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Complexation of Th(IV) and various lanthanides(III) by glycolic acid; potentiometric, ^{13}C-NMR and EXAFS studies†

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The complex formation of tetravalent thorium and various trivalent lanthanides by glycolate $HOCH_2CO_2^- \equiv A^-$, has been investigated by potentiometry, ^{13}C-NMR spectroscopy and EXAFS. The potentiometric data were used to deduce the stoichiometry and equilibrium constants for the reactions $pM^{n+}(aq) + rA^- \rightleftarrows M_pH_{-q}A_r^{np-q-r} + qH^+$ at 25 °C, in an ionic medium with a constant concentration of Na^+ equal to 3.00 M. Mononuclear complexes $Th(HOCH_2CO_2^-)_n$; $n = 1–4$, were identified in the $-\log[H^+]$ range 2.5–4.5. The equilibrium constants of these complexes obtained using a least-squares analysis of the experimental data agree well with previously published information; these test solutions also contain dinuclear ternary complexes $Th_2H_{-2}A_r$, $r = 2$, 4 and 6. The complex formation in the pH range 5–10 was studied at high and constant concentrations of glycolate, 0.50, 0.75 and 1.0 M, respectively. Under these conditions, in addition to the dinuclear species, also tetranuclear complexes $M_4H_{-q}A_8$ are formed, where q varies from 6 to 13 and 6 to 8 for the Th(IV) and Ln(III) systems, respectively. ^{13}C NMR spectra show that coordinated and free glycolate are in fast exchange at pH 4.5, while at higher pH there are two separate narrow peaks both in the CH_2 and CO_2^- regions for the coordinated ligand, indicating slow exchange between two equally populated sites. The peak integrals correspond to two bonded ligands per metal for both Th(IV) and Ln(III). EXAFS data were used to deduce bond distances within the tetranuclear Th complexes. These data together with the NMR-data indicate that the tetranuclear complexes have a cubane-like core "$M_4(OCH_2CO_2)_4$" to which additional glycolate, oxyacetate and hydroxide ligands are coordinated. The identification of new structure and bonding characteristics of α-hydroxycarboxylates, in particular at higher pH, may be used to explore new separation schemes between actinides in different oxidation states, but also for group separations between lanthanide(III) and actinide(III) ions.

Introduction

It is well known that actinide and lanthanide ions form strong complexes with glycolate ($HOCH_2CO_2^-$);[1–3] the same is true for other α-hydroxycarboxylate ligands. The chemistry of these reactions is important in nuclear waste management and separation technology, for the understanding and modeling of transport of lanthanides and actinides released from nuclear waste to ground and surface water systems. In this context one should note that α-hydroxycarboxylates occur in nature as a result of microbiological degradation of organic material. We have selected glycolate as a model ligand for this large group, that also includes humic and fulvic acids. α-Hydroxycarboxylates are used for group separations of trivalent actinides and lanthanides, or for the separation of the individual elements within each group. Complex formation with these ligands may involve the deprotonation of the α-OH group to form chelates containing both a metal carboxylate and a metal oxo-group bond. The dissociation constant of aliphatic OH-groups is much smaller ($pK = 15–17$) than that of aromatic OH-groups ($pK = 11–12$), nevertheless deprotonation of the α-OH proton has been shown to take place already at pH ~ 3 in the UO_2^{2+}–glycolate system.[4] Deprotonation is also known in complexes of multi-chelate ligands like citrate, and tartrate. Complexes with α-OH deprotonated glycolate have been characterized both in the solid state[5] and solution;[6] the high solubility of Er(III) in test-solutions containing 1 M glycolate and 1 M NaOH indicates that strong complexes are formed, presumably containing $^-OCH_2CO_2^-$ as a ligand. However, quantitative information on the stoichiometry and equilibrium constants of these complexes is scarce; an exception is a study[7] of the glycolate systems of Cm(III) and Eu(III) using time resolved fluorescence spectroscopy.

The present study is focused on the determination of the stoichiometry and stability constants in the ternary M–glycolate–hydroxide system, where M = Th(IV), Sm(III), Eu(III), Dy(III) and Lu(III), and the structure and bonding in these complexes. The complex formation reactions have been studied using standard potentiometric techniques (*vide infra*) to investigate reactions of the type

$$pM^{n+}\,(aq) + rA^- \rightleftarrows M_pH_{-q}A_r^{np-q-r} + qH^+ \qquad (1)$$

where A^- is glycolate $HOCH_2CO_2^-$. However, from experiments of this type it is not possible to decide if the species $M_pH_{-q}A_r$ (in the following charges will often be omitted) are formed by proton dissociation from coordinated water or glycolate. This information must be obtained using other methods, in the present study ^{13}C NMR spectra and EXAFS-data. The structure and bonding in the complexes and the possible differences between actinide(III) and lanthanide(III) complexes have been studied using the Cm(III) and Eu(III)–glycolate–hydroxide systems as models.[7]

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† Electronic supplementary information (ESI) available: ^{13}C-NMR spectra of the free ligand; species distribution curves; a table of the components of the samples used in the buffer titrations. See http://www.rsc.org/suppdata/dt/b2/b204717a/

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Experimental

Chemicals used

A stock solution of perchloric acid was made by diluting a 70% concentrated $HClO_4$ solution and analyzing this using NaOH. A sodium perchlorate solution was prepared from analytical grade $NaClO_4 \cdot H_2O$ (Merck p.a.) and analyzed by weighing samples dried at 393 K. The $Th(ClO_4)_4$ stock solution was prepared as follows: 0.425 mol $HClO_4$ was added to 0.1 mol $Th(NO_3)_4 \cdot H_2O$ solid; after evaporation the residue was dissolved in 250 ml triple-distilled water. The concentration of Th(IV) was analyzed by ion exchange, and the free acid concentration determined potentiometrically; the data were analyzed using a LETAGROP least-squares refinement.[8] Ln(III) perchlorate stock solutions were made as described elsewhere.[9] The metal ion and the free acid concentrations were determined by the same procedure as above, except for Eu(III), where the concentration was measured by ICP. Glycolic acid of analytical grade was used to prepare the stock solution of sodium glycolate by neutralization with NaOH and the same stock solution was used throughout the experiments.

Potentiometric studies

General procedures for the measurements. All EMF (Electro-Motive Force) measurements were made in a thermostatted box at 298 ± 0.05 K using an automatic titration system. The glass 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 the Gran-method by the titration of 3 M $NaClO_4$ against 0.1 M $HClO_4$.[10] Two different titration approaches were used as described below. In each titration equilibrium was assumed when the EMF value remained constant within 0.2 mV h^{-1} with the maximum waiting time 30 minutes in the Th(IV)–glycolate system and 0.5 mV h^{-1} with a maximum waiting time of 5 minutes in some $-\log[H^+]$ ranges for the Sm(III) and Eu(III) glycolate systems. In the latter case, we had to use a shorter waiting time in order to avoid precipitation of lanthanide tris-glycolate and hydrous oxide. The effect of longer waiting times was tested for the Dy(III) system where the solubility problems were smaller than for Sm and Eu. Except in the narrow $-\log[H^+]$ region between 9 and 10, equilibrium was reached within half an hour. The change in the EMF between 5 and 30 minutes was small, less than 0.8 mV in the whole $-\log[H^+]$ region. This had a significant effect on the data analysis only at $-\log[H^+] > 9.5$ when the total concentration of Dy(III) was larger than 10 mM. For this reason we only used the EMF data below $-\log[H^+] < 9.5$ in all Ln(III)–glycolate systems. When 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, 3 M $NaClO_4$ solution and G4 filter in order to avoid contamination by CO_2. All measurements were carried out at constant sodium ion concentration, $[Na^+] = 3.00$ M, adjusted with $NaClO_4$.

The potentiometric studies are complicated by hydrolytic reactions of the metal ions and by the formation of solid phases, hydroxides and M(glyc)$_3$ (s)/M(glyc)$_4$ (s). This means that only certain ranges in M_{tot}, A_{tot}, $-\log[H^+]$ can be studied; the subscript "tot" denotes a total concentration. These concentration ranges varied with M and the difference between thorium and the lanthanides was, as expected, large. The two different titration procedures used are outlined below.

Titrations using buffers of HA/A$^-$. This method was only used to study the thorium system; in the following HA and A$^-$ denote glycolic acid and glycolate, respectively. A summary of the experimental conditions used is given in Table S1 (ESI). The experimental method and the analysis of the data are described by Magon *et al.*[11,12] The analysis was made in two steps; first we assumed that only mononuclear complexes MA_n were formed. If this assumption is correct, the average number of coordinated ligands, $n\bar{l}$ should be a function of $[A^-]$ only, where $n\bar{l}$ and $[A^-]$ are calculated from the known analytical total concentration of M_{tot}, $A_{tot} = C_{HA} + C_A$, where C_{HA} and C_A denote total concentrations of glycolic acid and glycolate, respectively, and the measured hydrogen ion concentration $[H^+]$. We have

Table 1 The models tested in the least-squares refinement of the buffer titration for the Th–glycolate system. The data from the least-squares analysis are given as, $\log\beta_{p,-q,r} \pm 3\sigma$, where σ is the estimated standard deviation. *p*, *q*, *r* are the stoichiometric coefficients in eqn. (1)

p	*q*	*r*	$\log\beta_{pqr}$ refined	Reported value	Ref.
1	0	1	4.27 ± 0.08	4.11 ± 0.02	12
1	0	2	7.66 ± 0.07	7.44 ± 0.05	12
1	0	3	10.4 ± 0.08	10.2 ± 0.09	12
1	0	4	12.2 ± 0.09	12.0 ± 0.08	12
1	0	5	—	13.4 ± 0.11	12
2	2	2	4.48 ± 0.11	—	
2	2	4	11.0 ± 0.18	—	
2	2	6	15.7 ± 0.19	—	
2	2	0	−4.96 ± 0.43	−5.10 ± 0.17	17

$$n\bar{l} = (C_{HA} + C_A - [A^-] - [HA])/M_{tot} \quad (2)$$

$$[A^-] = K(C_{HA} - [H^+] + C_H)/[H^+] \quad (3)$$

where *K* is the dissociation constant of HA and C_H the excess concentration of perchloric acid in the test solutions. The experimental results in Fig. 1 show that $n\bar{l}$ is not only a function of $-\log[A^-]$, it also depends on M_{tot} and C_{HA}. However, the curves indicate that the predominant complexes are mononuclear and that ternary species make only minor contributions. It is in principle possible to analyze the system using graphical methods as described in ref. 13, however, in the present case the available experimental concentration ranges are limited and we therefore had to test various chemical models using least-squares methods to select the model that best describes the experimental data and previously known chemical features. The equilibrium constants are given in Table 1.

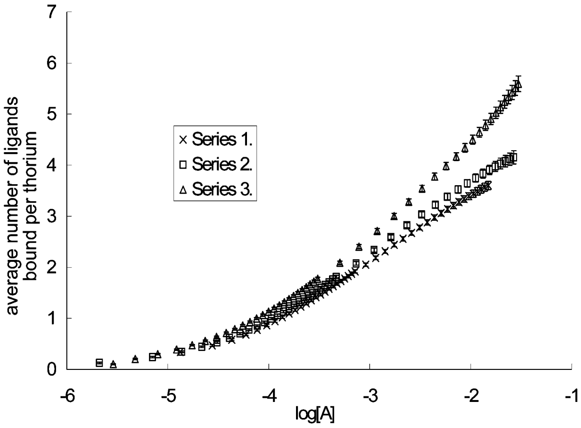

Fig. 1 The experimental data $n\bar{l}$, the average number of glycolate bound per Th(IV) plotted against $\log[A^-]$.

Titrations in test solutions with a large excess of glycolate. These experiments were made in test solutions containing an initial concentration of glycolate, C_A, equal to 0.50, 0.75 or 1.00 M and varying concentrations, M_{tot}, of the metal ions studied. To these test solutions known volumes of 0.100 M NaOH were added until a hydroxide precipitate was formed. After each addition the hydrogen ion concentration, as $-\log[H^+]$, was measured. By using a large excess of the component A, the

Table 2 The conditional equilibrium constants $\log\kappa_{p,-q} \pm 3\sigma$ for the Th–glycolate system at a total concentration of glycolate equal to 1.00 and 0.75 M, deduced from the final chemical model

		$\log\kappa_{p,-q} \pm 3\sigma$	
p	q	$[A^-] = 1$ M	$[A^-] = 0.75$ M
1	1	−5.31 ± 0.07	—
2	2	−9.03 ± 0.29	—
4	6	−26.8 ± 0.13	−25.9 ± 0.10
4	8	−39.8 ± 0.12	−38.8 ± 0.07
4	9	−46.4 ± 0.09	−45.3 ± 0.11
4	10	−54.4 ± 0.09	−52.4 ± 0.08
4	11	−63.2 ± 0.07	−60.2 ± 0.16
4	12	−73.2 ± 0.32	−69.0 ± 0.59
4	13	−84.4 ± 0.32	—

ternary system M–A^-–OH^- is effectively transformed into a two-component system M–OH^- for which conditional equilibrium constants can be determined at each total concentration of A. From the set of conditional constants the stoichiometry and the equilibrium constants of the ternary system can be deduced as outlined below.

The conditional equilibrium constants $\kappa_{p,-q}$ refer to the reactions

$$p\text{“M(aq)”} \rightleftarrows \text{“M}_p\text{H}_{-q}\text{”} + q\text{H}^+ \qquad (4)$$

where

$$[\text{“M(aq)”}] = \sum_{n=0}^{N} [\text{MA}_n] \qquad (5)$$

$$[\text{“M}_p\text{H}_{-q}\text{”}] = \sum_{r=0}^{R} [\text{M}_p\text{H}_{-q}\text{A}_r] \qquad (6)$$

N and R are the maximum value of the stoichiometric coefficients n and r. The experimental values of $\log\kappa_{p,-q}$, are reported in Table 2.

[“M”] is calculated from the known values of the equilibrium constants for the complexes MA_n and the free ligand concentration A^-; the latter is very close to the known total concentrations 0.50, 0.75 and 1.00 M, respectively. We have

$$[\text{"M"}] = [\text{M}^{n+}]\cdot\left(1 + \sum_{n=1}^{N}\beta_n[\text{A}^-]^n\right) = [\text{M}^{n+}]\cdot \text{X} \qquad (7)$$

Substituting eqn. (7) into the equilibrium expression for $\kappa_{p,-q}$ we obtain

$$\kappa_{p,-q} = \frac{[\text{"M}_p\text{H}_{-q}\text{"}][\text{H}^+]^q}{[\text{M}^{n+}]^p\cdot \text{X}^p} = K_{p,-q}/\text{X}^p \qquad (8)$$

where $K_{p,-q}$ is a new conditional equilibrium constant, with the free metal ion concentration $[M^{n+}]$ as a reactant. We also have

$$K_{p,-q} = \beta_{p,-q,0} + \beta_{p,-q,1}[\text{A}^-] + \beta_{p,-q,2}[\text{A}^-]^2\cdots\beta_{p,-q,R}[\text{A}^-]^R \qquad (9)$$

At high concentrations of A^-, we may safely assume that the stoichiometric coefficient n has attained its maximum value R. Hence eqn. (9) is

$$K_{p,-q} = \beta_{p,-q,0} + \beta_{p,-q,R}[\text{A}^-]^R \approx \beta_{p,-q,R}[\text{A}^-]^R \qquad (10)$$

where the first term refers to the binary M–OH^- complexes; this is negligible under the experimental conditions used as indicated in Table 3.

The determination of the equilibrium constants $\kappa_{p,-q}$ (see Table 4) and $K_{p,-q}$ follows the same procedure as described before.[14,15] The experimental quantities are the average number of protons lost per metal ion and the free hydrogen ion concentration

$$n_{-\text{H}} = \frac{C_{\text{OH}} - K_\text{w}/[\text{H}^+] + [\text{HA}]}{\text{M}_\text{tot}} = \frac{C_{\text{OH}} - K_\text{w}/[\text{H}^+] + [\text{H}^+]\cdot C_\text{A}/K}{\text{M}_\text{tot}} \qquad (11)$$

where C_{OH} is the total concentration of NaOH in the test solution, C_A the total concentration of ligand approximately equal to that of NaA, and K the dissociation constant of HA. The third term in the numerator represents the small (0.1%, or less) concentration of HA present in the stock solution of NaA. Experimental data of n_{-H} *vs.* $-\log[H^+]$ at different total concentrations of M are shown in Fig. 2(a)–(c), from which it is

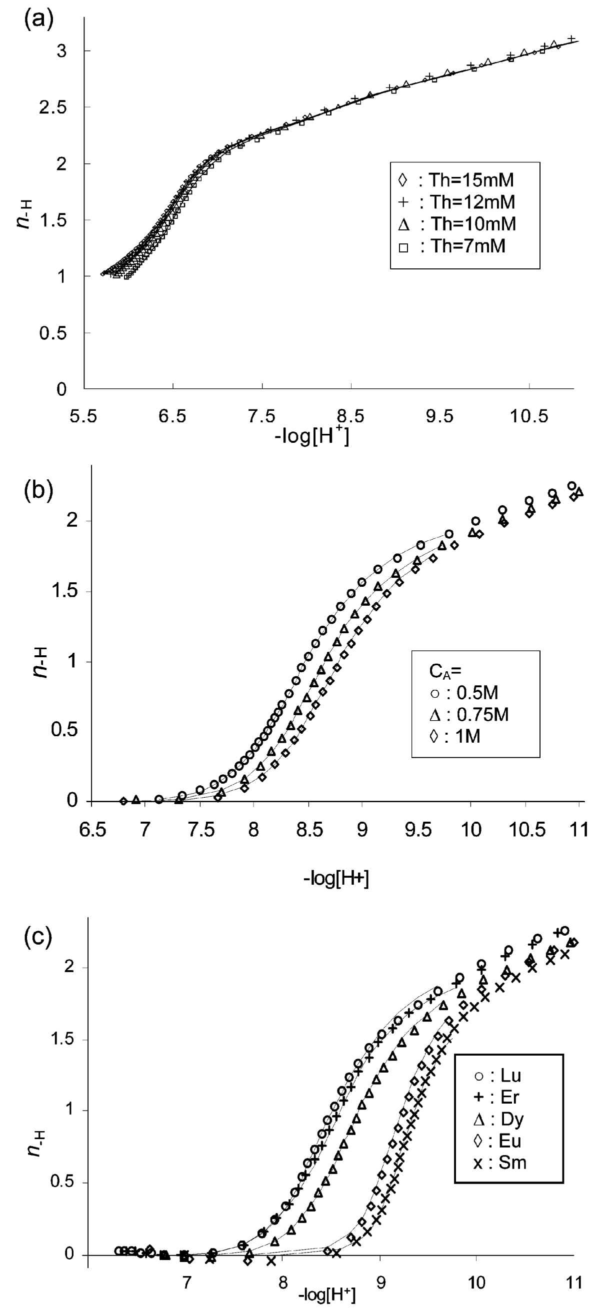

Fig. 2 The experimental data n_{-H}, the average number of consumed OH^- per metal ion, plotted against $-\log[H^+]$: (a) the Th(IV) system, (b) the Dy(III) system; the experimental conditions are given in Table S1 (ESI), and (c) the various lanthanide systems; the initial concentration of the metal was 7.5 mM in each system.

Table 3 The values of $\log K_{p,-q}$ and calculated R. $\beta_{p,-q,r}$, the equilibrium constants of the ternary complexes $Th_pH_{-q}L_r$ calculated from values of R are also shown

	$\log K_{p,-q}$ calculated			$\log\beta_{p,-q,r}$ calculated	
Stoichiometry	$[A^-] = 1$ M	$[A^-] = 0.75$ M	R calculated from $\log K_{p,-q}$	$[A^-] = 1$ M	$[A^-] = 0.75$ M
“Th_4H_{-6}”	21.6 ± 0.15	20.5 ± 0.27	8.40 ± 0.8	21.6 ± 0.15	21.5 ± 0.27
“Th_4H_{-8}”	8.63 ± 0.14	7.63 ± 0.10	8.01 ± 0.4	8.63 ± 0.14	8.63 ± 0.20
“Th_4H_{-9}”	2.03 ± 0.11	1.14 ± 0.01	7.13 ± 0.9	2.03 ± 0.11	2.14 ± 0.01
“Th_4H_{-10}”	−5.97 ± 0.11	−5.96 ± 0.08	[a]	−5.97 ± 0.11	−4.96 ± 0.08
“Th_4H_{-11}”	−14.8 ± 0.10	−13.8 ± 0.18	[a]	−14.8 ± 0.10	−12.8 ± 0.18
“Th_4H_{-12}”	−24.8 ± 0.33	−22.6 ± 0.35	[a]	−24.8 ± 0.33	−21.6 ± 0.35
“Th_4H_{-13}”	−36.0 ± 0.33	[a]	[a]	−36.0 ± 0.33	[a]

[a] No value could be calculated.

Table 4 The conditional equilibrium constants $\log\kappa_{p,-q} \pm 3\sigma$ for various lanthanide–glycolate systems at a total concentration of glycolate equal to 1.00 M, deduced from the final chemical model

Model		Sm	Eu		Dy		Er	Lu
p	*q*	$[A^-] = 1$ M	$[A^-] = 1$ M	$[A^-] = 1$ M	$[A^-] = 0.75$ M	$[A^-] = 0.5$ M	$[A^-] = 1$ M	$[A^-] = 1$ M
2	2	−16.6 ± 0.10	−16.3 ± 0.14	−14.9 ± 0.04	−14.6 ± 0.01	−14.2 ± 0.01	−14.4 ± 0.05	−14.4 ± 0.06
4	6	−49.0 ± 0.16	−48.1 ± 0.23	−44.9 ± 0.08	−44.0 ± 0.03	−42.9 ± 0.03	−43.7 ± 0.11	−43.1 ± 0.09
4	7	−58.1 ± 0.08	−57.4 ± 0.31	−54.0 ± 0.12	−53.0 ± 0.03	−51.7 ± 0.04	−52.5 ± 0.12	−52.2 ± 0.19
4	8	—	−67.1 ± 0.22	−63.7 ± 0.13	−62.8 ± 0.04	−61.2 ± 0.04	−62.2 ± 0.13	−61.4 ± 0.12

apparent that n_{-H} is a function both of $[H^+]$ and M_{tot}, *i.e.* polynuclear complexes “M_pH_{-q}” are formed. Different chemical models were tested using the least-squares program PC-LAKE[16] and the one in best agreement with the experimental data was selected.

It is difficult to determine the concentration of HA in the stock solution of NaA; an error will show up very clearly in the calculated value of n_{-H} which then does not approach zero asymptotically. For the lanthanides we could use this fact to determine the concentration of HA, because their hydrolysis is so weak that the $-\log[H^+]$ ranges where HA and hydrolysis complexes co-exist do not overlap. The situation is different for Th(IV) which is much more extensively hydrolyzed, here the two concentration ranges overlap strongly and the effect of hydrolysis is very significant, this means that also the equilibrium constants for the binary Th–OH^- complexes can be determined from the experimental data in the ternary systems. We have used prior information on the thorium hydrolysis[17] as a guide when testing different chemical models and selecting the one in best agreement with the experimental data and other chemical information.

At high pH the n_{-H} *vs.* $-\log[H^+]$ curves for different values of M_{tot} coincide, indicating that a series of homonuclear complexes are formed

$$n_{-H} = \frac{\sum_{1}^{P}\sum_{1}^{Q} q["M_pH_{-q}"]}{\sum_{1}^{P}\sum_{0}^{Q} p["M_pH_{-q}"]} = \frac{\sum_{1}^{P}\sum_{1}^{Q} q\cdot\kappa_{p,-q}\frac{["M"]^p}{[H^+]^q}}{\sum_{1}^{P}\sum_{0}^{Q} p\cdot\kappa_{p,-q}\frac{["M"]^p}{[H^+]^q}} = \frac{\sum_{1}^{Q} q\kappa_{p,-q}[H^+]^{-q}}{p\sum_{1}^{Q}\kappa_{p,-q}[H^+]^{-q}} \tag{12}$$

The experimental data for thorium are more precise than those for the lanthanides, *cf.* Fig. 2, however, both indicate that a tetranuclear complex “M_4H_{-q}” is predominant over a large pH range.

^{13}C-NMR spectroscopy

The NMR spectra provide information on the amount of coordinated ligand, its mode of bonding and rate of exchange. The ^{13}C-NMR spectra were recorded on a Bruker DMX500 spectrometer on a triple channel (^{1}H, ^{13}C, ^{15}N) 10 mm probe head at 275 K, in general using 10% D_2O solutions to get the locked mode. The test solutions were measured in 10 mm tubes for both the Th(IV) and Lu(III) systems. The latter was used as the model system for other Ln(III)–glycolate system for which the application of ^{13}C-NMR spectroscopy was not straightforward. Inverse gated proton decoupling was used to avoid Nuclear Overhauser effects with a relaxation delay of 10 s to obtain quantitative spectra. The ratio of coordinated and free glycolate was obtained from the integrals of the carbonyl peaks. The total metal concentration in the samples was 50 mM for Th(IV) and 77 mM for Lu(III) at $[A^-] = 1.0$ M. Their proton concentration was measured using a pH meter (Orion). The spectra were measured in the $-\log[H^+]$ range 4.5–9.5 for the Th(IV) system, *cf.* Fig. 3, and at $-\log[H^+] = 9.0$ for Lu(III), *cf.* Fig. S1 (ESI).

EXAFS measurements

EXAFS spectra were measured only for the Th–glycolate system. The concentration of $Th(ClO_4)_4$ was 50 mM in 1 M sodium glycolate and the ionic medium had a constant concentration of $Na^+ = 3$ M. The pH of the sample was adjusted to 10.8 with NaOH in order to avoid precipitation during the time between preparation and measurement. The EXAFS data were recorded at the Rossendorf Beamline (ROBL) at the ESRF in Grenoble. The transmission spectrum was measured at room temperature using a water-cooled Si(111) double-crystal monochromator of fixed-exit type ($E = 5$–35 keV). Higher harmonics were rejected using two Si and Pt coated mirrors. For energy calibration of the sample spectra, the spectrum from a Pb foil was recorded simultaneously. The ionization energy of the Th L_{III} electron, E_0, was arbitrarily defined as 16315 eV. The data were treated using the EXAFSPAK software.[18] Theoretical backscattering phase and amplitude functions, d(k) and F(k), used in data analysis were calculated using the FEFF6 program. The EXAFS oscillations were isolated using standard procedures for pre-edge subtraction, spline removal, and data normalization. The signal-to-noise ratio in the spectra is fairly large due to lack of beam-time and therefore only the main structure features could be explored. New experiments are planned and these will be extended also to the lower pH region. The EXAFS spectrum and its Fourier transform are shown in Fig. 4 and the bond distances and the number of them in the legend. We made an attempt to analyse the contribution of

Table 5 The refined parameters used for the theoretical curve shown in Fig. 4 using $S_0^2 = 1.00$

Shell	N	R/Å	σ^2/Å^2	ΔE_0/eV
Th–O$_1$	3.2	2.32	0.0084	−15.4
Th–O$_2$	6.3	2.43	0.0069	
Th–C	1.3	3.36	0.0025	
Th–Th	0.9	3.97	0.00345	

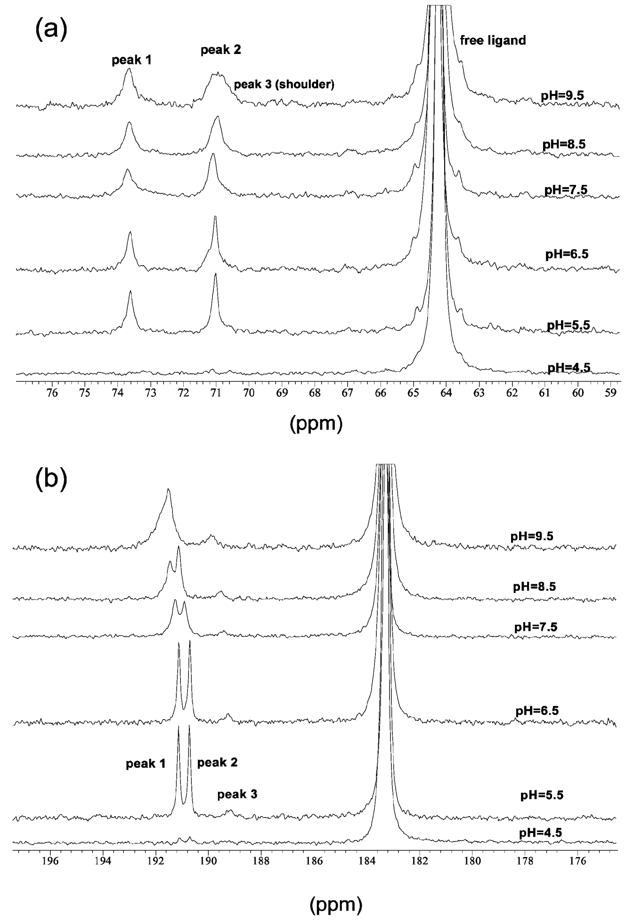

Fig. 3 ^{13}C-NMR spectra of the Th–glycolate system at different −log[H$^+$]: (a) for CH$_2$, (b) for carbonyl carbon. The total concentrations of Th and glycolate were 50.0 mM and 1.00 M, respectively. The spectra were measured at 275 K.

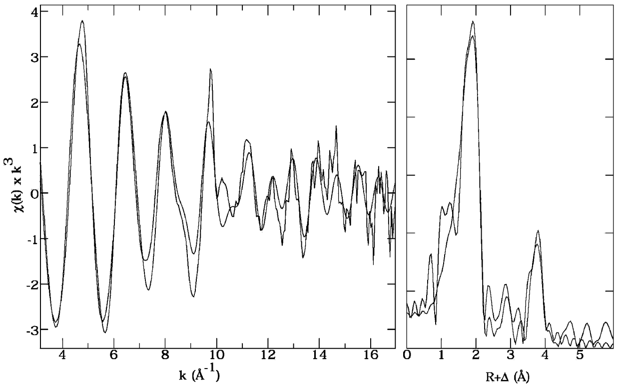

Fig. 4 EXAFS spectra obtained at pH = 10.5. The black and gray lines shown in the figure are the experimental spectra and theoretical fit, respectively. The theoretical curve has been calculated for the FT-range 3.14–17 Å^{-1} using the refined parameters in Table 5.

multiple scattering pathways by using only the "Th$_4$O$_4$" core, but this results in a much poorer fit; a more detailed structure models is necessary before MS pathways can be included.

Results and discussion

The mononuclear complexes ThA$_n$; n = 1–4 are predominant in the buffer titrations allowing a precise determination of the equilibrium constants given in Table 1; they are also in fair agreement with those of an earlier study by Magon *et al.*[11,12] where a smaller range of M$_{tot}$ and H$_{tot}$ was explored. The binary hydrolysis species Th$_2$(OH)$_2^{6+}$ is present in significant concentration in the test solutions and its equilibrium constant log$\beta_{2,-2}$ = −4.96 ± 0.43 could therefore be determined. This is consistent with that from a previous study, log$\beta_{2,-2}$ = −5.10 ± 0.17, providing a check on the consistency of the chemical model used. The uncertainty in the equilibrium constants is always given at the 3σ level. Magon *et al.* did not include hydroxide complexes when interpreting their data, which may explain some of the differences between our study and theirs. We expect glycolate to be coordinated to the Th$_2$H$_{-2}$-core and have therefore tested models comprising ternary dinuclear complexes Th$_2$H$_{-2}$A$_r$, where only complexes with r = 2, 4 and 6 occurred in significant amounts in the investigated test solutions, *cf.* Fig. S2 (ESI).

Additional and more precise information on the stoichiometry of the ternary complexes were obtained from the titrations at high total concentrations of glycolate. The conditional equilibrium constants $\kappa_{p,-q}$ for the Th(IV) system are given in Table 2; the predominant species are tetranuclear at −log[H$^+$] > 6. At lower −log[H$^+$], one mononuclear and one dinuclear complex is formed, "ThH$_{-1}$" and "Th$_2$H$_{-2}$", respectively. The equilibrium constants $K_{p,-q}$ and $\beta_{p,q,r}$ and the value of R from eqn. (10) are all given in Table 3. For the Th-system we could only determine R (8 ± 1) for the tetranuclear complex. This estimate is based on the assumption that the activity coefficients of reactants and products are constant in all test solutions even when the total concentration of glycolate is varied. This rather crude approximation results in an estimated error of ±1 in the stoichiometric coefficient R.

In the corresponding lanthanide systems we used Dy as a model because the experimental problems indicated previously were less severe here than for the other lanthanides studied. We assumed that the stoichiometry of the Dy-complexes were representative of all lanthanides in view of the well-known chemical similarity between the elements in this group. The different equilibrium constants are given in Tables 4, 6 and 7 and also in this case we found R = 8 ± 1 for the tetranuclear complexes, while R was 5.4 ± 0.4 ≈ 6 for the dinuclear complex.

As indicated above, it is not straightforward to determine the number of coordinated A-ligands, the same is true when deciding if the proton dissociation takes place from coordinated water or A$^-$. The potentiometric data alone are not sufficient, however by using the ^{13}C-NMR data the desired information can be extracted. The spectra and the distribution diagrams for the NMR test solutions (C_{Th} = 50 mM, C_{Lu} = 77 mM and [A$^-$] = 1 M) drawn using the MEDUSA program[19] are shown in Figs. 3 and 5 and S1 and S3 (ESI). For the Th(IV) glycolate system at log[H$^+$] = 4.5, we could not identify separate peaks for the complex and the free ligand, there was one single peak in the CH$_2$ and the carbonyl carbon regions. This indicates a rapid exchange between free and coordinated glycolate in this test solution where "Th" = ThA$_4$(aq), "ThH$_{-1}$" = ThA$_4$(OH)$^-$ are predominating, and with "Th$_2$H$_{-2}$" as a minor component. Szabó and Grenthe[4] reported the same kind of fast exchange between the free ligand and the carboxylate-coordinated ligand in the U(VI)–glycolate system. At −log[H$^+$] = 5.5 and 6.5, where the tetranuclear complexes "Th$_4$H$_{-6}$" and "Th$_4$H$_{-8}$" predominate, we observe two separate narrow peaks with a ratio of approximately 1 : 1, both from the CH$_2$ and CO$_2^-$ groups from coordinated glycolate, *cf.* Fig. 3(a) and (b), indicating two non-equivalent coordinated ligands in the tetranuclear complex that are in slow exchange with one another and with free glycolate. In the Lu(III)–glycolate system (Fig. S1) we also observed two separate peaks in the ratio 1.2 : 1. The large change in chemical

Table 6 $\log K_{p,-q}$ values and corresponding R values calculated from the "conditional" equilibrium constants $\kappa_{p,-q}$ in the Dy(III) system

	Calculated $\log K_{p,-q}$			Calculated R	
Stoichiometry	$[A^-] = 1$ M	$[A^-] = 0.75$ M	$[A^-] = 0.5$ M	$[A^-] = 1$ and 0.5 M	$[A^-] = 1$ and 0.75 M
Dy_2H_{-2}	−0.01 ± 0.04	−0.67 ± 0.03	−1.61 ± 0.03	5.4 ± 0.2	5.4 ± 0.4
Dy_4H_{-6}	−15.1 ± 0.10	−16.2 ± 0.06	−17.7 ± 0.06	8.7 ± 0.4	8.6 ± 0.9
Dy_4H_{-7}	−24.2 ± 0.13	−25.2 ± 0.06	−26.5 ± 0.07	7.5 ± 0.5	7.6 ± 1.2
Dy_4H_{-8}	−34.0 ± 0.14	−34.9 ± 0.06	−35.9 ± 0.07	6.5 ± 0.5	7.4 ± 1.2

Table 7 Equilibrium constants for lanthanide(III)–glycolate systems at $[Na^+] = 3$ M. The accuracy of the $\log \beta_{p,-q,R}$ values is ± 0.15, ± 0.2, ± 0.2 and ± 0.4, for $\log\beta_{2,-2,6}$, $\log\beta_{4,-6,8}$, $\log\beta_{4,-7,8}$, and $\log\beta_{4,-8,8}$, respectively, estimated as written in the text

		$\log\beta_{p,-q,R}$			
M^{3+}		$M_2H_{-2}A_6$	$M_4H_{-6}A_8$	$M_4H_{-7}A_8$	$M_4H_{-8}A_8$
	Sm	−1.83	−19.5	−28.5	[a]
	Eu	−0.34	−16.1	−25.4	−35.1
Dy	$[A^-] = 0.5$ M	0.20	−15.3	−24.1	−33.5
	$[A^-] = 0.75$ M	0.08	−15.2	−24.2	−33.9
	$[A^-] = 1.0$ M	0.01	−15.1	−24.2	−34.0
	Er	0.53	−13.8	−22.6	−32.3
	Lu	1.20	−12.0	−21.0	−30.2

[a] The model could not be introduced.

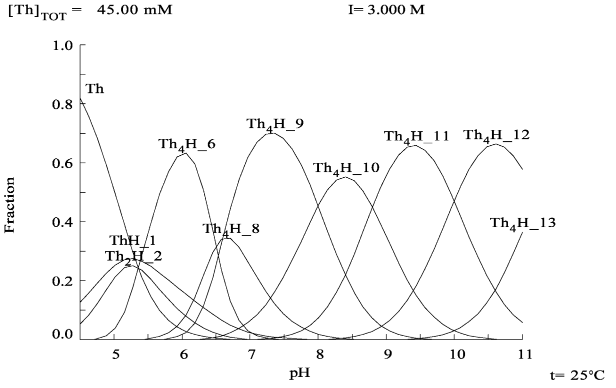

Fig. 5 Distribution diagram for the Th–glycolate system calculated using the equilibrium constants given in Table 3.

shift and the slow rate of exchange between free and coordinated ligand is a strong indication of a change in its mode of bonding, presumably through deprotonation of the α-OH group. We could determine the number of coordinated $^-OCH_2CO_2^-$ ligands per metal ion from the concentrations of the different "M_pH_{-q}" species obtained from the potentiometric data and that of coordinated $^-OCH_2CO_2^-$ obtained from the sum of integrals of the $^{13}CO_2^-$ peaks from the complexes, these data are given in Table 8. The fast rate of exchange between free and coordinated ligand at $-\log[H^+] = 4.5$ indicates that the complex "ThH_{-1}" does not contain coordinated $^-OCH_2CO_2^-$, and that the deprotonation takes place from a coordinated water. Note that "EuH_{-1}" and "CmH_{-1}" studied by Stumpf *et al.*[7] show the same characteristics.

Three models indicated in Table 8 were tested, the deviation between the experimental values of the concentration of coordinated $^-OCH_2CO_2^-$ and that calculated from the different models (Table 8) is larger than the estimated experimental errors in the integration and the error in the individual concentrations of the different "Th_pH_{-q}" species. The error is strongly affected by the uncertainty of the concentration of "Th_4H_{-6}" because this is very sensitive to the pH as indicated by the distribution diagram (Fig. 5). Model 2 is in fair agreement with the experimental data but the experimental value indicates only seven oxyacetate ligands per tetranuclear complex, where we expected eight from our model. We do not know if this is due to experimental errors that we have not detected, or that there are 0.7 non-bridging oxyacetates and 0.3 OH^- outside the tetranuclear core.The small peak [peak 3, in Fig. 3(b)] at 189 ppm may belong to a complex that could not be identified by potentiometry due to its small concentration.

The analysis so far shows that both the di- and tetra-nuclear complexes contain between two and eight coordinated $^-OCH_2CO_2^-$ ligands. In addition these complexes contain coordinated $HOCH_2CO_2^-$ as indicated by the value of R in Table 3. The experimental results also indicate that the ternary complexes formed by Th and Ln(III) have the same constitution, except at pH > 8.5 where Th contains additional OH-groups, no doubt a result of its stronger hydrolytic reactions. However, the higher charge of Th also results in the formation of much stronger complexes than for the trivalent lanthanides.

Structure and bonding

The EXAFS data show the presence of a single Th–Th distance at 3.97 Å, and two Th–O distances at 2.32 and 2.43 Å respectively. There are approximately three of the shorter Th–O distances and six of the longer. There is a third shell at 3.36 Å, presumably a Th–C distance. All these distances are close to those found in the solid compounds $M_2(OCH_2CO_2)_2(HOCH_2CO_2)_2{\cdot}4H_2O$, M = Dy, Er, that contain bridging oxoacetate ligands.[5,20] There are only 1.3 carbons per Th, lower than the expected two or three. The reason for this discrepancy is mainly due to the small contribution of this shell to the EXAFS scattering. These facts indicate that the "M_4H_{-q}" has a cubane-like structure with a "$Th_4(OCH_2CO_2)_4$" core similar to the "$Ln_4(OH)_4$" unit found in several lanthanide complexes,[21–23] and the $Yb_4(OR)_4$-core found in a Yb(III)–alkoxide–phosphide complex with triple bridging alkoxide groups.[24] Thorium seems to have the normal eight to nine coordination found in other complexes. Only tetranuclear complexes "Th_4H_{-11}" and "Th_4H_{-12}" are predominant in the EXAFS test solution, where NMR-data indicate that there are still about two coordinated oxoacetate groups per thorium. From the stoichiometry both structures containing "$Th_4(OH)_4$" and "$Th_4(OCH_2CO_2)_4$" cores are possible. However, we can rule out the structure with a "$M_4(OH)_4$"-core, in the pH range 5.5–8, where the predominant

Table 8 Concentrations (in mM) of the different complexes in the NMR test solutions for the Th–glycolate system, A and Y stand for glycolate with non-deprotonated and deprotonated OH-groups, $HOCH_2CO_2^-$ and $^-OCH_2CO_2^-$, respectively

				Concentration of the different species/mM				
	Stoichiometric models			Th				Lu
(M_pH_{-q})	Model 1	Model 2	Model 3	pH = 5.5	pH = 6.5	pH = 7.5	pH = 8.5	pH = 9.5
"M"	MA_4(aq)	MA_4(aq)	MA_4(aq)	3.20				
"MH_{-1}"	$M(OH)A_4^-$	$M(OH)A_4^-$	$M(OH)A_4^-$	4.96	0.95	0.06		
"M_2H_{-2}"	$M_2(OH)_2A_6$	$M_2Y_2A_4$	$M_2Y_2A_4$	4.20	0.25			
"M_4H_{-6}"	$M_4Y_6A_2$	$M_4Y_6A_2$	$M_4Y_6A_2$	7.03	3.86			7.35
"M_4H_{-7}"	M_4Y_7A	M_4Y_7A	M_4Y_7A					7.27
"M_4H_{-8}"	M_4Y_8	M_4Y_8	M_4Y_8	0.07	3.86	0.97	0.02	4.62
"M_4H_{-9}"		$M_4Y_8A(OH)$	M_4Y_9		3.06	7.70	1.94	
"M_4H_{-10}"		$M_4Y_8A_2(OH)_2$	M_4Y_{10}		0.10	2.43	6.12	
"M_4H_{-11}"		$M_4Y_8A_3(OH)_3$	M_4Y_{11}			0.12	3.06	
"M_4H_{-12}"			M_4Y_{12}				0.10	
Concentration of deprotonated glycolate "$^-OCH_2CO_2^-$"/mM		From NMR spectra		$58._6 \pm 4$	$74._3 \pm 5$	$74._3 \pm 5$	$77._4 \pm 5$	$127._7 \pm 9$
		Calculated from model 1		$42._7 \pm 4$				
		Calculated from model 2		$51._1 \pm 3$	79.8	89.8	90	132.1
		Calculated from model 3		$51._1 \pm 3$	83.1	100.5	113.7	

tetranuclear species are "Th_4H_{-q}", q = 6–10. The NMR data show that all these species contain between six and eight coordinated oxoacetates (corresponding to the release of six to eight protons), hence there are not enough coordinated hydroxide to form a "$M_4(OH)_4$"-core. The EXAFS data are also consistent with a structure that contains bridging oxoacetate ligands. The same type of bridges may also be present in the dinuclear complexes as indicated by the lanthanide structures mentioned above.[5,20]

At pH = 8.5–9.5, where more than two protons per Th are released, the NMR spectra still contain two separate peaks with a ratio of 1 : 1 for CH_2 while the CO_2^- peaks coalesce. The line broadening indicates a faster rate of exchange between the different ligand sites. In this pH region the tetranuclear complexes "Th_4H_{-n}" n = 8–12 still contain eight $^-OCH_2CO_2^-$, however, there are additional protons released from coordinated water. This could result in a change of the bridge structure, but we do not have sufficient information to corroborate such a change.

Comparison with TRLFS data

These data are described by Stumpf *et al.*;[7] they identified three different Cm(III) complexes, $Cm(HOCH_2CO_2)_4$; $\log\beta_{1,0,4} = 6.7$, $Cm(HOCH_2CO_2^-)_4(OH)$; $\log\beta_{1,-1,4} = -1.9$ and $Cm(OH)(HOCH_2CO_2^-)_3(OCH_2CO_2^{2-})$; $\log\beta_{1,-2,4} = -12.1$. In the corresponding Eu(III) system only the first and third complexes were identified. The equilibrium constant for the reaction

$$Cm(HOCH_2CO_2)_4H_2O \rightleftarrows Cm(OH)(HOCH_2CO_2^-)_4 + H^+; \log K_1 = -8.6 \quad (13)$$

is much smaller than that of the corresponding Th(IV) system, $\log K = -5.31$, which is in agreement with the much stronger hydrolytic reactions of Th(IV). Stumpf *et al.*[7] also reported that the attainment of equilibrium for the reaction

$$Cm(OH)(HOCH_2CO_2^-)_3(^-OCH_2CO_2^-) + 2H^+ \rightleftarrows Cm(HOCH_2CO_2^-)_4 \quad (14)$$

from high pH to low, takes more than one day. In the corresponding Eu system equilibrium is attained much faster, both at trace concentrations and at a total concentration of Eu of 1 mM. The difference between Eu and Cm is a chemical characteristic and not dependent on different total concentrations of the two metal ions. This difference can presumably be exploited for group separation of trivalent actinides and lanthanides. If the pH of a solution at high pH containing a mixture of actinides and lanthanides is decreased rapidly, the actinides will retain their high-pH speciation during several minutes up to hours, while the lanthanides quickly transforms to the low-pH speciation. The chemistry of the two groups is thus distinctly different for a sufficiently long time to achieve a separation. In the Th-system equilibrium in all test solutions was reached within 30 minutes, much faster than in the Cm system. We suggested that this difference is in part due to the different stoichiometry of the complexes, in part on the difference in total concentration of the reactants. The protonation of coordinated oxoacetete in U(VI) complexes has been investigated by Szabó and Grenthe.[4] The protonation is a reaction of second order and therefore dependent on the concentration of the complex and this differs by more than four orders of magnitude between the Cm(III) and Th(IV) complexes; the former are therefore expected to equilibrate much slower than the latter. The different behavior of tri- and tetra-valent actinides is illustrated in Figs. 2(a)–(c). From the information of the equilibrium constants one can optimize the chemical conditions to obtain the best separation both between actinides and lanthanides and the individual elements within each group.

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