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Aqueous complexation of trivalent lanthanide and actinide cations by *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)ethylenediamine

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Abstract

The aqueous complexation reactions of trivalent lanthanide and actinide cations with the hexadentate ligand *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN) have been characterized using potentiometric and spectroscopic techniques in 0.1 M $NaClO_4$. At 25°C, the stability constant of $Am(TPEN)^{3+}$ is two orders of magnitude larger than that of $Sm(TPEN)^{3+}$, reflecting the stronger interactions of the trivalent actinide cations with softer ligands as compared to lanthanide cations.

Keywords: Americium; Lanthanides; Stability constants; Complexation; Soft donors

1. Introduction

The great chemical similarity of the trivalent lanthanide (Ln^{3+}) and actinide (An^{3+}) cations makes practical and efficient separations of trivalent lanthanides from the transplutonium actinides a difficult hydrometallurgical problem. The difficulty arises because these cations form primarily ionic bonds. As such, bond strengths and ultimately the degree of Ln/An separation is predominately governed by the charge density of the cations [1,2]. Under the conditions commonly encountered in the separation processes, all of the Ln and important transplutonium An cations are trivalent. Any difference in the charge density arises solely from changes in the ionic radii caused by the lanthanide and actinide contractions. Unfortunately, the f-element contractions cause Am^{3+} and Cm^{3+}, the most abundant An^{3+} cations, to have almost the same radii (and charge density) as the common fission product lanthanides Nd^{3+}, Pm^{3+}, and Sm^{3+} [3].

Since the electrostatic bonding of Ln^{3+} and An^{3+} is so similar, the only methods capable of real Ln^{3+}/An^{3+} separations exploit the slightly greater degree of covalency that appears to exist in An bonds. Although they still prefer hard Lewis bases, the trivalent actinides bind softer Lewis bases more strongly than the trivalent lanthanides. Because the energy required for a useful separation is small, this effect can be exploited for successful separations [4]. The difficulty in exploiting soft donor systems for Ln/An separations is the large concentration of water molecules present in aqueous systems. Water contains ca. 55 mol/l of hard oxygen donors which both Ln and An cations generally prefer over soft donors. However, incorporating multiple acidic soft donors into a ligand might allow the formation of stable f-element–soft donor complexes in aqueous solution, overcoming the large excess of water molecules through the formation of multiple chelate rings at pH values low enough to preclude the formation of Ln^{3+} or An^{3+} hydroxo complexes. This would allow a unique opportunity to study f-element complexation by non-oxygen donors in an aqueous system.

An ideal ligand for this approach appears to be the hexanitrogen donor *N*,*N*,*N′*,*N′*-tetrakis(2-pyridylmethyl)-ethylenediamine (TPEN), the 2-pyridylmethyl analogue of ethylenediaminetetraacetic acid, H_4EDTA. TPEN has previously been studied as a complexant for a number of transition metal cations [5], and recent rough measurements of its stability constants with a number of lanthanide cations [6] indicate that TPEN is able to form lanthanide complexes in aqueous solution despite the abundance of water molecules. There are also two reports of crystal structure determinations on Ln–TPEN complexes [7,8]. To investigate the potential of this ligand for Ln/An separations, we determined the stability constants of the 1:1

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TPEN complexes of La^{3+}, Sm^{3+}, and Am^{3+} and the hydration number of the Eu^{3+} complex in 0.1 M $NaClO_4$.

2. Experimental

Stock solutions of $La(ClO_4)_3$, $Sm(ClO_4)_3$, and $Eu(ClO_4)_3$ were prepared by dissolving the rare earth oxides (99.99%) in a slight excess of warm perchloric acid. The metal concentrations were determined by EDTA titration using xylenol orange indicator. The free acid concentration of each metal stock solution was determined by passing an aliquot through a bed of cation resin in the H^+ form, titrating the total acid in the effluent, and correcting for the amount of acid liberated by the exchange of the lanthanide cation. A 6.64×10^{-3} M stock solution of ^{243}Am was prepared from laboratory stocks of this nuclide, and the radiochemical purity was determined by α- and γ-spectrometry. At the end of each experiment, the Am concentration was measured by liquid scintillation counting with α/β discrimination after a 50- to 100-fold dilution. The ligand TPEN was synthesized and characterized as reported previously [7]. Its concentration was determined by potentiometric titration. Purification of the background electrolyte, $NaClO_4$ (GFS Chemicals), has also been described previously [9]. Solutions of acid and base for the titrations were prepared by dilution of Ultrex 70% $HClO_4$ (Baker) or 50% NaOH (Aldrich).

The p[H] ($p[H]=-\log H^+$ concentration in molarity) was measured in each titration with a Ross semimicro combination electrode (Orion) filled with saturated NaCl. The electrode was calibrated by titration of 0.01 M $HClO_4$/0.09 M $NaClO_4$ with 0.02 M NaOH/0.09 M $NaClO_4$ at the desired temperature. All potentiometric titrations were conducted under N_2 and the temperature was controlled to ±0.1°C with a circulating water bath. Lanthanide titrations were conducted on 20 ml of 1×10^{-3} M $Ln(TPEN)^{3+}$ at 5.0, 15.0, 25.0, and 35.0°C. Potentiometric titrations on 6 ml of 1×10^{-3} M $Am(TPEN)^{3+}$ solutions were conducted only at 25.0°C due to the limited amount of Am available. Spectrophotometric p[H] titrations of the Am complex were also preformed. The absorption spectra of TPEN solutions containing 5×10^{-4} M Am^{3+} were measured at different p[H] values in 1.000 cm quartz cuvettes between 495 and 520 nm and 25±1°C using an OLIS Cary-14 spectrophotometer. All uncertainties are reported at the 95% confidence level.

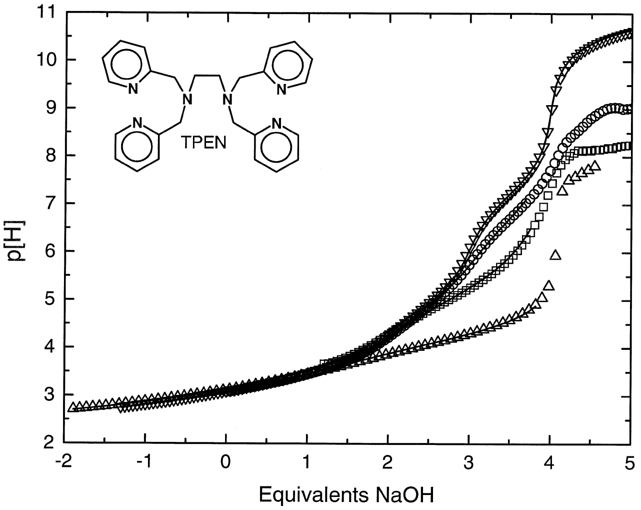

Fig. 1. Representative potentiometric titrations of TPEN at 25.0°C. (▽) 1.00×10^{-3} M TPEN, (○) 1.00×10^{-3} M TPEN with 1.04×10^{-3} M La^{3+}, (□) 9.40×10^{-4} M TPEN with 9.73×10^{-4} M Sm^{3+}, (△) 8.34×10^{-4} M TPEN with 1.41×10^{-3} M Am^{3+}. Solid lines are best fits of experimental data.

Time-resolved laser-induced fluorescence measurements were made on H_2O and D_2O solutions of 1.0×10^{-4} M $Eu(TPEN)^{3+}$ with a 10-fold excess of TPEN, buffered at p[H] (or p[D]) 6.2 with 0.01 M *N*-morpholinoethanesulfonic acid in 0.1 M $NaClO_4$. The lifetime of the $^5D_0$ state was measured following excitation at 355 nm and the data were analyzed as described previously [10].

3. Results and discussion

The protonation constants of TPEN and the stability constants of the metal–TPEN complexes (Table 1) were calculated from the potentiometric titration curves (Fig. 1) using the program Psequad [11]. The pK_w values for 5, 15, and 35°C and $I=0.1$ M were obtained by fitting the data of Harned and Mannweiler [12]. The first hydrolysis

Table 1
Logarithmic stability constants of TPEN complexes and pK_a values in 0.1 M $NaClO_4$ at various temperatures

Species	5°C	15°C	25°C	35°C
$HTPEN^+$	7.617±0.026	7.356±0.005	7.225±0.004	7.020±0.010
H_2TPEN^{2+}	5.208±0.032	4.992±0.008	4.873±0.007	4.793±0.014
H_3TPEN^{3+}	3.726±0.053	3.451±0.034	3.328±0.016	3.307±0.036
H_4TPEN^{4+}	3.530±0.072	3.202±0.106	3.029±0.031	2.907±0.076
$La(TPEN)^{3+}$	3.58±0.07	3.55±0.04	3.52±0.02	3.50±0.05
$Sm(TPEN)^{3+}$	4.83±0.05	4.76±0.03	4.70±0.02	4.64±0.02
$Am(TPEN)^{3+}$ (pot)[a]			6.69±0.03	
$Am(TPEN)^{3+}$ (sp)[a]			6.77±0.01	

[a] pot, determined by potentiometric titration; sp, determined by spectrophotometric titration.

constants of La^{3+} and Sm^{3+} at $I = 0.1$ M were approximated by the constants for $I = 0.5$ M and 25°C ($10^{-9.11}$ and $10^{-8.38}$, respectively), while the value reported for Am^{3+} at $I = 0.1$ M and 25°C ($10^{-6.98}$) was used [13]. The data from the metal titrations were truncated between p[H] 5.5 and 7.1, depending on the metal, to reduce the impact of metal hydrolysis on the analysis. Multiple speciation models, which included the complexes $M(TPEN)^{3+}$, $M(OH)^{2+}$, $M(TPEN)_2^{3+}$, $M(HTPEN)^{4+}$, and $M(OH)(TPEN)^{2+}$, were tested on the 25°C metal titration data. Of these, only $M(TPEN)^{3+}$ was a major complex, and $M(OH)^{2+}$ was a minor species under the conditions studied. These were the only metal complexes considered at the other temperatures.

Spectrophotometric titrations of the $Am(TPEN)^{3+}$ complex between p[H] 2.7 and 5.0 (Fig. 2) were conducted to test the validity of the potentiometric data. The spectra were analyzed using the program Squad [14]. Despite the presence of an excess of ligand in some experiments, the only absorbing species present in the p[H] range studied were Am^{3+} and $Am(TPEN)^{3+}$. The $Am(TPEN)^{3+}$ stability constant derived from the spectrophotometric titrations (Table 1) is in good agreement with the value calculated from the potentiometric titrations.

The TPEN complexes have modest stability constants in aqueous solution, but they show good Ln/An selectivity. Despite the similar ionic radii of hexacoordinate Sm^{3+} (1.098 Å) and Am^{3+} (1.115 Å) [3], the stability constant of the reaction

$$M^{3+} + TPEN \rightleftharpoons M(TPEN)^{3+} \quad (1)$$

is 100 times larger for M = Am than for M = Sm at 25°C. A purely electrostatic model [15] would predict the stability constant of $Am(TPEN)^{3+}$ to be ca. 5% or 0.03 log units smaller per donor than that of $Sm(TPEN)^{3+}$. The observed difference is also much larger than the five-fold difference observed for the $EDTA^{4-}$ or $DTPA^{5-}$ complexes of these metal ions [13], and illustrates the impact of replacing acetate groups with 2-pyridylmethyl groups. The hard, negatively charged oxygen donors make carboxylic acid based ligands superior to the softer, neutral 2-pyridylmethyl moieties for forming electrostatic bonds with Ln^{3+} or An^{3+}. Replacing the acetate groups of $EDTA^{4-}$ with 2-pyridylmethyl groups decreases the stability of the complexes by more than 11 orders of magnitude. However, the presence of only nitrogen donors results in significantly stronger binding of the softer An^{3+} compared to the Ln^{3+}.

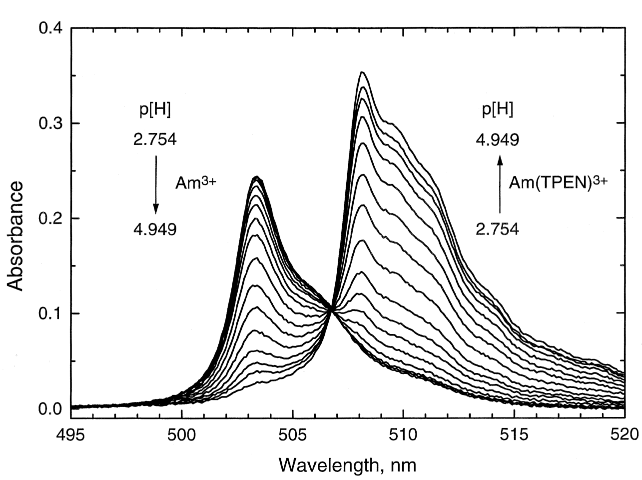

Fig. 2. Spectrophotometric titration of 9.20×10^{-4} M TPEN, 5.51×10^{-4} M Am^{3+} between p[H] 2.754 and 4.949 in 0.1 M $NaClO_4$ at 25°C.

The formation constants of $La(TPEN)^{3+}$ and $Sm(TPEN)^{3+}$ at each temperature were used to calculate the enthalpy and entropy of complexation (Table 2) for both lanthanide complexes. The enthalpies are modestly exothermic, much less so than might be expected for a hexadentate nitrogen donor, and even less exothermic than the $La(EDTA)^{-}$ and $Sm(EDTA)^{-}$ complexes (−12 and −14 kJ/mol, respectively, for $I = 0.1$ M) [13]. The complexation entropies are likewise much smaller than those of the $Ln(EDTA)^{-}$ complexes (+274 J/mol K for $Sm(EDTA)^{-}$ and +255 J/mol K for $La(EDTA)^{-}$ at $I = 0.1$ M) [13]. Despite this, more than half of the complexation free energy is associated with the entropy term for both $La(TPEN)^{3+}$ and $Sm(TPEN)^{3+}$.

The small ΔH and ΔS values for the TPEN complexes could signal a low degree of cation dehydration and that few of the TPEN nitrogen donor atoms are coordinated to the Ln^{3+} centers. For aqueous f-element complexes, the complexation entropies mostly reflect changes in the hydration [16–18]. In aqueous solution, the trivalent f-element aquo cations exist as highly hydrated species with 8–10 water molecules coordinated in the cation's inner coordination sphere. Complexation by other ligands displaces water molecules from the inner sphere, but this dehydration is often not complete. To the extent allowed by the steric requirements of the non-aquo ligands, enough water molecules remain in the inner coordination sphere to maintain a total coordination number of 8–10. For example, the complex between Eu^{3+} and the hexadentate ligand $EDTA^{4-}$ has an average hydration number of 2.6 in solution, for a total coordination number of 8.6 [1]. Thus, the hydration number can give an insight into the denticity of the non-aquo ligands. If the hydration number of $Ln(TPEN)^{3+}$ is low (3 or less), we can conclude that all six nitrogen donors in TPEN are coordinated, and that the

Table 2
Thermodynamic parameters for the formation of f-element–TPEN complexes in 0.1 M $NaClO_4$ at 25.0°C

Complex	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol K)
$La(TPEN)^{3+}$	−20.1±0.1	−4.9±0.3	+51±1
$Sm(TPEN)^{3+}$	−26.8±0.1	−10.3±0.3	+55±1
$Am(TPEN)^{3+}$	−38.4±0.2	−22[a]	

[a] Estimated using ΔS for $Sm(TPEN)^{3+}$.

coordination numbers of the Ln– and An–TPEN complexes are the same.

In light of this, two plausible models could explain the larger stability constant of the Am complex. In one model the number of M–N bonds is the same for both $Am(TPEN)^{3+}$ and $Sm(TPEN)^{3+}$, but the Am–N bonds are inherently stronger. In the other model, $Sm(TPEN)^{3+}$ actually has fewer M–N bonds than $Am(TPEN)^{3+}$ because Ln^{3+} bind nitrogen donors less readily than do An^{3+}. With fewer M–N bonds, the Ln^{3+} complexes would naturally have smaller stability constants (and complexation entropies) than the corresponding An^{3+} species or other Ln^{3+} complexes with hexadentate ligands. A potential way to differentiate between the possible models is by measuring the number of water molecules in the inner coordination sphere of the complexed metal.

The hydration number of $Eu(TPEN)^{3+}$ was measured by time-resolved laser-induced fluorescence in an attempt to differentiate between these two models. Applying the known relationship between Eu^{3+} luminescence decay constants and the number of inner sphere water molecules [19] to the observed decay constants ($k_{H_2O} = 2.39 \pm 0.07$ ms^{-1}, $k_{D_2O} = 0.63 \pm 0.01$ ms^{-1}), we calculate an average of 1.8 ± 0.5 water molecules in the Eu^{3+} inner coordination sphere. A single peak for the $^5D_0 \rightarrow {}^7F_0$ emission at 579.95 ± 0.07 nm (Fig. 3) indicates the presence of only one luminescing Eu species. Complexation of Eu^{3+} by TPEN results in only modest changes in the emission spectrum of Eu^{3+} in comparison with that of aquated Eu^{3+}.

The low hydration number of $Eu(TPEN)^{3+}$ is strong evidence for full hexacoordination of TPEN in the Ln^{3+} complexes and, by inference, also in the more stable $Am(TPEN)^{3+}$ complex. Since the solution structures of the Sm^{3+} and Am^{3+} complexes appear to be similar, and the cations are nearly the same size, the greater stability of the Am^{3+} complex should arise from intrinsically stronger Am–N bonds. How much stronger are the Am–N bonds? The free energy of Am^{3+}–TPEN complexation is 12 kJ/mol more favorable (Table 2) than for the corresponding Sm complex. If we assume $\Delta S_{Sm(TPEN)} = \Delta S_{Am(TPEN)}$, as observed for $Sm(EDTA)^-$ and $Am(EDTA)^-$ [13], the difference in ΔG arises from the difference in ΔH for the two complexes.

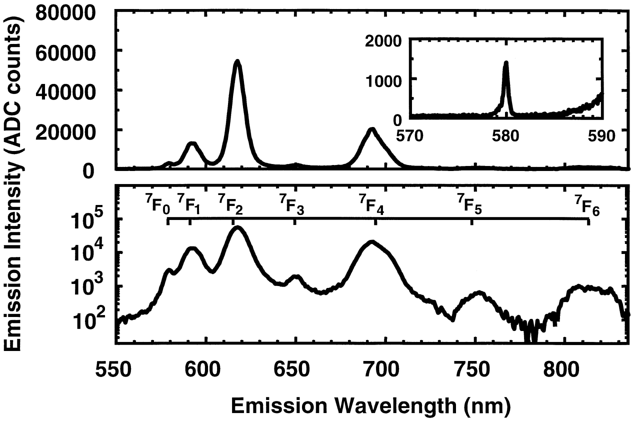

Fig. 3. Observed emission spectrum of the $^5D_0$ state of Eu^{3+} in 10^{-4} M $Eu(TPEN)^{3+}$ in D_2O at 22°C, following pulsed excitation at 467 nm, shown with linear (upper panel) and logarithmic (lower panel) intensity axes. The data were recorded using 3.8 nm spectral bandpass. The insert in the upper panel shows data recorded at 0.11 nm spectral bandpass to better determine the wavelength of the $^5D_0 \rightarrow {}^7F_0$ peak. The assignments for the observed bands are shown in the lower panel along with tick marks that denote the expected [20] centers of aquated Eu^{3+} emission bands.

While the selectivity of TPEN for An^{3+} over Ln^{3+} is an enthalpic effect, the weakness of the Ln–TPEN complexes, as compared to the Ln–EDTA complexes, is mostly an entropic effect. Based on the residual inner-sphere hydration of $Eu(TPEN)^{3+}$ and $Eu(EDTA)^-$ (1.8 and 2.6, respectively), ΔS should be larger for the Ln–TPEN complexes if metal dehydration is the primary determinant of the entropy. Instead, the opposite trend in ΔS is observed ($\Delta S_{Eu(EDTA)^-} = +294$ J/mol K). Furthermore, the complexation entropies reported for the TPEN complexes of a series of divalent 3d transition metals (Mn^{2+}–Zn^{2+}) are also much smaller than those of the corresponding EDTA complexes [5,13]. This indicates that the much lower entropies of the TPEN complexes derive from differences in the complexation-induced dehydration of EDTA and TPEN. Smaller entropy changes could be attributable to weaker hydration of the 2-pyridylmethyl groups in uncomplexed TPEN or to a more strongly hydrated $Ln(TPEN)^{3+}$ complex. The former is the more likely explanation for the small complexation entropies because the absence of any groups capable of hydrogen bonding on the surface of a complexed TPEN molecule makes the latter possibility unlikely. Consequently, although metal dehydration is a primary factor for determining differences in ΔS within a class of ligands, the thermodynamic parameters of the Ln–TPEN complexes underscore the point that the magnitude of the entropy change is also determined by the hydration state of the free ligand, which is determined by the types of donors present in the ligand.

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