	0.1448	0.1469
330	0.7700	0.7187	0.6723	0.5610	0.5331	0.5155	0.4973	0.4792	0.5117	0.5220	0.5552	0.5488	0.3948	0.1195	0.1262	0.1187	0.1190
320	0.6655	0.5864	0.5373	0.4633	0.4358	0.4153	0.4067	0.3954	0.4150	0.4202	0.4525	0.4517	0.3296	0.1073	0.1098	0.1021	0.1014
310	0.5420	0.4527	0.4098	0.3749	0.3508	0.3299	0.3343	0.3320	0.3322	0.3285	0.3531	0.3571	0.2654	0.1001	0.0980	0.0902	0.0883
300	0.4142	0.3344	0.3048	0.3050	0.2565	0.2655	0.2865	0.2932	0.2693	0.2536	0.2683	0.2746	0.2095	0.0980	0.0947	0.0868	0.0834

290	0.2975	0.2346	0.2227	0.2580	0.2460	0.2246	0.2663	0.2832	0.2290	0.1986	0.2021	0.2111	0.1802	0.1178	0.1316	0.1233	0.1184
280	0.2012	0.1556	0.1690	0.2508	0.2481	0.2260	0.2975	0.3285	0.2370	0.1870	0.1810	0.2048	0.2695	0.2631	0.3926	0.3851	0.3741
270	0.1549	0.1358	0.1931	0.3777	0.3913	0.3765	0.4935	0.5446	0.4039	0.3203	0.2907	0.3128	0.3970	0.3783	0.5807	0.5734	0.5611
260	0.2883	0.3293	0.4306	0.5850	0.5915	0.5810	0.6827	0.7202	0.5730	0.4767	0.4288	0.4331	0.4534	0.3682	0.5459	0.5372	0.5270
250	0.4727	0.4878	0.5820	0.6693	0.6635	0.6450	0.7377	0.7707	0.6569	0.5783	0.5648	0.5814	0.5827	0.4126	0.6151	0.6056	0.5938
240	0.6286	0.6078	0.6749	0.7864	0.7796	0.7615	0.8674	0.9076	0.7976	0.7088	0.6981	0.7188	0.7061	0.5124	0.7120	0.7019	0.6893
230	0.9887	0.9590	1.0334	1.2131	1.2098	1.1939	1.3208	1.3738	1.2473	1.1337	1.1112	1.1314	1.0964	1.0283	1.0770	1.0654	1.0578
220	2.3475	2.3456	2.4133	2.5690	2.5543	2.5396	2.6257	2.6716	2.6102	2.5227	2.5232	2.5415	2.4432	2.5836	2.3141	2.3233	2.2960
210	2.6956	2.6765	2.7309	2.8204	2.8272	2.8022	2.8716	2.8935	2.8073	2.7558	2.7408	2.7539	2.7412	2.6494	2.7365	2.7285	2.7200
200	2.3299	2.3253	2.3745	2.4610	2.4540	2.4423	2.4952	2.5242	2.4407	2.3967	2.3685	2.3980	2.3962	2.2841	2.3707	2.3679	2.3647

Ligand 2b-Thorium(IV)

λ/pH	1.552	1.719	2.227	3.447	3.675	3.862	4.041	4.683	6.879	7.121	7.188	7.413	7.619	9.597	10.238	10.509	10.526	10.642
550	0.0128	0.0190	0.1282	0.0883	0.0804	0.0813	0.8100	0.0462	0.0199	0.0174	0.0141	0.0136	0.0076	0.0033	0.0061	0.0065	0.0039	0.0064
540	0.0133	0.0203	0.1382	0.0950	0.0865	0.0857	0.0850	0.0491	0.0207	0.0183	0.0148	0.0140	0.0078	0.0035	0.0070	0.0076	0.0051	0.0076
530	0.0137	0.0219	0.1490	0.1022	0.0935	0.0915	0.0899	0.0525	0.0218	0.0196	0.0155	0.0147	0.0079	0.0036	0.0094	0.0111	0.0094	0.013
520	0.0146	0.0238	0.1612	0.1110	0.1018	0.0990	0.0959	0.0575	0.0238	0.0218	0.0167	0.0163	0.0089	0.0066	0.0189	0.0236	0.0259	0.0321
510	0.0154	0.0264	0.1760	0.1222	0.1123	0.1088	0.1040	0.0641	0.0273	0.0251	0.0195	0.0193	0.0112	0.0178	0.0538	0.0710	0.0883	0.1044
500	0.0168	0.0299	0.1959	0.1379	0.1273	0.1225	0.1166	0.0747	0.0350	0.0320	0.0263	0.0259	0.0181	0.0483	0.1486	0.2003	0.2581	0.2990
490	0.0189	0.0356	0.2240	0.1618	0.1503	0.1442	0.1365	0.0929	0.0509	0.0475	0.0415	0.0410	0.0358	0.1000	0.2888	0.3882	0.5035	0.5806
480	0.0225	0.0448	0.2632	0.1984	0.1862	0.1786	0.1689	0.1244	0.0817	0.0787	0.0719	0.0721	0.0734	0.1726	0.4478	0.5996	0.7718	0.8862
470	0.0304	0.0619	0.3216	0.2576	0.2449	0.2358	0.2245	0.1794	0.1402	0.1386	0.1312	0.1333	0.1491	0.2771	0.6255	0.8304	1.0568	1.2073
460	0.0464	0.0919	0.4051	0.3457	0.3326	0.3226	0.3108	0.2663	0.2372	0.2387	0.2316	0.2376	0.2779	0.4125	0.7927	1.0332	1.2971	1.4737
450	0.0775	0.1437	0.5201	0.4743	0.4612	0.4510	0.4391	0.3949	0.3834	0.3912	0.3855	0.3976	0.4764	0.5812	0.9202	1.1711	1.4416	1.6227
440	0.1315	0.2241	0.6562	0.6346	0.6222	0.6138	0.6055	0.5646	0.5806	0.5968	0.5943	0.6140	0.7370	0.7672	0.9983	1.2276	1.4751	1.6409
430	0.2171	0.3387	0.8063	0.8174	0.8059	0.8008	0.8003	0.7622	0.8156	0.8418	0.8438	0.8720	1.0329	0.9509	1.0271	1.2098	1.4090	1.5421
420	0.3323	0.4880	0.9442	0.9906	0.9802	0.9810	0.9940	0.9607	1.0523	1.0859	1.0916	1.1256	1.3018	1.0988	1.0112	1.1339	1.2691	1.3621
410	0.4690	0.6542	1.0524	1.1299	1.1208	1.1292	1.1582	1.1292	1.2480	1.2805	1.2875	1.3206	1.4782	1.1766	0.9613	1.0201	1.0927	1.1407
400	0.5899	0.8020	1.1096	1.2029	1.1946	1.2091	1.2531	1.2264	1.3524	1.3769	1.3822	1.4075	1.5154	1.1747	0.8954	0.9001	0.9148	0.9247
390	0.6741	0.9047	1.1167	1.2155	1.2072	1.2251	1.2812	1.2530	1.3627	1.3745	1.3764	1.3904	1.4422	1.1130	0.8232	0.7871	0.7562	0.7367
380	0.7076	0.9415	1.0685	1.1590	1.1487	1.1683	1.2287	1.1954	1.2708	1.2703	1.2683	1.2721	1.2733	1.0027	0.7490	0.6862	0.6234	0.5857
370	0.6907	0.9128	0.9784	1.0475	1.0356	1.0535	1.1133	1.0709	1.1068	1.0994	1.0935	1.0923	1.0614	0.8722	0.6748	0.6004	0.5175	0.4690
360	0.6441	0.8395	0.8673	0.9046	0.8912	0.9052	0.9557	0.9066	0.9073	0.8990	0.8916	0.8869	0.8430	0.7373	0.6037	0.5267	0.4327	0.3817
350	0.5920	0.7429	0.7474	0.7515	0.7368	0.7473	0.7885	0.7324	0.7069	0.6986	0.6902	0.6855	0.6391	0.6068	0.5291	0.4551	0.3615	0.3137
340	0.5528	0.6453	0.6392	0.6120	0.5956	0.6038	0.6352	0.5763	0.5352	0.5280	0.5197	0.5155	0.4733	0.4910	0.4545	0.3895	0.3032	0.2616
330	0.5394	0.5650	0.5528	0.4974	0.4799	0.4889	0.5251	0.4479	0.3948	0.388	0.3799	0.3771	0.3403	0.3860	0.3781	0.3248	0.2496	0.2152
320	0.5460	0.5027	0.4906	0.4126	0.3944	0.4037	0.4385	0.3518	0.2912	0.2856	0.2772	0.2755	0.2435	0.2962	0.3039	0.2628	0.1998	0.1739
310	0.5520	0.4548	0.4547	0.3604	0.3407	0.3485	0.3755	0.2876	0.2180	0.2123	0.2035	0.2015	0.1729	0.2194	0.2356	0.2057	0.1562	0.1385
300	0.5390	0.4133	0.4443	0.3398	0.3185	0.3258	0.3501	0.2536	0.1722	0.1665	0.1564	0.1547	0.1275	0.1586	0.1815	0.1640	0.1290	0.1210

290	0.4895	0.3671	0.4599	0.3483	0.3253	0.3297	0.3426	0.2446	0.1503	0.1429	0.1314	0.1296	0.1019	0.1253	0.1843	0.1933	0.1897	0.2023
280	0.4118	0.3375	0.5488	0.4390	0.4126	0.4143	0.4187	0.3146	0.2019	0.1904	0.1752	0.1712	0.1406	0.1710	0.2929	0.3486	0.3878	0.4322
270	0.4052	0.4342	0.7788	0.7279	0.7020	0.7061	0.7215	0.6175	0.5088	0.4975	0.4797	0.4787	0.472	0.4000	0.4205	0.4664	0.4980	0.5367
260	0.4185	0.5339	0.8755	0.8470	0.8249	0.8330	0.8611	0.7572	0.6624	0.6543	0.6377	0.6380	0.6208	0.5315	0.5222	0.5309	0.5243	0.5407
250	0.3990	0.5486	0.9052	0.8415	0.8144	0.8238	0.8568	0.7327	0.6156	0.6073	0.5889	0.5888	0.5601	0.5645	0.6243	0.6310	0.6122	0.6264
240	0.5837	0.6848	1.0524	0.9767	0.9462	0.9561	0.9895	0.8516	0.7128	0.7045	0.6833	0.6848	0.6629	0.6608	0.7093	0.7194	0.6985	0.7148
230	1.0849	1.1677	1.5844	1.5407	1.5103	1.5257	1.5662	1.4191	1.2863	1.2827	1.2626	1.2719	1.2813	1.2725	1.2590	1.2590	1.2043	1.2057
220	2.6350	2.6240	2.8287	2.8066	2.7887	2.8083	2.8670	2.7381	2.6347	2.6293	2.6197	2.6317	2.6146	2.5945	2.5493	2.5424	2.4563	2.4318
210	2.7648	2.8174	3.0123	2.9603	2.9379	2.9513	2.9672	2.8685	2.7821	2.7691	2.7626	2.7579	2.7460	2.7384	2.7626	2.7801	2.7704	2.7576
200	2.4049	2.4675	2.6595	2.5973	2.5636	2.5790	2.6140	2.5079	2.4103	2.4067	2.3954	2.4063	2.3786	2.3810	2.4152	2.4114	2.3977	2.4063

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