Characterization of 2,3-Dihydroxyterephthalamides as M(IV) Chelators

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Received March 19, 2004

The ligand N,N'-diethyl-2,3-dihydroxyterephthalamide (ETAM) has been characterized as a chelator for Zr(IV), Ce(IV), and Th(IV). The K⁺ salts of the complexes [Zr(ETAM)₄]⁺, [Ce(ETAM)₄]⁺, and [Th(ETAM)₄]⁺ were prepared in a MeOH solution containing H₂ETAM, the corresponding M(acac)₄, and 4 equiv of KOH. Single-crystal X-ray diffraction analyses are reported for K₄[Zr(ETAM)₄] (C₂/c, Z = 8, a = 27.576(3) Å, b = 29.345(3) Å, c = 15.266(2) Å, α = 90°, β = 118.688(4)°, γ = 90°), [Me₃BnN]₄[Th(ETAM)₄] (P₂₁/c, Z = 2, a = 13.7570(3) Å, b = 13.9293(3) Å, c = 26.9124(6) Å, α = 99.941(1)°, β = 94.972(1)°, γ = 103.160(1)°), and the dimeric (NMe₄)₄[Th(ETAM)₃MeOH]₂ (P₂₁/c, Z = 4, a = 18.2603(9) Å, b = 18.5002(9) Å, c = 19.675(1) Å, β = 117.298(1)°). Solution thermodynamic studies were used to determine formation constants (log Kₑ and esd) for Th(IV)—ETAM log K₁₁₀ = 17.47(1), log K₁₂₀ = 13.23(1), log K₁₃₀ = 8.28(3), log K₁₄₀ = 6.57(6), and log β₁₄₀ = 45.54(5). These results support the hypothesis that the terephthalamides are high-affinity chelators for the actinide(IV) ions and thus promising ligands for use in nuclear waste remediation.

Introduction

The purification of radioactive fission materials and spent fuels from the nuclear industry has resulted in large volumes of highly radioactive waste that must ultimately be safely stored in a geological repository. Reducing the volume of this waste is a major goal of nuclear waste remediation, and this can be aided through the selective removal of actinide metals from the complex waste mixtures that contain a variety of organic and inorganic components. A biomimetic approach based on the observation that Fe(III) and Pu(IV) are both hard metal ions with the same charge-to-size ratio and a preference for oxygen donor ligands has successfully been applied to the development of actinide sequestering agents. Siderophores are powerful bacterial chelators of iron, and many of the most potent of these chelators incorporate catecholamide (CAM) ligand groups (Figure 1). The extraordinary Fe(III) chelating properties of the CAMs prompted the development of other catecholate-based ligands containing additional carboxyl or sulfate groups and the characterization of these ligands as powerful chelators for Fe(III) and An(IV) ions confirmed the validity of this biomimetic approach to M(IV) chelation.

Early studies with the catechol dianion and the eight-coordinate, tetravalent metals U(IV), Ce(IV), Th(IV), and Hf(IV) indicated that catechol itself is a strong chelator of high oxidation state metals. A derivative of the naturally occurring catecholamide which contains a second amide

Figure 1. Structure of the catecholamide ligands and N,N'-diethyl-2,3-dihydroxyterephthalamide (H₂ETAM) in its protonated and deprotonated forms.

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(1) This paper is no. 52 in the series “Specific Sequestering Agents for the Actinides.” For the previous paper, see: Guilmette, R. A.; Hakimi, R.; Durbin, P. W.; Xu, J.; Raymond, K. N. Inorg. Chem. 1996, 35, 4128–4136.
group, the 2,3-dihydroxyterephthalamide (TAM), was one of these ligands characterized as an Fe(III) chelator. In the progression from catechol, to catecholamide (CAM), to terephthalamide (TAM), the addition of electron-withdrawing amides lowers the protonation constants of the phenolic oxygens but does not decrease the effective strength of Fe(III) binding. Thus, the TAMs are also a logical candidate for actinide(IV) chelation. Previously, we have reported the syntheses and incorporation of these ligands into watersoluble polymers for the extraction of Pu(IV). Here, we present the coordination chemistry of a simple bidentate alkyl TAM ligand, N,N’-diethyl-2,3-dihydroxyterephthalamide (ETAM), with the tetravalent metals Zr(IV), Ce(IV), and Th(IV) as models for Pu(IV).

The size of the metals increases in the order Zr(IV) < Ce(IV) < Pu(IV) < Th(IV); thus, Ce(IV) is a convenient Pu(IV) analogue since the ionic radii of Ce(IV) and Pu(IV) are similar. And because the aqueous coordination chemistry of Ce(IV) parallels that of Pu(IV), giving identical shifts in the M(IV)/M(III) redox potentials.  

Experimental Section

General Methods. All reagents and solvents were purchased from either Aldrich Chemical Co. or Fisher Scientific and used as purchased. Solvents were dried over activated alumina and stored over 4 Å molecular sieves. All reactions were carried out under Ar, and all solvents were degassed by evacuating the flask and filling with argon 3 times. Water was distilled and further purified over 4 Å molecular sieves. All reactions were carried out under an atmosphere of purified Ar, and all solvents were degassed by evacuation of the flask and filling with argon 3 times. Water was distilled and further purified over 4 Å molecular sieves. All reactions were carried out under an atmosphere of purified Ar, and all solvents were degassed by evacuation of the flask and filling with argon 3 times. Water was distilled and further purified over 4 Å molecular sieves.

In each of the following cases, the ligand H$_2$ETAM (100 mg, 0.40 mmol) was dissolved in 10 mL of degassed MeOH. The metal acetylacetonate (M(acac)$_2$, 0.10 mmol) was dissolved in 5 mL of MeOH, filtered through a cotton plug to remove undissolved particles, and added to the ligand solution. The reaction was heated to reflux temperature for 16 h and then concentrated by means of evaporation to a tan solid. This was redissolved in MeOH and degassed, and 0.5 M KOH (0.6 mL, 0.3 mmol) was added. After the solution was stirred for 3 h, the solvent was evaporated, and the tan solid was dissolved in 0.5 mL of MeOH and applied to a Sephadex LH-20 column. The desired fraction was collected and evaporated to a tan solid.  

K$_4$[Zr(ETAM)$_4$]. Yield: 92 mg, 74%.  

1 H NMR (DMSO-d$_6$): δ 8.83 (t, 3H), 3.00 (q, 2H), 6.53 (s, 2H), 10.88 (s, t, NH), Anal. Calcd for K$_4$Zr(ETAM)$_4$·17H$_2$O: C, 37.08; H, 4.79; N, 7.94. Found: C, 37.17; H, 5.98; N, 7.04. MS [ESI$^+$] (m/z): 430.3, [ZrL$_4$]$^+$Crystals were grown from diffusion of diethyl ether into 2 mL of ethanol containing 4 mg of the complex.

K$_4$[Ce(ETAM)$_4$]. A black solid formed. Yield: 92 mg, 71% yield.  

1 H NMR (DMSO-d$_6$): δ 0.91 (t, 3H), 3.08 (q, 2H), 6.56 (s, 2H), 10.69 (t, NH), Anal. Calcd for K$_4$Ce(ETAM)$_4$·5H$_2$O: C, 41.55; H, 4.79; N, 7.94. Found: C, 41.49; H, 4.65; N, 8.08.

K$_4$[Th(ETAM)$_4$]. A tan solid formed. Yield: 100 mg, 72% yield.  

1 H NMR (DMSO-d$_6$): δ 0.91 (t, 3H), 3.09 (q, 2H), 6.63 (s, 2H), 10.87 (t, NH), Anal. Calcd for K$_4$Th(ETAM)$_4$·11H$_2$O: C, 36.31; H, 4.95; N, 7.06. Found: C, 36.38; H, 4.73; N, 6.90. FAB-MS(–) (m/z): 1349.2, [Th$_2$L$_6$]$^+$. Crystals of the [Th(ETAM)$_4$]$^+$-complex were prepared as the tetrakis(trimethylbenzylammonium) salt by using a stoichiometric amount of [Me$_3$BnN]OH as the base instead of KOH during the metal complex synthesis. Crystals were grown from diffusion of either methyl tert-butyl ether or diethyl ether into 1 mL of methanol.  

(Me$_4$N)$_2$[Th(ETAM)$_4$]. H$_2$ETAM (76 mg, 0.30 mmol) was dissolved in 10 mL of degassed MeOH. Th(acac)$_2$ (62 mg, 0.10 mmol) was dissolved in 5 mL of MeOH and added with filtering to the ligand solution. The reaction was heated to reflux temperature for 16 h and then concentrated by means of evaporation to a tan solid. This was redissolved in MeOH and degassed, and 0.5 M KOH (0.6 mL, 0.3 mmol) was added. After the solution was stirred for 3 h, the solvent was evaporated, and the tan solid was dissolved in 0.5 mL of MeOH and applied to a Sephadex LH-20 column. The desired fraction was collected and evaporated to a tan solid (94 mg, 86% yield). Anal. Calcd (found) for K$_4$Th$_2$(ETAM)$_4$·16H$_2$O: C, 35.88 (35.38); H, 4.85 (4.59); N, 6.97 (6.76). FAB-MS(–) (m/z): 1021. Crystals were grown from diffusion of either methyl tert-butyl ether or diethyl ether into 1 mL of methanol containing 4 mg of the K$^+$ salt of the complex and 4 mg of NMe$_2$Cl.

Structure Determination and Refinement. All X-ray structure data sets were collected on a Siemens SMART area detector diffractometer.  

Crystals were mounted on quartz capillaries in Paratone oil and were cooled in a nitrogen stream on the diffractometer. Peak integrations were performed using the Siemens SAINT software package.  

Space group determinations were done using the software XPREP. The two Th structures were solved and refined using the teXsan software package, and the Zr structure was solved and refined using SHELXTL. All hydrogen atoms were fixed at calculated positions and their thermal parameters refined isotropically. For [Zr(ETAM)$_4$]$^+$, only the Zr, oxygen, and nitrogen atoms of the ligand were refined anisotropically. For [Th(ETAM)$_4$]$^+$ and the [Th(ETAM)$_4$]$^+$$^+$dimer, all non-hydrogen atoms were fixed at their geometrically determined positions.
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| Table 1. Crystal Structure Details for K₂[Zr(ETAM)₄], [Me₂BnN]₄[Th(ETAM)₄], and [NMe₄]₄[Th(ETAM)₃MeOH]₂ |
|-----------------|-----------------|-----------------|
| K₂[Zr(ETAM)₄]  | [Me₂BnN]₄[Th(ETAM)₄] | [NMe₄]₄[Th(ETAM)₃MeOH]₂ |
| fw             | 1336.64          | 1834.02          | 1529.63          |
| temp, °C       | -114             | -124             | -117             |
| cryst syst     | monoclinic       | triclinic        | monoclinic       |
| space group    | C2/c             | P1              | P2/c             |
| unit cell dimens |                  |                  |                  |
| a, Å           | 27.576(3)        | 13.7570(3)       | 18.2603(9)       |
| α, deg         | 90               | 99.941(1)        | 90               |
| b, Å           | 29.345(3)        | 13.9293(3)       | 18.5020(9)       |
| β, deg         | 118.688(4)       | 94.972(1)        | 117.298(1)       |
| c, Å           | 15.2662(2)       | 26.9124(6)       | 19.675(1)        |
| γ, deg         | 90               | 103.160(1)       | 90               |
| V, Å³          | 10837.0(2); 8    | 4903.4(2); 2     | 5906.3(5); 4     |
| d, Å/cm³       | 1.638            | 1.242            | 1.72             |
| cryst size, mm | 0.27 × 0.40 × 0.15 | 0.23 × 0.17 × 0.12 | 0.16 × 0.10 × 0.09 |
| abs corr μ, cm⁻¹ | 5.92            | 15.9             | 26.25            |
| refcns collen  | 17 366           | 25 460           | 24 261           |
| indep reflcns | 7210 [R(int) = 0.1371] | 15 569 [R(int) = 0.0444] | 8795 [R(int) = 0.074] |
| data/param     | 2605/364         | 11 123/874       | 4195/585         |
| goodness-of-fit ab | 1.016e         | R1 = 0.1110°    | R1 = 0.0526     |
| final R indices ab |               | wR2 = 0.2069    | R2 = 0.0326     |
|               |                 |                  | R4 = 0.0060     |
|               |                 |                  | R4 = 0.0300     |

* Solved using SHELXTL; goodness-of-fit on F²; final R indices [I > 2σ(I)].
* Solved using TEXAN; goodness-of-fit on F; final R indices [I > 3σ(I)].

Atoms were refined anisotropically. The crystallographic details of each structure are given in Table 1.

Solution Thermodynamics. Equilibrium constants were measured at 25 °C in aqueous solution with a supporting electrolyte of 0.1 M KCl for Th(IV). They were determined as cumulative formation constants (βₘₙₗₜₜ, where M, L, and H refer to the metal, ligand, and proton, respectively):

\[ \beta_{\text{mln}} = \frac{[M^nL^mH^n]}{[M]^n[L]^m[H]^n} \]

For convenience, these are discussed as stepwise association constants, either for complex formation (Kₙ₀₁₀) or ligand protonation (K₀₁₀ₖ).

| Apparatus. A temperature-controlled 100 mL titration flask with attached quartz UV—vis cell has been described in detail elsewhere. An Accumet pH-meter (model AR15 or 15) and a Corning attached quartz UV spectrophotometer were used for electrode potential measurements. Metrohm autoburets (Dosimat 665/765) were used for titrant dosing. For the collection of absorbance data, a Hewlett-Packard 8452a spectrophotometer (diode array) was used. The lamp was always turned on for at least 1 h before use to allow the lamp to come to operating temperature, and all absorbance measurements were less than 1.1 absorbance units. The autoburets, pH meters, and spectrophotometer were controlled by a personal computer using modules of the LABVIEW programming environment, allowing automated titration execution. Acid and base solutions (0.1 M HCl and KOH) were prepared using J.T. Baker Dilut-it stock solutions. An Ag/AgCl reference electrode and standard electrode calibration was performed with a Corning 91041-000 electrode.

Electrode Calibration. The standard electrode calibration was conducted before each titration by following published protocols. The electrode was calibrated by adding 2.000 mL of HCl (ca. 0.1 M) to 50.0 mL of 0.1 M KCl, and the solution was titrated with KOH (ca. 0.1 M) to pH 11.6. The data were analyzed using the program GLEE allowing refinement of E° and slope. For low-pH titrations, a correction was made for the junction potential.

Th(IV) ETAM Titrations. Into 50 mL of 0.1 M KCl was added an aliquot of 0.024089 M H₂ETAM solution in MeOH (0.05189 mL, 0.00125 mmol), an aliquot of a 0.0506 M Th(IV) stock solution (0.0049 mL, 0.00025 mmol), HEPES (4.4 mg, 0.019 mmol), MES (4.7 mg, 0.022 mmol), NH₄Cl (1.6 mg, 0.03 mmol), and 1.000 mL of 0.0988 M HCl. This was titrated with 0.1003 M KOH from pH 2.8 to 10.5 and then back to pH 2.8 with 0.0988 M HCl, with a constant pH increment of 0.05 such that 67—82 data points, each consisting of pH and absorbance spectrum, were collected in each of the forward and reverse titrations. This was repeated 5 times, and a final concentration of 0.0506(2) M Th(IV) was calculated for the stock solution.

Th(IV) Stock Solution. A Th(IV) solution was prepared by dissolving ThCl₄ in HCl and HNO₃ such that the [Th(IV)] was approximately 5 mM and the [H⁺] was 0.2 M. In a 40 °C temperature-controlled cell, 2.5 mL of the Th(IV) solution was diluted into 50 mL of doubly distilled H₂O and 4 drops of a 0.1% pyrocatechol violet solution were added. The solution was titrated with 0.1018 M EDTA until the pink color disappeared. This was repeated 5 times, and a final concentration of 0.0506(2) M Th(IV) was calculated for the stock solution.

(21) LABVIEW, 5.0.1 ed.; National Instruments Corp.; Austin, TX.
As seen in previously characterized metal complexes, the square antiprismatic coordination geometry is illustrated by the hydrogen bond with the catecholate oxygen. The approach of the ligands on top intersect each other with an angle of 147°, indicating that the geometry most closely resembles a square antiprism, as is clear from the ORTEP diagrams.

The quantitative shape measure has been introduced to compare the eight-coordinate polyhedra of several Ce(IV) hydroxyxypyrindinone (HOPO) crystal structures with idealized eight-coordinate polyhedra. The three idealized polyhedra for eight-coordinate metal complexes are square antiprism, bicapped trigonal prism, and trigonal dodecahedron. For the shape measure $S$, the dihedral angles of adjacent planes from crystal structure coordinates are calculated and compared to the dihedral angles of the $D_{4d}$, $D_{2d}$, and $C_{2v}$ geometries:

$$S = \min \left[ \frac{1}{m} \sum_{i=1}^{m} (\delta_i - \theta)^2 \right]$$

Here $m$ = number of edges, $\delta$ = angle between normals of adjacent faces, $\delta_i = \text{observed dihedral angle along the } i\text{th edge of } \theta$, and $\theta = \text{same angle of corresponding ideal polytopal shape } \theta$. The smallest $S$ value is the one closest to describing the coordination geometry. In the case of $[\text{Zr(ETAM)}_4]^{4-}$, the following shape measures were calculated: $S(D_{4d}) = 12.8°$, $S(C_{2v}) = 16.9°$, $S(D_{2d}) = 17.3°$. This indicates that the geometry most closely resembles a square antiprism, as is clear from the ORTEP diagrams.

Crystals of the K$^+$ salt of the analogous Th(IV) complex of a quality suitable for characterization by XRD were never obtained even from a variety of crystallization methods in various solvent, so the [Th(ETAM)$_4$]$^{4-}$ as the tetrakis(trimethylbenzylammonium) salt was prepared using a stoichiometric amount of [Me$_3$BnN]OH as the base instead of KOH during the metal complex synthesis. This structure, shown in Figure 3, is also eight-coordinate, although the structure has a coordination geometry different from that of the Zr structure and the angle between the catecholate ring, phenolic oxygens, and Th(IV) is 180°. The shape measure ($S$) was used to analyze the coordination geometry, which is not as obvious in this structure. This provided values of $S(D_{4d}) = 22.6°$, $S(C_{2v}) = 18.6°$, and $S(D_{2d}) = 15.6°$, indicating that the coordination geometry around the Th(IV) lies between bicapped trigonal prismatic ($C_{2v}$) and trigonal dodecahedron ($D_{2d}$) but closer to $D_{2d}$. The Th(IV)–oxygen bond lengths are between 2.38 and 2.49 Å.

These Zr(IV) and Th(IV) ETAM structures have coordination geometries which differ from each other and those found in the four crystal structures of $[\text{M(catecholato)}_4]$$^{4-}$, where M = U(IV), Th(IV), Ce(IV), and Hf(IV). The catecholate complexes all have $D_{2d}$ (trigonal dodecahedron) symmetry and all have identical unit cell contents. Th–oxygen bond lengths in the Th catecholate structure of 2.4 Å are close to 2.14 to 2.27 Å. One of the K$^+$ counterions sits in the cleft above the four catecholate oxygens and is coordinated by each oxygen. The remaining K$^+$ counterions are coordinated by amide oxygens from neighboring complexes (not shown) and in this way link all of the $[\text{Zr(ETAM)}_4]^{4-}$, forming large voids in the extended structure that accommodate disordered solvent.

Results and Discussion

Synthesis and X-ray Crystal Structures of M(IV) ETAM Complexes. Three complexes with composition $K_4[\text{M(ETAM)}_4](M = \text{Zr(IV), Ce(IV), Th(IV)})$ were prepared by a ligand exchange reaction in which the appropriate M(acac)$_4$ and 4 equiv of H$_2$ETAM were heated in refluxing MeOH for 16 h and then treated with 4 equiv of methanolic HCl at constant pH increments such that 25 data points were collected.

The structure of $K_4[\text{Zr(ETAM)}_4]$ shown in Figure 2 illustrates the square antiprismatic coordination geometry. As seen in previously characterized metal–TAM complexes, the amide is oriented such that the amide proton forms a hydrogen bond with the catecholate oxygen. The approach of the ligands to the Zr(IV) center forms an angle of ~115° between the catecholate plane, phenolic oxygens, and Zr(IV) with the Zr(IV) lying 0.76 or 0.87 Å out of the plane of the catechol ring. In the view shown, the planes of the two ligands on top intersect each other with an angle of 147°.

those of the Th TAM structure. The Hf–oxygen bond lengths of 2.2 Å are close to those of the Zr TAM complex (Hf(IV) and Zr(IV) are the same size). In the [U(catecholato)₄]⁴⁻ structure, a small difference was seen in the U(IV)–oxygen bond lengths; however, this distortion was not present in the Th(IV) or Ce(IV) catecholate structures. This difference in U–oxygen bond lengths was attributed to a ligand field effect from the 5f² electrons. The Hf(IV) structure also had a small distortion, but this was attributed to the small size of Hf(IV) and the close contacts between adjacent catechol ligands. Th(IV) and Hf(IV) are f⁰ and d⁰ metals so there is no electronic preference for a particular coordination geometry. In the TAM structures presented here, the difference is attributed to the different counterions: the K⁺ ion coordinates to the catecholate oxygens in the Zr(IV) structure and distorts the ligands, which in turn affects the geometry around the metal.

If the Th ETAM complex is instead prepared with a 3:1 ratio of H₂ ETAM–Th(IV), light tan cube-shaped crystals readily form after diffusion of diethyl ether into a methanol solution of the complex. The complex crystallizes in P₂₁/c, shown in Figure 4, as a dimer with the formula [NMe₄]⁺[Th(ETAM)₃MeOH]₂. Four dimers are present in the unit cell, and the dimer sits on a special position with inversion symmetry. The coordination environment around the Th(IV) ion consists of two TAM units bound in the expected catecholate fashion. The third TAM also binds Th(IV) with its catecholate oxygens; however, one of the catecholate oxygens bridges to the second Th(IV) center. The amide ortho to this phenolic oxygen is oriented such that the carbonyl oxygen also binds to the second Th(IV) in a salicylate mode (detail shown in Figure 4b). In all other TAM and CAM metal complex structures, the amide is oriented with the oxygen pointing away from the metal such that the amide proton can hydrogen bond to the deprotonated, coordinating catecholate oxygen. In total, each Th(IV) is coordinated by five phenolic oxygens, two bridging phenolic oxygens, one amide oxygen, and one MeOH, for a total coordination number of 9, consistent with the larger size of Th(IV) as compared to Zr(IV) (ionic radius of 1.01 Å vs 0.86 Å).¹¹

Stability Constant Determination for Th(IV) ETAM Complex. The formation constants for the Th ETAM complex were determined by acid and base titrations of a solution containing Th(IV) and H₂ ETAM, and the constants are summarized in Table 2. The pH-dependent sequential addition of ETAM⁻ ligands to the Th(IV) center was monitored by the distinct changes in the UV–vis spectrum between 250 and 280 nm and 340 and 375 nm attributed to the π to π* transition of the ligand (Figure 5).⁵ The concentration of Th(IV) and H₂ ETAM were carefully chosen to avoid precipitation of the neutral Th(ETAM)₂ during the titration while still maintaining sufficient intensity in absorbance values. Due to these low concentrations, not enough buffering is afforded by H₂ ETAM so three noncoordinating buffers, MES, HEPES, and NH₄Cl, were added at ~0.4 mM to ensure sufficient buffering. A second “low pH” titration
from pH 3.1 to 1.5 was conducted to confirm $K_{110}$, and in this case the disappearance of the ThL$_2$ complex was monitored spectrophotometrically. The data fit very well to a simple model of sequential addition of ligand to the metal center. Inclusion of mixed hydroxo–ligand–Th(IV) species or dimers did not agree at all with the observed data. H$_2$ETAM is a high-affinity chelator for Th(IV) with an overall formation constant log $\beta_{140}$ of 45.54. The speciation diagram shown in Figure 6 (calculated with [Th(IV)] = 1 µM and [ETAM$^{2-}$] = 10 µM) illustrates how the composition of the solution changes with pH showing that the complex is not fully formed until pH 10 but starts forming at pH 1.

The relative strength of ETAM as a chelator of Th(IV) can also be evaluated by calculating pM. The pM value is defined as the negative logarithm of the free metal concentration and can be calculated for any pH, concentration of metal, and concentration of ligand. While the standard concentrations for a pM calculation are 1 µM metal and 10 µM ligand at a pH of 7.4, in this case it is more useful to calculate pM over the entire pH range since waste samples can vary widely. Shown in Figure 7 is a plot of pM vs pH for the Th(IV) ETAM system, calculated with metal and ligand concentrations of 1 and 10 µM, illustrating the amount of actinide that would be expected to remain in a waste stream after treatment with a TAM.

Acknowledgment. The authors acknowledge the assistance of Dr. Darren Johnson with the X-ray crystallography, Dr. Brendon O’Sullivan with the solution thermodynamics, and Dr. Jide Xu with synthetic advice. We also thank Dr. Anne E. V. Gorden for the preparation of this manuscript. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy (DOE), under Contract No. DE-AC03-76SF00098. Additionally, this research was supported in part under Grant No. SF17SP23, Environmental Management Science Program, Office of Science and Technology, Office of Environmental Management, U.S. DOE.

Supporting Information Available: CIF files with the details for the datasets from the crystals of ZrETAM, ThETAM, and the dimeric Th$_2$ETAM$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

Figure 5. Representative spectra from the Th(IV) ETAM UV–vis spectrophotometric titration.

Figure 6. Speciation diagram for the Th(IV)–ETAM system calculated with [Th(IV)] = 1 µM and [ETAM$^{2-}$] = 10 µM.

Figure 7. Graph of pM vs pH for Th ETAM calculated with [M(IV)] = 1 µM and [ETAM$^{2-}$] = 10 µM.

Conclusion

Understanding the basic coordination chemistry of the TAMs with actinide cations is crucial for determining their potential utility for us as actinide chelators in nuclear waste remediation. The simple bidentate 2,3-dihydroxyterephthalamide ligand ETAM has been evaluated in solution and the solid state as a M(IV) chelator. The complexes of Zr(IV), Ce(IV), and Th(IV) are straightforward to synthesize through a ligand exchange reaction, providing useful models for Pu(IV). The crystal structures show that these complexes can adopt different coordination geometries and coordination number. In the absence of a sufficient amount of ligand to saturate the coordination sphere of Th(IV), the hydrogen bond between the amide proton and catecholate oxygen can be broken to allow the ligand to coordinate through the amide carbonyl oxygen. Solution thermodynamic studies reveal that the TAMs have very high binding constants with Th(IV) and therefore should be well suited for chelating Pu(IV) in a variety of waste streams. With the appropriate choice of amide substituents, the TAMs should be well suited as liquid–liquid extractants for Pu(IV) or incorporation onto a solid support.