

Lanthanide(III) complexation by the ligand 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol: an unusual thermodynamic behaviour across the rare-earth series

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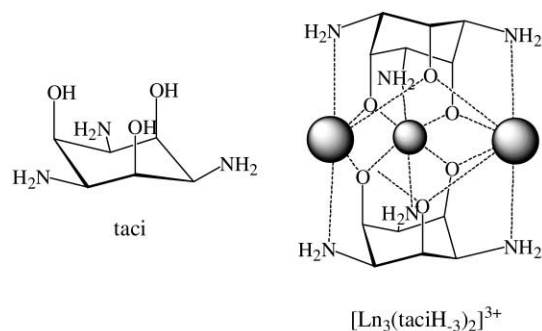
1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol (taci) gives trinuclear sandwich-type complexes of trivalent lanthanide cations $[\text{Ln}_3(\text{taciH}_{-3})_2]^{3+}$ in aqueous solution, whose stability constants experience a very great increase across the rare-earth series. To have a better insight into factors controlling lanthanide recognition, the enthalpy changes of the complexation reaction were measured by microcalorimetry. This thermodynamic analysis demonstrates that the discrimination is mainly due to enthalpic effects; the entropic contribution shows little variation. The X-ray structure of the lutetium complex $[\text{Lu}_3(\text{taciH}_{-3})_2(\text{H}_2\text{O})_6](\text{SO}_4)_{1.5}$ is also presented and gives crucial structural information for the smallest lanthanide cations.

Introduction

Trivalent lanthanide coordination chemistry has received a growing interest in the few past decades, because of the characteristic magnetic and photophysical properties of their compounds.¹ For example, a lot of work has been done to understand the coordination properties of N,O ligands like polyaminocarboxylates for trivalent lanthanide cations.^{2–5} Some interesting results on phenolato group as an anionic O-donor have also been reported.⁶

1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol, taci, is a rigid polyamino-polyalcohol ligand offering several coordination modes for metal binding, depending on the size and the hard/soft character of the cation.^{7,8} In the course of our investigations of lanthanide(III) complexes of sugars^{9–12} and cyclohexane-based ligands,^{13–16} this molecule has attracted our attention because it gives some original trinuclear lanthanoid complexes with an unusual sandwich-type structure (see Scheme 1).¹⁷ In these complexes, each of the three metal cations binds to an amino group and two alkoxo groups of each of the two deprotonated ligands. The coordination sphere is completed by peripheral ligands such as H_2O or counter ions. Recently in our laboratory, an extensive study of lanthanide(III)

complexes of taci has shown that $[\text{Ln}_3(\text{taciH}_{-3})_2]^{3+}$ was the only metallic complex present in solution across the entire 4f series, and that the stability constants for complex formation were extremely dependent on the radius of the cation, as evidenced in Fig. 1.¹⁸ The global increase in the affinity constants from lanthanum(III) to lutetium(III) is classical and reflects the well-known electrostatic trend,^{19,20} but the high discrimination that taci displays between heavy and light lanthanides is very uncommon. To get a better insight into factors controlling lanthanide discrimination by taci we decided to measure the thermodynamic parameters of the complexation reaction by microcalorimetry, since the evolution of the complex formation constants is the combination of enthalpic and entropic effects.



Scheme 1

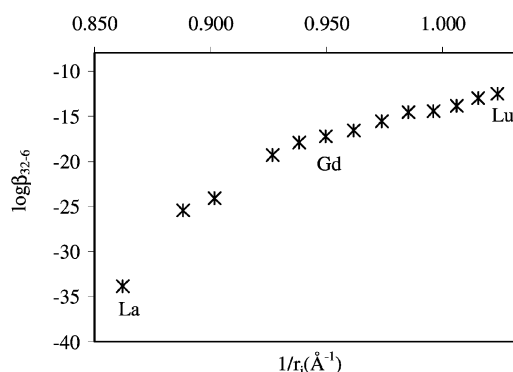


Fig. 1 $[\text{Ln}_3(\text{taciH}_{-3})_2]^{3+}$ complex formation constants ($\log \beta_{32-6}$) in aqueous 0.1 mol L^{-1} KCl at 298 K.

In this contribution, we report the Gibbs energy, enthalpy and entropy changes of the complexation reaction of trivalent lanthanide cations by 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol in water at a constant ionic strength of 0.1 mol L^{-1} and 298.15 K. Furthermore, X-ray diffraction studies of the lutetium(III) complex are presented and its molecular structure is compared

Table 1 Thermodynamic functions for reaction (1) at 298 K in aqueous 0.1 mol L⁻¹ KCl

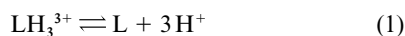
	tach ^a	taci
$\Delta_r G^\circ/\text{kJ mol}^{-1}$	148	127 ^b
$\Delta_r H^\circ/\text{kJ mol}^{-1}$	146.7	126(2)
$\Delta_r S^\circ/\text{J mol}^{-1} \text{K}^{-1}$	-4	-3(6)

^a Calculated from values reported in ref. 21. ^b Calculated from the log *K* values reported in ref. 18.

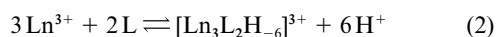
to those of the lighter lanthanide complexes of taci. The progress of the thermodynamic parameters across the rare-earth series will be discussed in terms of electrostatic interactions that are strongly altered by the cation coordination sphere contraction evidenced in the X-ray structures from lanthanum to lutetium.

Results

The total dissociation enthalpy of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol trihydrochloride (taci(HCl)₃) corresponding to reaction (1) was first measured by microcalorimetry, by titration with sodium hydroxide. The results for the proton dissociation of the three ammonium functions are given in Table 1. These values are similar to those measured for 1,3,5-triaminocyclohexane (tach), existing as the triequatorial form in water solution.²¹ This observation is consistent with the expected conformation of taci in solution, *i.e.* the conformation in which hydroxy groups are in the axial position and amino groups are in the equatorial position.



The formation constants of lanthanide complexes of taci (reaction (2)) have already been determined by means of pH-titrations.¹⁸ The enthalpy changes associated with this reaction have been measured by microcalorimetry for seven representative cations of the rare-earth series in water at a constant ionic strength of 0.1 mol L⁻¹ KCl and 298.15 K. The corresponding values of $\Delta_r S^\circ$ have been deduced using the values of $\Delta_r G^\circ$ and $\Delta_r H^\circ$. The thermodynamic measurements are summarized in Table 2.



X-Ray diffraction studies of the lanthanum and the gadolinium complexes have been published by Hegetschweiler and coworkers.¹⁷ So as to evaluate the evolution of the complex structure across the entire lanthanide series, we have determined the X-ray structure of the lutetium complex of taci. The structure of the discrete $[\text{Ln}_3(\text{taciH}_{-3})_2(\text{H}_2\text{O})_6]^{3+}$ cations are virtually identical for Gd and Lu (Fig. 2). In the trinuclear species, the three metal centres form an approximately equilateral triangle, which is encapsulated by the two deprotonated taci ligands. As for the gadolinium complex, two water molecules complete the coordination sphere of each lutetium cation. Selected interatomic distances are given in Table 3.

Table 2 Thermodynamic functions for lanthanide complexation by taci according to reaction (2) at 298 K in 0.1 mol L⁻¹ KCl. $\beta_{32-6} = [[\text{Ln}_3\text{L}_2\text{H}_6]^{3+}][\text{H}^+]^6/[\text{Ln}^{3+}]^3[\text{L}]^2$

Ln	log β_{32-6}	$\Delta_r G^\circ/\text{kJ mol}^{-1}$	$\Delta_r H^\circ/\text{kJ mol}^{-1}$	$\Delta_r S^\circ/\text{J mol}^{-1} \text{K}^{-1}$
La	-33.83	193	291(8)	329(25)
Pr	-25.45	145	267(8)	409(25)
Sm	-19.29	110	233(8)	413(25)
Gd	-17.25	98	219(8)	405(25)
Dy	-15.54	89	211(8)	411(25)
Er	-14.43	82	215(8)	445(25)
Lu	-12.5	71	203(8)	442(25)

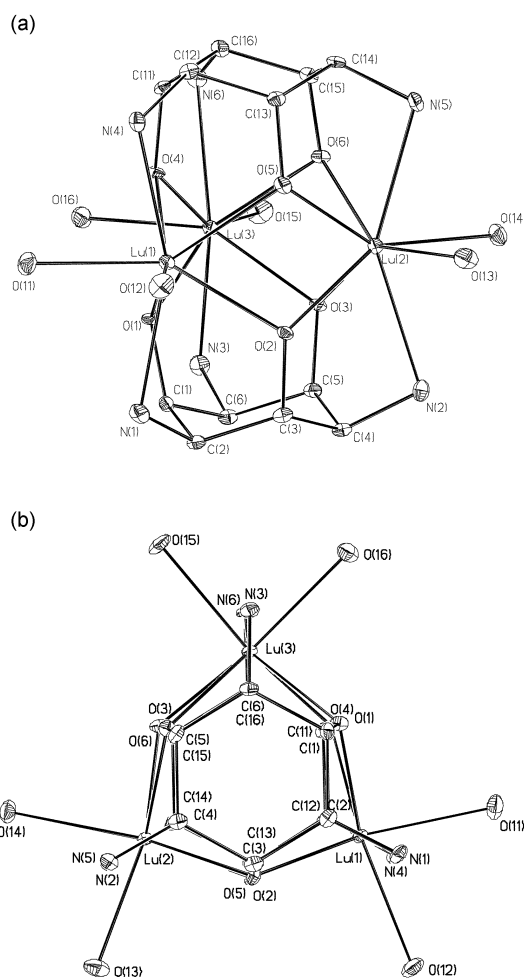


Fig. 2 ORTEP drawing of $[\text{Lu}_3(\text{taciH}_{-3})_2(\text{H}_2\text{O})_6]^{3+}$ with labelling schemes. Thermal ellipsoids for non-hydrogen atoms are drawn at the 30% probability level.

Discussion

The large increase in the stability constants of the lanthanide complexes of taci across the rare-earth series is very uncommon (see Fig. 1). The examination of these constants shows a good discrimination among the light lanthanides (La to Gd) whereas the affinity constants have a lower evolution for the heavier lanthanides (Gd to Lu). To compare taci to other well-known ligands, we have examined the residual free metal concentration in solution, because the comparison of stability constants of complexes having different stoichiometries is meaningless. The analysis of the $\text{pM} = -\log[\text{M}^{3+}]$ values across the entire series confirms the break at Gd in the discrimination capability of taci. The differences in pM values for two successive lanthanide cations from La to Gd, are higher for taci than for edta, which is one of the ligands exhibiting a consistent trend across the entire lanthanide series,^{22,23} and after Gd these differences decrease a lot. As an illustration, Fig. 3 represents the evolution of pM for selected cations (La, Gd and Lu) for lanthanide

Table 3 Selected bond lengths (Å) and angles^a (°) of [Lu₃(taciH₋₃)₂(H₂O)₆](SO₄)_{1.5}(H₂O)₈ with estimated standard deviations

	Range	Mean
Lu...Lu	3.6008(5)–3.6139(5)	3.607
Lu–O(taci)	2.219(5)–2.325(5)	2.27
Lu–OH ₂	2.309(6)–2.379(6)	2.34
Lu–N	2.482(7)–2.528(6)	2.51
Lu...Lu...Lu	59.829(9)–60.188(9)	60.0
N–Lu–O	67.3(2)–69.7(2)	68.6
N–Lu–O'	131.1(2)–133.4(2)	132.1
N–Lu–N'	146.4(2)–148.4(2)	147.6
N–Lu–OH ₂	75.4(2)–80.3(2)	77.9
O–Lu–O	78.2(2)–82.0(2)	79.6
O–Lu–O' (<i>cis</i>)	65.0(2)–65.8(2)	65.3
O–Lu–O' (<i>trans</i>)	110.4(2)–115.8(2)	113.7
O–Lu–OH ₂ (<i>cis</i>)	85.7(2)–91.8(2)	89.6
O–Lu–OH ₂ (<i>trans</i>)	143.4(2)–149.1(2)	146.3
H ₂ O–Lu–OH ₂	80.3(2)–85.0(2)	82.0
Lu–O–Lu	102.9(2)–107.8(2)	105.0

^a Intraligand angles are indicated as X–Lu–Y, interligand angles as X–Lu–Y' (X, Y = O, N).

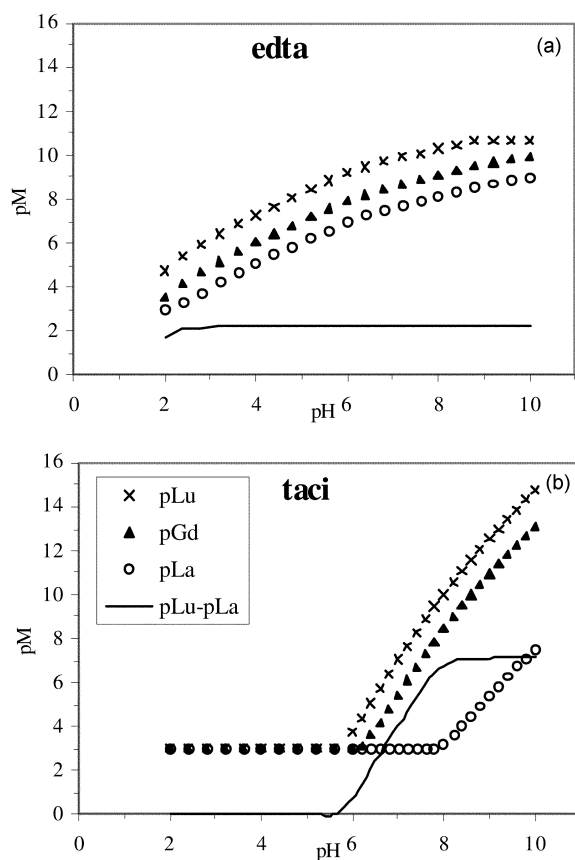


Fig. 3 $pM = -\log[M^{3+}]$ calculated in aqueous KCl 0.1 mol L⁻¹ at 298 K with $[L]_0 = 1 \text{ mmol L}^{-1}$ and $[M]_0 = 1 \text{ mmol L}^{-1}$ for edta (a) and taci (b). The stability constants given in refs. 18 and 23 were used for calculations.

complexation by taci (b) and edta (a). The discrimination of lanthanides by taci is clearly evidenced by the different pH forming of the complexes (La: ~8, Lu: ~5.5). Taci complexes are of course formed at a higher pH than those of edta because of ligand alcohol deprotonation, but once they are formed ($pH > 8$), the difference in pM ($pLu-pLa$) is much greater for taci than for edta.

The complexation of a trivalent lanthanide cation Ln^{III} with a ligand in water has been described as two successive steps.^{1,19,24} The first one corresponds to the dehydration of the cation and the ligand and the second one to the reaction or

combination between the desolvated species. In the case studied here, a third term contributes to the calculated thermodynamic properties referring to reaction (2): the alcohol functions of the ligand (taci) are indeed deprotonated upon complexation. Under the experimental conditions used, the alcohol groups are not deprotonated in the absence of metal, and thus the determination of the corresponding thermodynamic properties was not possible. It is therefore difficult to discuss the absolute value or the sign of $\Delta_r H^\circ_2$ or $\Delta_r S^\circ_2$ and to compare them to other known ligands. On the other hand, it is possible to see how the thermodynamic properties of formation of $[Ln_3L_2H_{-6}]^{3+}$ vary across the lanthanide series, inducing the discrimination of taci for the 4f cations. According to numerous studies on lanthanide(III) complexation,^{4,19,24} it is known that the global free energy of the complexation process is dominated by the combination step leading to the increase of formation constants with increasing atomic number of the cation.

The evolution of the Gibbs energy, enthalpy and entropy changes of reaction (2) is presented in Fig. 4. The progress of $\Delta_r G^\circ$ follows the well-known electrostatic trend and is mainly enthalpy-driven, the entropic term shows little variation across the 4f series. In this particular case, lanthanide(III) discrimination is thus mainly of enthalpic origin. However, entropic effects cannot be completely neglected, especially for lanthanum that has a much lower entropy change ($\Delta_r S^\circ$) than the other lanthanides. Both enthalpic ($\Delta_r H^\circ$) and entropic ($-T\Delta_r S^\circ$) factors are decreasing across the 4f series, and their overall evolutions do not compensate giving rise to the good selectivity between heavy and light lanthanides.

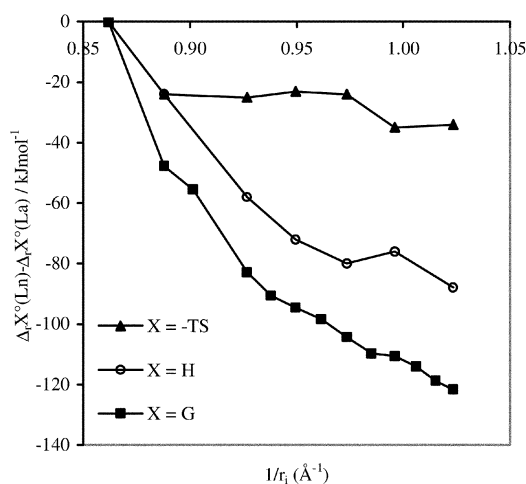


Fig. 4 Thermodynamic parameters of reaction (2) in kJ mol⁻¹.

$\Delta_r G^\circ$ and $\Delta_r H^\circ$ greatly decrease from La to Gd and then decrease more slightly from Gd to Lu. The high decrease of $\Delta_r H^\circ$ is characteristic of the electrostatic interaction between the Ln^{III} cations and the ligand which is rising with the hardness of the cation. This evolution across the 4f series is quite uncommon, since most of the studies show that the enthalpy and entropy changes on formation of the complexes of the lanthanide cations and many ligands are more influenced by changes in the hydration of cations and ligand anions than by the reaction of the two desolvated partners. This leads generally to irregular variations of the enthalpy and entropy of complexation across the rare-earth series.¹ In the case of lanthanide(III) complexes of taci, the predominant effect in the complexation enthalpy evolution is the electrostatic interaction between the cation and the ligand. Orvig and coworkers have reported a similar observation *i.e.* a very great decrease in enthalpy and thus in free energy of complexation with some phenolate based ligands (TRNS).⁶

At about Gd the enthalpy and Gibbs energy of reaction (2) start to flatten out. This non-monotonic evolution may be

attributed to the combination step and/or to the dehydration step. It has been indeed demonstrated that the hydration number of the free lanthanide cations changes from nine to eight between Sm and Gd.^{25,26} This change in the cation coordination number strongly affects the entropic and enthalpic contributions of the dehydration step and may contribute to the change in the slope of $\Delta_r G^\circ$ of reaction (2) at gadolinium.

Moreover, the expected electrostatic trend may also be altered by specific intramolecular interactions, especially in such compact polynuclear complexes. A careful examination of the X-ray structures of the lanthanum, gadolinium¹⁷ and lutetium species helps to evidence the variation in the internal energies of the complexes across the 4f series. The decrease in the value of the Ln^{III}–O–taci and N–taci bond lengths from La to Lu is, respectively, 0.17 and 0.19 Å (0.07 and 0.08 Å from Gd to Lu). These values are in agreement with the expected contraction of 0.18 Å (0.076 Å) calculated from Shannon ionic radii for eight-coordinated ions.²⁷ Simultaneously, this coordination sphere contraction moves closer the two negatively charged platforms when the cation radius is decreasing. In the three structures, the planes (O1 O2 O3), (O4 O5 O6), (N1 N2 N3), (N4 N5 N6) and (Ln1 Ln2 Ln3) are almost parallel, with a deviation of only 0.5 to 1°. For lanthanum, the distance between the planes (O1 O2 O3) and (O4 O5 O6) which is also the distance between two “face to face” alcoholate oxygens (O1–O4, O2–O5, O3–O6) is 2.71 Å, and the contraction of the Ln^{III} radius induces an increased repulsion between these negative groups since the same distance for gadolinium is 2.54 Å and is only 2.45 Å for lutetium. Another consequence of the Ln^{III} radius contraction is the increased repulsion between the three Ln^{III} cations which form an equilateral triangle with Ln ··· Ln distances of 3.932 (La), 3.734 (Gd) and 3.607 (Lu). These secondary interactions eventually imply an enthalpic destabilization term with the heavier lanthanide cations. A related thermodynamic trend along the lanthanide series has been described for dipicolinate complexes in which secondary interactions between the negatively charged carboxylate side arms are destabilizing the heavy lanthanide complexes.¹⁹

Conclusion

The ligand 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) displays an unusual selectivity between the light and the heavy lanthanides. The thermodynamic analysis presented in this paper demonstrates that this discrimination is mainly due to enthalpic effects, the entropic contribution remaining fairly constant across the rare-earth series. Contrary to many ligands, that show an enthalpic evolution characteristic of the dehydration step, taci shows a strongly decreasing complexation enthalpy from lanthanum to lutetium, which is typical of the electrostatic interaction between the trivalent cation and the ligand.

The resolution of the X-ray structure of the lutetium complex gives crucial structural information for the smallest lanthanide cations. The discrete molecular structures of gadolinium and lutetium complexes are formally identical. However the lanthanide radius contraction implies a coordination sphere contraction of the trinuclear sandwich complex, which moves the three Ln^{III} cations and the two triply charged ligands closer to each other. These secondary interactions are destabilizing the heavy lanthanide complexes and may explain that the decrease in the free energies and enthalpies of complexation is less marked at the end of the rare-earth series.

Experimental

Synthesis

Hydrated lanthanide chlorides were obtained from Aldrich and used without further purification. 1,3,5-Triamino-1,3,5-tri-

Table 4 Selected crystallographic data

[Lu ₃ (taciH ₋₃) ₂ (H ₂ O) ₆](SO ₄) _{1.5} (H ₂ O) ₈	
Formula	Lu ₃ C ₁₂ H ₅₂ N ₆ O ₂₆ S _{1.5}
<i>M_w</i>	1269.60
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> /Å	27.810(2)
<i>b</i> /Å	15.4654(9)
<i>c</i> /Å	20.360(1)
β /°	129.027(1)
<i>V</i> /Å ³	6802.7(7)
<i>Z</i>	8
<i>D_c</i> /g cm ⁻³	2.479
μ (Mo-K α)/mm ⁻¹	8.835
<i>T</i> /K	223(2)
Data/parameters	8003/505
<i>R</i> ₁ / <i>wR</i> ₂ ^a	0.0318/0.0801

^a Structure was refined on F_o^2 using all data: $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

deoxy-*cis*-inositol sulfate (taci(H₂SO₄)_{1.5}), 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) and 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol trihydrochloride (taci(HCl)₃) were synthesized according to published procedures.²⁸

[Lu₃(taciH₋₃)₂(H₂O)₆](SO₄)_{1.5}(H₂O)_{7.5}. Triethylamine (0.35 mL, 2.525 mmol) was added to a suspension of the sulfate salt of taci (0.091 g, 0.280 mmol) in methanol (30 mL) and the resulting mixture was refluxed for 30 min. Then lutetium nitrate hexahydrate (0.152 g, 0.421 mmol) was added and the stirring was continued for 1 h. The resulting white powder (0.087 g) was collected by filtration. Slow diffusion of methanol in a aqueous solution of this powder afforded a few crystals suitable for X-ray crystallography. Microanalysis results on samples including both crystals and powder were unsatisfactory due to the heterogeneous nature of the latter. ¹H NMR (400 MHz, D₂O): δ 3.91 (s, 6H, CHO), 2.93 (s, 6H, CHN)

Crystallography

The crystal was analyzed using a Bruker SMART CCD area detector three-circle diffractometer (Mo-K α radiation, graphite monochromator, $\lambda = 0.71073$ Å). The cell parameters were obtained with intensities detected on three batches of 15 frames with exposure time 60 s. The crystal–detector distance was 5 cm. For three settings of ϕ and 2θ , 1265 narrow data frames were collected for 0.3° increments in ω with exposure time 60 s. A full hemisphere of data was collected for each complex. Unique intensities with $I > 10\sigma(I)$ detected on all frames using SAINT program²⁹ were used to refine the values of the cell parameters. Lorentz and polarization corrections were made. The substantial redundancy in data allowed empirical absorption corrections to be applied using multiple measurements of equivalent reflections with SADABS Bruker program.³⁰ Space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure (Table 4).

The structures were solved by direct methods program SHELXTL,³¹ which revealed most of the complex atoms. Difference Fourier synthesis led to the location of all remaining non-hydrogen atoms. All non-hydrogen atoms were anisotropically refined on F^2 and hydrogen atoms were geometrically fixed. Final *R* indices and residual electronic density are listed in Table 4.

The one and a half sulfate counterions are partially disordered. The sulfate ion built around unit occupancy atom S1 was refined with six sites for the oxygen atoms, whereas the sulfate ion built around the half occupancy atom S2 is disordered with four oxygen atoms of water molecules. Six other

water molecules, of which one was refined with two sites, are present in the cell.

CCDC reference number 207019.

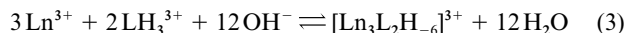
See <http://www.rsc.org/suppdata/dt/b3/b303414c/> for crystallographic data in CIF or other electronic format.

Microcalorimetry

Materials. All solutions were prepared in 0.1 mol L⁻¹ aqueous KCl using water purified by passing through a Millipore Milli-Q reverse-osmosis cartridge system (resistivity 18 MΩ cm). Stock solutions of the lanthanide salt, 3 × 10⁻³ mol L⁻¹, were analyzed for cation concentration by titration with Titriplex III (Merck) following classical methods. The ligand was checked for purity by NMR and elemental analysis before titration. Stock solutions of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol trihydrochloride (taci(HCl)₃), 2 × 10⁻³ mol L⁻¹, were also analyzed for ligand concentration by titration with KOH.

Thermodynamic measurements. The measurements were performed at 298.15 K using a microcalorimeter (Thermometric 2277 Thermal Activity Monitor) equipped with a titration vessel. Suurkuusk and Wadsö³² have described this heat-conduction calorimeter and analyzed its performance.

The experiments were carried out using a 1 mL glass vessel fitted with a gold stirrer. The vessel was charged with 450 μL of taci(HCl)₃ (2.00 × 10⁻³ mol L⁻¹) and 450 μL of LnCl₃ (3.00 × 10⁻³ mol L⁻¹) both in aqueous 0.1 mol L⁻¹ KCl solution. A solution of NaOH (about 0.03 mol L⁻¹), prepared from a 1 : 1 concentrated solution diluted with triply distilled water, was injected with a Thermometric Lund pump equipped with a 250 μL Hamilton syringe fitted with a gold cannula. 25 injections of 10 μL were made for a titration experiment, with a time of 60 min between each injection, a time sufficient to reach the equilibrium and to return to the baseline of the thermogram. The total heat measured during the experiment, corresponding to the complete reaction (3), corrected for the heat of dilution



of NaOH, leads to the Δ_rH° of this reaction. Knowing the values of Δ_rH° of reaction (1) and of the reaction of water autoprotolysis, *i.e.* 56.5 kJ mol⁻¹, the value of Δ_rH° of reaction (2) is calculated.

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