Potentiometric and ^{1}H and ^{19}F NMR studies of the Th(IV)–5-sulfosalicylate–OH$^-$–F$^-$ system †

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The complex formation between Th(IV) and 5-sulfosalicylate, (SSA)$^{3-}$, has been investigated, in both the presence and absence of fluoride, by potentiometry, ^{1}H and ^{19}F NMR spectroscopy. The potentiometric data were used to deduce the stoichiometry and equilibrium constants for the reactions pTh^{4+}(aq) + r(SSA)$^{3-}$ $\rightleftharpoons$ Th$_p$H$_{-q}$(SSA)$_r^{4p-q-3r}$ + qH$^+$ at 25 °C, in an ionic medium with a constant concentration of Na$^+$ equal to 1.00 M. Three mononuclear complexes, Th(HSSA)$^{2+}$, Th(SSA)$^+$ and Th(SSA)$_2^{2-}$, were identified in the $-$log[H$^+$] range 1.7–3.5. Their stability constants obtained by least-squares refinement of the experimental data agree well with previously published information; their magnitude, and additional NMR data, indicate coordination at the carboxylate end only in Th(HSSA)$^{2+}$, and the formation of chelates involving deprotonation of the aromatic OH group in the other two species. A maximum of two SSA ligands are coordinated even at high ligand concentration. However, this does not indicate tetrahedral coordination around Th, additional fluoride can coordinate to these complexes even at very low free fluoride concentrations. We expect that additional fluorides may coordinate at higher fluoride concentration, but these systems could not be investigated by potentiometry due to precipitation. We could demonstrate the coordination of one fluoride to these complexes. We suggest that Th is nine- or ten-coordinated in these species as in other mononuclear Th-complexes. The bi- and tetra-nuclear complexes, Th$_2$(OH)$_2$(SSA)$_4^{6-}$ and Th$_4$(OH)$_4$(SSA)$_{10}^{18-}$, were identified at pH > 3.5 using both potentiometric data and ^{1}H NMR spectra. The binuclear complex can bind three fluoride ions per Th, indicating nine-coordination with a bridging "Th$_2$(OH)$_2$" core. The tetranuclear complex Th$_4$(OH)$_4$(SSA)$_{10}^{18-}$ cannot bind additional fluoride, and from this we can suggest that Th(IV) is eight-coordinated. The stoichiometry and the NMR data show that the complex has a "cubane-like" hydroxide core "Th$_4$(OH)$_4$". This structure is different from the previously investigated tetranuclear glycolate complex with a "Th$_4$(OR)$_4$" core, where OR is $^-$OCH$_2$COO$^-$.

Introduction

It is well known that actinide ions such as thorium(IV) or uranium(VI) form strong complexes with organic ligands containing phenolate and carboxylate groups. The chemistry of the reactions is important in nuclear waste management because these ligands, mainly humic and fulvic acids (HA/FA), occur in nature as a result of microbiological degradation of organic material. We recently reported[1] on the complex formation of Th(IV) with glycolate (HOCH$_2$COO$^-$) that was used as a model ligand for natural organic materials. This study suggested the existence of di- and tetra-nuclear Th(IV) complexes with bridging hydroxide or oxyacetate ligands, the latter formed through deprotonation of the α-OH group in the ligand (pK = 15–17); based on the experimental evidence we suggested structures based on oxyacetate bridges. HA/FA contains aromatic hydroxide and carboxylate groups and we have therefore extended the previous study to include 5-sulfosalicylate (SSA) as a model ligand. It is known that this ligand can bind at the carboxylate end only, but also form a bidentate chelate through the carboxylate and deprotonated phenolate groups.[2,3] As the dissociation constant of aromatic OH groups (pK = 11–12) is much larger than that of aliphatic groups, the formation of ternary complexes similar to those in the glycolate system, could be expected at lower pH. In addition, the much larger size of the SSA ligand might affect the coordination geometry. In previous investigations on the complex formation between SSA^{3-} and Th(IV) the formation of a very strong mononuclear Th(SSA)$^+$

complex has been reported,[2] the value of the equilibrium constant (logβ_1 = 12.30) indicates the formation of a chelate involving both the carboxylate and phenol groups

The present study is focused on the determination of the stoichiometry and stability constants in the ternary Th(IV)–SSA^{3-}–hydroxide system and the structure and bonding in the complexes formed; it covers a much larger pH range than the previous studies. The complex formation reactions have been studied using standard potentiometric techniques (*vide infra*) to investigate reactions summarized in eqn. (1):

$$p\text{Th}^{4+}(\text{aq}) + r\text{SSA}^{3-} \rightleftharpoons \text{Th}_p\text{H}_{-q}(\text{SSA})_r^{4p-q-3r} + q\text{H}^+ \quad (1)$$
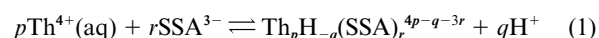
However, from experiments of this type it is not possible to decide if the species Th$_p$H$_{-q}$(SSA)$_r$ are formed with proton dissociation from coordinated water or the phenol group of SSA; information of this type has been obtained by ^{1}H NMR spectroscopy. At most two SSA ligands per Th(IV) were bonded in the mononuclear complexes; the other coordination positions presumably being occupied by water. In order to estimate this number we determined how many additional fluorides could be coordinated by using potentiometric titrations. The stoichiometry thus obtained gives indications of the possible coordination geometry; additional structure information was obtained using ^{19}F NMR spectroscopy.

Experimental

Chemicals used

Stock solutions of perchloric acid, sodium perchlorate and thorium perchlorate were prepared and analyzed as described in our previous study.[1] 5-Sulfosalicylic acid of analytical grade (Sigma Co. Ltd.) was used to prepare the stock solution of sodium 5-sulfosalicylate by neutralization with NaOH, the

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† Electronic supplementary information (ESI) available: Table S1: a summary of experimental conditions used in titrations using buffers of H$_2$SSA$^-$/HSSA^{2-}. See http://www.rsc.org/suppdata/dt/b3/b301188g/
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Table 1 The chemical models tested in the least-squares refinement of the Th(IV)–SSA system. The data from the least-squares analysis are given as $\log \beta_{pqr} \pm 3\sigma$, where σ is the estimated standard deviation. The protonation constants for the formation of H_3SSA, H_2SSA^- and $HSSA^{2-}$ are 14.29 ± 0.08, 13.52 ± 0.06 and 11.28 ± 0.05, respectively

p	q	r	Exptl. series[a]	$\log \beta_{pqr}$ (refined)	Composition identified in the titration
1	−1	1	(A)	15.47 ± 0.17	$Th(HSSA)^{2+}$
1	0	1	(A)	13.38 ± 0.14	$Th(SSA)^+$
1	0	2	(B)	23.34 ± 0.11	$Th(SSA)_2^{2-}$
2	2	4	(B)	38.03 ± 0.43	$Th_2(OH)_2(SSA)_4^{6-}$
			(C)	37.37 ± 0.18	
4	4	10	(C)	86.88 ± 0.51	$Th_4(OH)_4(SSA)_{10}^{18-}$

[a] Exptl. series: (A) titrations using buffer of $H_2SSA^-/HSSA^{2-}$, (B) titrations in test solutions with $C_{SSAM,tot} = 50$ mM, (C) titrations in test solutions with a large excess of SSA.

same stock solution was used throughout the experiments. The stock solution of NaF was made from solid NaF that was of analytical grade (Merck).

Potentiometric studies

General procedures for the potentiometric measurements. All EMF measurements were made in a thermostatted box at 298.0 ± 0.05 K using an automatic titration system. The glass, fluoride and reference (Ag/AgCl) electrodes were from Metrohm. The electrode slope was calibrated by an acid–base titration; E_0 was determined after each titration using Gran's method[4] by the titration of 1 M $NaClO_4$ with 0.1 M $HClO_4$. The protonation constants of SSA^{3-} were determined by potentiometric titrations by adding 0.100 M NaOH to test solutions of H_3SSA. The equilibrium constants are given in Table 1. In order to investigate the complex formation with Th(IV) in as wide a $-\log[H^+]$ range as possible, three different types of titrations were performed, as described below. In titrations where NaOH was used as titrant we purged the test solutions continuously with nitrogen that was purified by passage through 10% NaOH, 10% H_2SO_4, 1 M $NaClO_4$ solutions and a G4 filter in order to avoid contamination by CO_2. All measurements were carried out at constant sodium ion concentration, $[Na^+] = 1.00$ M, that was adjusted with $NaClO_4$. The measured EMF values were treated using the least-squares program PC-LAKE[5] to test different chemical models, and the one in best agreement with the experimental data was selected.

(A) Titrations using buffer of $H_2SSA^-/HSSA^{2-}$. A summary of the experimental conditions used is given in Table S1 (ESI†). The principle of the experimental method and the analysis of the data have been described both by Magon *et al.*[6] and in our previous paper.[1] The titrations were made in the range $1.70 < -\log[H^+] < 2.63$ and equilibrium was assumed when the EMF value remained constant within 0.2 mV h^{-1} with a maximum waiting time of 30 min. At the high hydrogen ion concentrations used the species $Th(HSSA)^{2+}$ and $Th(SSA)^+$ are the predominant species, as confirmed by the plot of $-\log[H^+]$ *vs.* C_{Htot} given in Fig. 1.

(B) Titrations in test solutions at $C_{SSA,tot} = 50$ mM. These experiments were performed in test solutions containing an initial concentration of SSA, $C_{SSA,tot}$, equal to 50.00 mM and varying Th(IV) concentrations, $C_{Th,tot}$, equal to 4.00, 6.00, 9.00 and 17.00 mM. In a preliminary experiment, 0.1 M NaOH was sequentially added to these test solutions to investigate the time of equilibration and the point where a hydroxide precipitate was formed. It turned out that equilibrium, as indicated by the drift of the measured EMF values, was not attained within 24 h at $-\log[H^+] > 3.5$. A similar finding was also reported by Cassol *et al.*[2] Therefore, these experiments were conducted using a batch technique. As a precipitate appeared at pH 6.0, we could only investigate the region $2.5 < -\log[H^+] < 5.5$. The test solutions were stored in 50 ml glass flasks for 1 week in a thermostatted box at 298.0 ± 0.05 K, and then their EMF

values were measured. The experimental data are plotted in Fig. 1(b), where the full-drawn curves have been calculated using the chemical model and the corresponding equilibrium constants given in Table 1.

(C) Titrations in test solutions with a large excess of SSA. The formation of hydroxide precipitates could be avoided by using a large excess of 5-sulfosalicylate, thus enabling us to explore the complex formation at higher pH. These experiments were carried as batch experiments at $5.5 < -\log[H^+] < 10.5$ in test-solutions containing an initial concentration of SSA of 0.17 M and varying Th(IV) concentrations equal to 4.00, 8.00 and 11 mM. Dissolved carbon dioxide was removed by N_2 gas from all test solutions prior to the addition of NaOH; the test solutions were stored in 50 ml polypropylene bottles that were filled with purified nitrogen gas and then sealed hermetically. The experimental data are shown in Fig. 1(c), where the full-drawn curves have been calculated using the chemical model and the corresponding equilibrium constants given in Table 1.
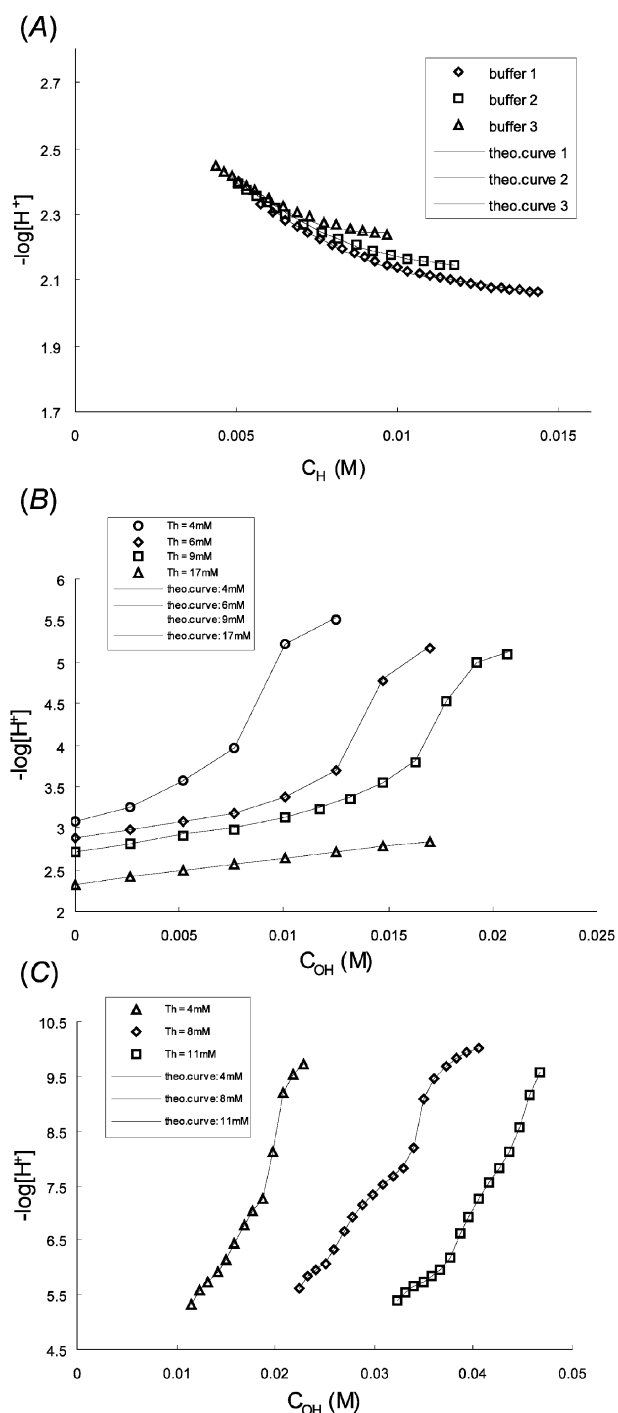
(D) Titrations of Th(IV)–SSA^{3-} test solutions with fluoride. This experiment was carried out to obtain information if there is coordinated water in the binary and ternary Th(IV) –SSA– OH^- complexes, that can be replaced by fluoride and thereby provide more information on the coordination number and structure of these complexes. The titrations were performed in three different pH ranges; pH = 3.8–3.9, 4.0–6.0 and 10.0–10.2, where mono- bi- and tetra-nuclear complexes, respectively, are predominant. The total concentration of SSA was 0.100 M, and that of thorium 4.00 or 10.00 mM, respectively; the fluoride concentration was varied using a 0.200 M NaF solution as a titrant. The fluoride electrode was calibrated after each titration using a standard solution of NaF–SSA, with known concentration of fluoride. Because of the very strong complex formation with SSA, we can safely assume that the number of the coordinated SSA per thorium does not change on addition of fluoride, and that the fluoride coordination takes place by exchange with coordinated water as in many other systems.[7–10] The fluoride coordination can then be described by eqn. (2):

$$Th_pH_{-q}(SSA)_r^{4p-q-3r} + nF^- \rightleftharpoons [Th_pH_{-q}(SSA)_rF]^{4p-q-3r-n} \quad (2)$$
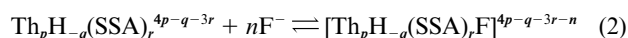
with a conditional equilibrium constant, $-\log K_{cond}$. A change in the number of dissociated protons, q, will result in a change of pH. However, no such change was experimentally observed, indicating that fluoride cannot be coordinated at the OH^- sites. The number of coordinated fluorides per thorium–SSA complex, $\bar{n}_F$, can then be calculated using eqn. (3):
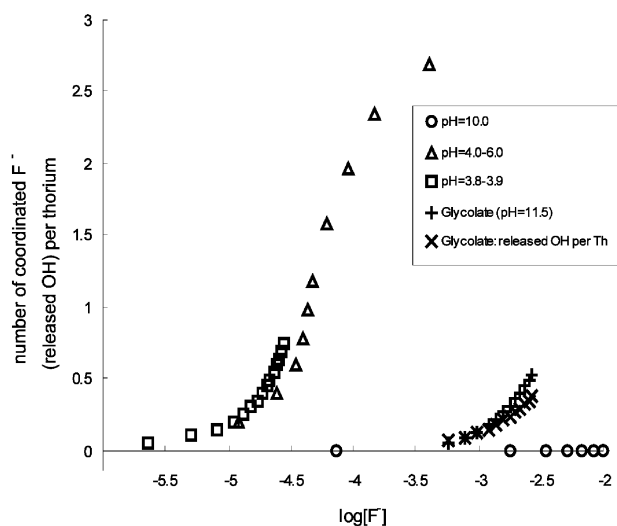
$$n_F = \frac{C_F - [F^-] - ([H^+][F^-]/K_a)}{\sum_p p[Th_pH_{-q}(SSA)_r^{4p-q-3r}]} = \frac{C_F - [F^-] - ([H^+][F^-]/K_a)}{C_{Th}} \quad (3)$$

where K_a is the dissociation constant of HF. $\bar{n}_F$ provides an estimate of the number of coordinated water ligands in the

Fig. 2 The experimental data $\bar{n}_F$, the number of the coordinated F^- per thorium, plotted against $\log[F^-]$. The data on the left hand side refer to the Th(IV)–SSA system where $Th_2(OH)_2(SSA)_4F_n$, $n = 1$–3, are predominant. The data on the right hand side refer to the Th(IV)–glycolate system at pH = 11.5 where tetranuclear complexes $Th_4(OCH_2COO)_8(OHCH_2COO)_4(OH)_{4-n}F_n$ are predominant.

Fig. 1 The experimental data $-\log[H^+]$ plotted against C_H or C_{OH}, the total concentrations of H^+ or OH^-: (A) Titrations using a buffer of H_2SSA^-/$HSSA^{2-}$, (B) titrations in test solutions with at $C_{SSA,tot} = 50$ mM, and (C) titrations in test solutions with a large excess of SSA. The full drawn curves were calculated from the equilibrium constants β_{pqr} given in Table 1.

data were treated by least-squares refinement in order to estimate the conditional equilibrium constants, K_{cond}. The data for the systems where binuclear complexes are also present were not sufficiently precise to determine the six additional equilibrium constants for the fluoride containing species.

^{1}H and ^{19}F NMR spectroscopy

The NMR spectra provide information on the dynamics of ligand exchange, the number of coordinated ligands, and their mode of bonding and indications of the possible structures of the complexes formed. Both ^{1}H and ^{19}F NMR spectra were recorded in D_2O on a Bruker DMX500 spectrometer using a 5 mm tube. Two series of ^{1}H NMR experiments were made; the first series, shown in Fig. 3(a), using test solutions with total concentrations of SSA and Th(IV) equal to 75.0 and 25.0 mM, respectively; the second with test solutions where these concentrations were 100.0 and 10.0 mM (spectra shown in Fig. 3(b)). The ^{1}H NMR spectra were measured at 273 K to obtain a better peak resolution. The spectra and the corresponding distribution diagrams drawn using the MEDUSA program [11] are shown in Figs. 3 and 4, respectively. The dissociation constants of the phenol and carboxylic acid groups used for calculating the diagram were corrected for the D_2O solvent as described by Lowe and Smith [12] for salicylic acid. Corrections for temperature (273 K) were made using published [13] values of ΔH. A test solution with $C_{Th} = 50.00$ mM, $C_{SSA,tot} = 500.0$ mM and $C_F = 25$ mM was used to measure the ^{19}F NMR spectra. By using a ratio of two between the total concentrations of Th(IV) and fluoride we could ensure that there is only one coordinated fluoride per thorium in the system. The ^{19}F NMR spectra are shown in Fig. 5. The hydrogen ion concentration in a given test solution was varied by addition of a small amount of concentrated NaOH in D_2O; in this way the total concentrations of the other components were kept very near constant. The proton concentration of the solutions for NMR measurements was measured by using a pH meter (Orion) and a combined glass electrode (Ingold) in which the inner solution of KCl was replaced by 1 M NaCl to avoid precipitation of $KClO_4$. The value of $-\log[D^+]$ was calculated from the measured EMF as described previously. The obtained spectra were treated using WIN-NMR software,[14] assuming Lorentzian line shapes.

complex. Fluoride coordination was only observed in systems containing mononuclear and binuclear Th(IV)–SSA complexes, no fluoride was bonded in the system where the tetranuclear complex is predominant. The same experiment was carried out for Th–glycolate $(OHCH_2COO^-)$–F^- system under the condition at $C_{Th} = 5$ mM, $C_{glyc} = 500$ mM, $[Na^+] = 1$ M and pH = 11.5 where the tetranuclear $Th_4(OCH_2COO)_8(OHCH_2COO)_4(OH)_4$ is predominant.[1] In contrast to the SSA system we found coordination of fluoride. The values of $\bar{n}_F$ plotted against $-\log[F^-]$ is shown in Fig. 2. Only the data for the mononuclear complexes were used to estimate an equilibrium constant for the complexes formed in reaction (2). These potentiometric
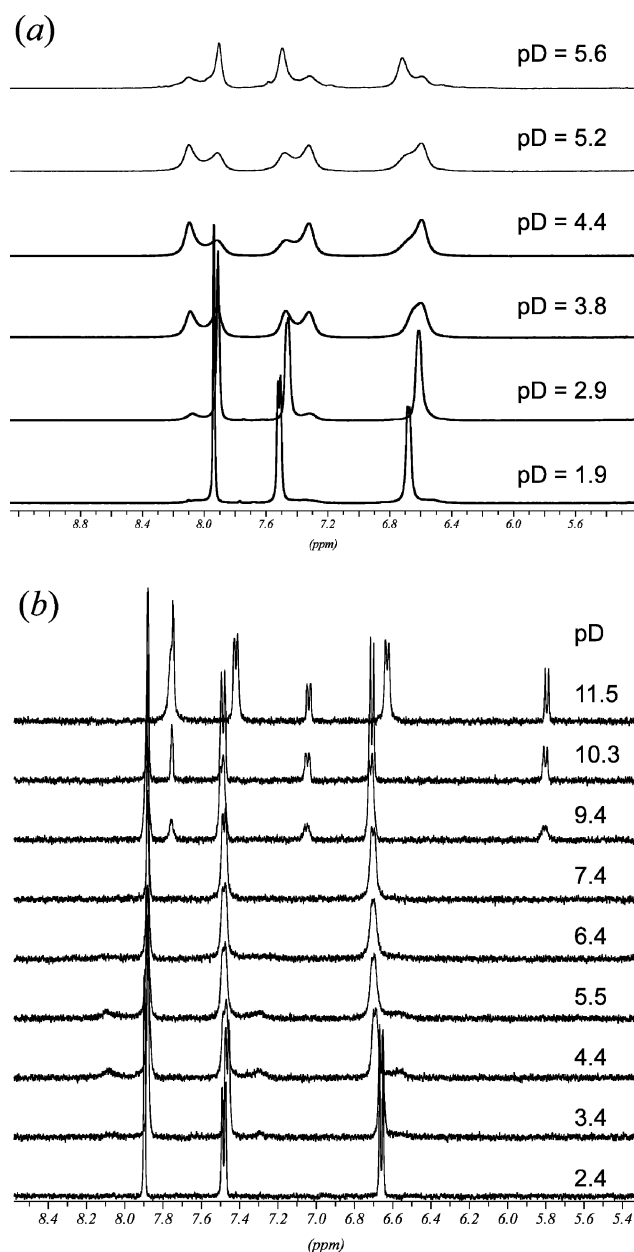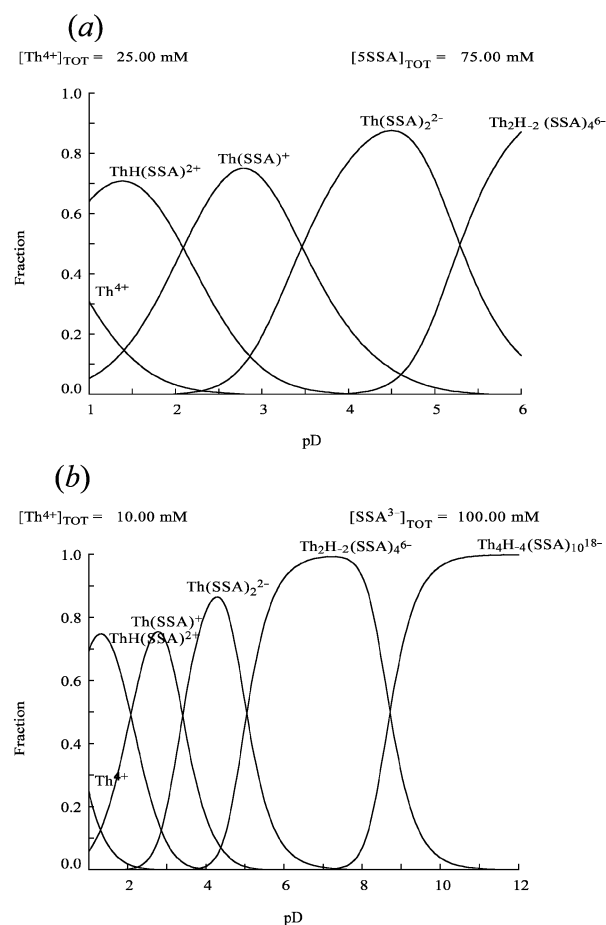
Fig. 4 Distribution diagrams calculated from the equilibrium constant β_{pqr} given in Table 1 for the conditions used in the ^{1}H NMR measurements. The dissociation constants of the phenol and carboxylic acid groups were corrected for the D_2O solvent and temperature (273 K).

$Th_2H_{-2}(SSA)_4^{6-}$; $\log\beta_{2,-2,4} \pm 3\sigma = 37.37 \pm 0.18$ and Th_4H_{-4}-$(SSA)_{10}^{18-}$; $\log\beta_{4,-4,10} \pm 3\sigma = 86.88 \pm 0.51$. A comparison between experimental and calculated titration curves is shown in Fig. 1. The difference between the stability constants of the binuclear complex $Th_2H_{-2}(SSA)_4^{6-}$ in the two titrations gives a measure of the uncertainty in the experiment and we have used the average value, $\log\beta_{2,-2,4} \pm 3\sigma = 37.70 \pm 0.33$ in the following discussions. The number of coordinated SSA ligands in the tetranuclear complex, $Th_4H_{-4}(SSA)_{10}^{18-}$, has been estimated to 10 from the potentiometric data; the main uncertainty derives from the experimental conditions used; $C_{Th,tot} = 11.0$ mM and $C_{SSA,tot} = 170.0$ mM, hence only 16% of the total concentration of SSA is coordinated to Th(IV), even when $Th_4H_{-4}SSA_{10}^{18-}$ is the predominant species. However, the stoichiometry is confirmed by the information from the ^{1}H NMR spectra as described below.

The constitution of the complexes

As mentioned before, it is not straightforward to determine if the release of a proton takes place from the phenol group or from coordinated water using potentiometric data. For instance, $Th(SSA)^+$ may be either $Th(OH)(HSSA)^+$ with the dissociated proton from coordinated water, or $Th(SSA)^+$ with the proton dissociated from the coordinated phenol group. A choice between these two alternatives may be obtained from the ^{1}H NMR spectra shown in Fig. 3. At pD = 1.9 all peaks from coordinated and free ligand coincide and cannot be deconvoluted. However from pH = 2.9 new set of signals are observed, and all peaks can be resolved. The predominant species at pD = 1.9 and 2.9 are $Th(HSSA)^{2+}$ and $Th(SSA)^+$, respectively. The

Fig. 3 ^{1}H NMR spectra at different pD: (a) $C_{Th,tot} = 25$ mM and $C_{SSA,tot} = 75$ mM, (b) $C_{Th,tot} = 10$ mM and $C_{SSA,tot} = 100$ mM. The spectra were measured at 273 K.

Results and discussion

Potentiometry

Three mononuclear complexes, $Th(HSSA)^{2+}$, $Th(SSA)^+$, $Th(SSA)_2^{2-}$ were identified in titrations A and B, and the corresponding equilibrium constants are given in Table 1. The stability constant for $Th(SSA)^{2+}$ ($\log K = 13.38$) differs significantly from that of a previous study by Cassol *et al.*,[2] $\log K = 12.30$. Possible reasons might be the smaller pH range (pH < 3.5) and the different temperature (20 °C) used by Cassol *et al.*, but more likely that the mono- and bi-nuclear complexes, $Th(HSSA)^{2+}$ and $Th_2H_{-2}(SSA)_4^{6-}$, were not included in their refinement. The stoichiometry of the complexes was determined from the experimental value of $-\log[H^+]$ and the total concentrations of the reactants. The number of coordinated SSA in the bi- and tetra-nuclear complexes was confirmed by NMR data as described in the following. The predominant complex in titration B is the complex $Th_2H_{-2}(SSA)_4^{6-}$ with the equilibrium constant $\log\beta_{2,-2,4} = 38.03 \pm 0.43$. Models with different stoichiometry do not give satisfactory fits to the experimental data. In titration C there are two complexes formed,
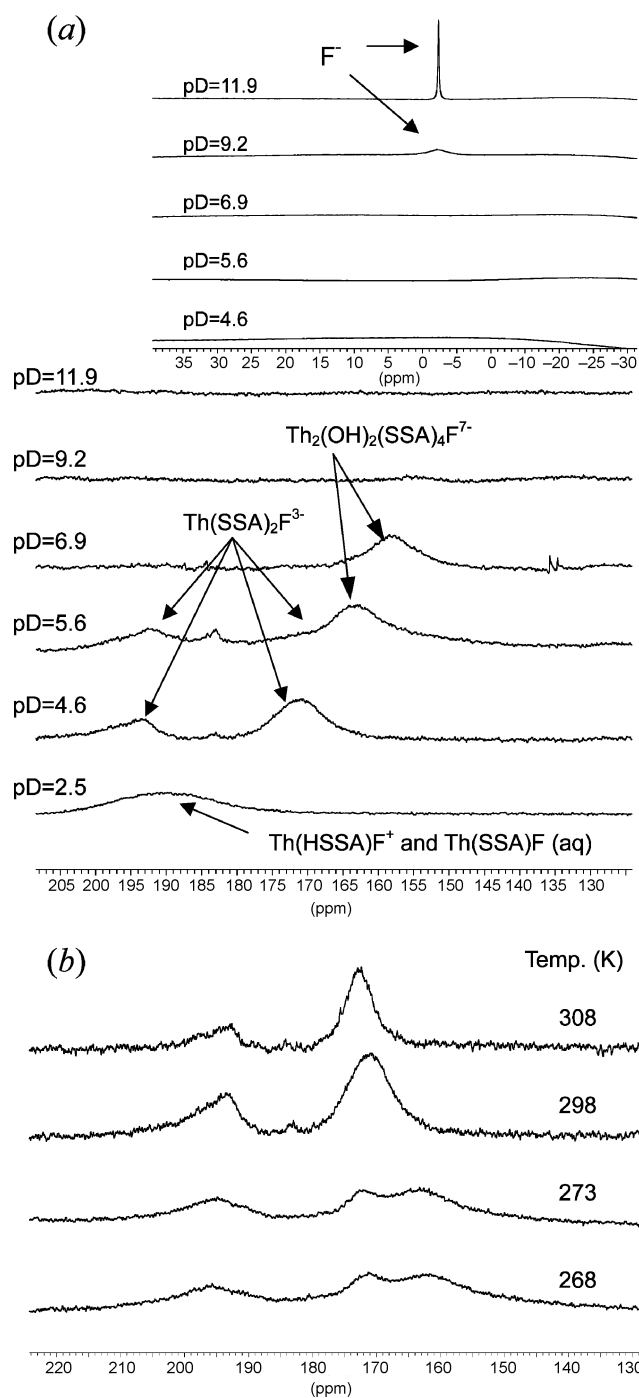
(a)

F⁻ →

pD=11.9

pD=9.2

pD=6.9

pD=5.6

pD=4.6

35 30 25 20 15 10 5 0 −5 0 −10 −20 −25 −30
(ppm)

pD=11.9

pD=9.2

$Th_2(OH)_2(SSA)_4F^{7-}$

pD=6.9

$Th(SSA)_2F^{3-}$

pD=5.6

pD=4.6

pD=2.5

$Th(HSSA)F^+$ and Th(SSA)F (aq)

205 200 195 190 185 180 175 170 165 160 155 150 145 140 135 130
(ppm)

(b)

Temp. (K)

308

298

273

268

220 210 200 190 180 170 160 150 140 130
(ppm)

Fig. 5 ^{19}F NMR spectra at C_{Th} = 50.00 mM, $C_{SSA,tot}$ = 500.0 mM and C_F = 25 mM: (a) at different pD, (b) at different temperature at pD = 4.6; note the different chemical shift scales.

relatively narrow line width of the average peak at pD = 1.9 indicates that there is a rapid exchange between the free and coordinated ligand in $Th(HSSA)^+$, where the ligand can only be coordinated through the carboxylate end; the observed rapid exchange is in agreement with the observations on α-hydroxy-carboxylate complexes reported recently;[1,10] where in both cases a rapid exchange was observed when the ligand was coordinated at the carboxylate end only. This conclusion is supported by the magnitude of the equilibrium constant (log K = 4.18) for reaction (4):

$$Th^{4+} + HSSA^{2-} \rightleftharpoons Th(HSSA)^{2+} \qquad (4)$$
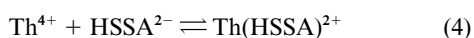
which is comparable in magnitude with those for the formation of Th(IV) acetate, (log K_1 = 3.88) and glycolate complexes[1] (log K_1 = 4.27). The constitution of $Th(SSA)^+$ can be either

$Th(OH)(HSSA)^+$ or $Th(SSA)^+$. In the first case the fast ligand exchange reaction, which results in the averaged single signal observed pD = 1.9, is in agreement with coordination at the carboxylate end only. However, the formation of Th(OH)-$(HSSA)^+$ is not in agreement with the known hydrolytic behavior of Th(IV); at pH 2.9 the hydrolysis of Th^{4+} is low,[15,16] about 5%, and one expects a similar or smaller hydrolysis also for $Th(HSSA)^{2+}$. On this ground we propose that $ThSSA^+$ contains chelated 5-sulfosalicylate coordinated with both the phenolate and carboxylate groups. In the previous studies[1,10] we noticed a slow rate of exchange when the coordinated α-hydroxycarboxylate ligand was deprotonated at the OH-end, a slow reactions is also found for the exchange in $Th(SSA)_2^{2-}$, indicating that the small changes in chemical shift and line broadening between pD = 1.9 and 2.9 are a result of a small difference in chemical shift between $Th(SSA)^{2+}$ and free SSA. At pD = 3.8 there is an additional complex, $Th(SSA)_2^{2-}$ according to the potentiometric data. In the NMR spectrum all peaks can be resolved, allowing a determination of the chemical shift and peak integral for the new complex. At pD = 5.2 and 5.6 we note a decrease of the peak at 6.6 ppm, while the peak at 6.7 ppm is increasing. Using the known speciation, the 6.6 ppm peak was identified with $Th(SSA)_2^{2-}$, and the 6.7 ppm peak with a new complex $Th_2H_{-2}(SSA)_4^{6-}$. By using the peak integrals we can compare the consistency of the potentiometric and NMR data. Denoting the peak integrals for $Th(SSA)_2^{2-}$ with P_1 and the peak integral for the sum of the other species with P_2 we have

$$\frac{P_1}{P_1 + P_2} = \frac{2[Th(SSA)_2^{2-}]}{\sum_{p,q,r} r[Th_pH_{-q}(SSA)_r^{4p-q-3r}]} = \frac{2[Th(SSA)_2^{2-}]}{C_{SSA,tot}} \qquad (5)$$

This ratio calculated from the NMR spectra and from the potentiometric equilibrium constants are given in Table 2; the agreement between the two sets is satisfactory, taking the experimental uncertainty into account. In the ^1H NMR spectra at pD = 7.4 shown in Fig. 3(b), only one average signal between coordinated and free SSA was observed for the different protons. The only possible explanation is that the complex has very nearly the same chemical shift as the free ligand, the broader peaks as compared to those at pD = 2.4, indicate slow exchange. Therefore we assume that the SSA ligand in $Th_2H_{-2}(SSA)_4^{6-}$ is chelated and that the constitution is $Th_2(OH)_2(SSA)_4^{6-}$. In the ^1H NMR spectra at pD ⩾ 9.4, where both $Th_2(OH)_2(SSA)_4^{6-}$ and $Th_4H_{-4}SSA_{10}^{18-}$ are present, a new set of the signals appears at 5.8, 7.0 and 7.7 ppm, the peak integrals of which indicate an average of 1.5_1 and 2.2_0 coordinated SSA ligands per Th at pD = 9.4 and 10.3, respectively. In the same way, the peak integrals at pD = 11.5 where only the tetranuclear complex is present, give 2.4_3 coordinated SSA per Th, corresponding to the stoichiometry $Th_4H_{-4}(SSA)_{9.7}$, which we assume is $Th_4H_{-4}(SSA)_{10}^{18-}$. The rate of exchange between this complex and free SSA is slow. This indicates all SSA in this complex are chelated, and its constitution is $Th_4(OH)_4(SSA)_{10}^{18-}$.

On the structure of the complexes in the Th(IV)–SSA system

The predominating coordination number of Th(IV) is eight, nine or ten, indicating that a maximum of four to five bidentate SSA ligands might be bonded to Th^{4+}. At low pH where $Th(SSA)_2^{2-}$ is predominant, we found that a maximum of two SSA ligand could be coordinated, even if the concentration of free SSA is increased up to 0.2 M. The additional coordination sites are occupied by water that can be replaced by fluoride. The conditional equilibrium constant, log K_{cond} = 4.68 ± 0.10, for coordination of fluoride could only be determined for the reaction $Th(SSA)_2^{2-} + F^- \rightleftharpoons ThF(SSA)_2^{3-}$, using the titration data at pH = 3.8–3.9, because of precipitation of ThF_4 (s)

Table 2 Comparison of the consistency of the potentiometric and NMR data. The values of $P_1/(P_1 + P_2)$, defined in eqn. (3) are given for each pD. The theoretical values were evaluated from the $-\log\beta$ values given in Table 1, obtained by potentiometric titrations

	pD	2.9	3.8	4.4	5.2	5.6
$\dfrac{P_1}{P_1 + P_2}$	From the peaks of ^{1}H NMR	0.11 ± 0.01	0.50 ± 0.03	0.59 ± 0.05	0.50 ± 0.04	0.37 ± 0.03
	Theoretical values from $\log\beta$	0.15	0.49	0.55	0.42	0.25 ± 0.045

or ThF(SSA) (s) around $\bar{n}_F = 1.0$. The binuclear complex $Th_2(OH)_2(SSA)_4^{6-}$ contains a double hydroxide bridge, resulting in a minimum coordination number of six for Th(IV), additional coordination sites must be occupied by water. The fluoride titration curve at pH = 4–6, where the binuclear complex is predominant, indicates the coordination of three fluorides per Th(IV), resulting in nine-coordination. The minimum coordination number is eight for Th(IV) in the complex $Th_4(OH)_4(SSA)_{10}^{18-}$ with a "cubane" core "$Th_4(OH)_4$", similar to that of "$Ln_4(OH)_4$" found in several lanthanide complexes.[17–19] The fact that fluoride and hydroxide (if a coordinated water is present) cannot coordinate to this complex (fluoride titration data at pH 10) indicates that this complex does not contain coordinated water and that Th(IV) indeed is eight-coordinated.

The ^{19}F NMR data shown in Fig. 5(a) and (b) recorded at different pD indicate the presence of different fluoride sites in the species present, consistent with the proposed coordination geometry. Fig. 5(a) shows that there is no signal for free fluoride at pH < 9.2, indicating that all fluoride is bonded. At pD = 9.2 there is free fluoride present in slow exchange with the coordinated fluoride in $Th_2(OH)_2(SSA)_4F^{7-}$. No fluoride is coordinated to the tetranuclear complex at pD = 11.9. The observations are in good agreements with the potentiometric result discussed above. Furthermore, two broad ^{19}F peaks were observed at pD = 4.6, where only one species, $Th(SSA)_2F^{3-}$, exists in the system. At lower temperature each of these peaks is broadened or separated into additional peaks as shown in Fig. 5(b). This may indicate the existence of structural isomers with different coordination sites for fluoride.

Two important idealized geometries in nine-coordinated complexes are the tricapped trigonal prism, and the mono-capped square antiprism, however, these are often distorted in "real life". A tentative structure model of the bi- and tetra-nuclear complexes, indicating the relationship between them is shown in Fig. 6. It is interesting to note that the proposed structure of the tetranuclear complex is different from that found in the previously studied Th(IV)–glycolate–OH$^-$ system,[1] where $Th_4(OCH_2COO)_8(OHCH_2COO)_4(OH)_4$, has a "$Th_4(OR)_4$" core, with the oxygen donor atom from the deprotonated aliphatic OH group. The additional coordinated hydroxide ions are non-bridging and may thus be replaced by fluoride as also observed experimentally *cf.* Fig. 2. Hydroxide is released when fluoride is coordinated, and the change in $-\log[H^+]$ can therefore also be used to estimate the number of coordinated fluorides as shown in Fig. 2. The discrepancy between the two curves for the average number of coordinated F$^-$ deduced from F$^-$ and H$^+$ potentiometry is probably within the experimental uncertainty at these very high pH values. The coordination of fluoride is not due to formation of binary ThF_n^{4-n} complexes, these being too weak ($\log\beta = 7.46$ for ThF^{3+}) to exist in significant amounts under the experimental conditions used.[20] The decrease in coordination number for Th from nine to ten in the mononuclear and from nine in the binuclear complexes to eight in the tetranuclear SSA complexes may well be due to steric crowding. The same suggestion is reasonable also for the change in geometry between the tetranuclear SSA and glycolate complexes; the SSA ligand is too large to allow the formation of a "$Th_4(OR)_4$" core.
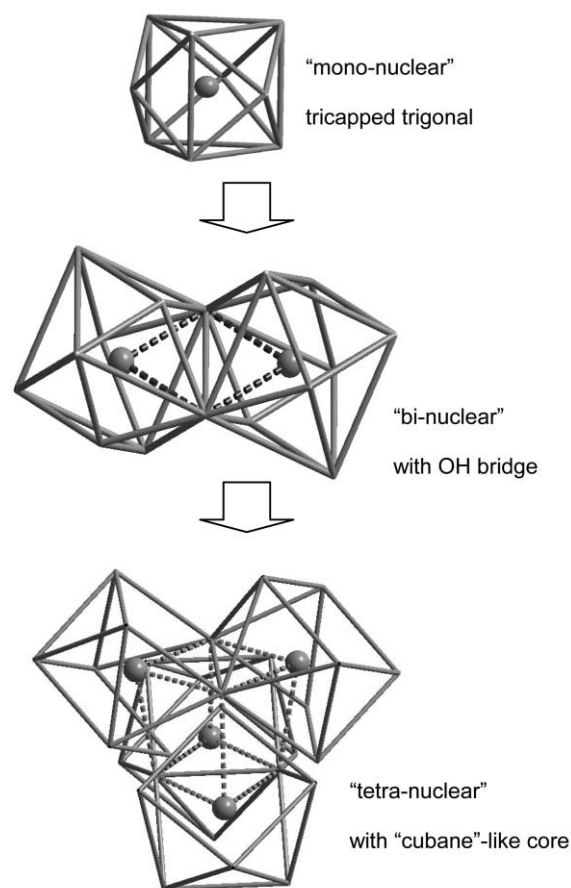
Fig. 6 Structure models for the mono-, bi- and tetra-nuclear complexes using a tricapped trigonal prism geometry for the first two, and a square antiprism geometry for the tetranuclear complex. The black coloring denotes Th and the dotted lines OH bridges.

Acknowledgements

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