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# Solid State Structure of Thorium(IV) Complexes with Common Aminopolycarboxylate Ligands

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The crystal structures of the complexes formed by reaction of thorium(IV) nitrate with iminodiacetic acid ($H_2$IDA), nitrilotriacetic acid ($H_3$NTA), and ethylenediaminetetraacetic acid ($H_4$EDTA) under hydrothermal conditions are reported. In [Th(HIDA)$_2$($C_2O_4$)]·$H_2O$ (**1**), the metal atom is chelated by two carboxylate groups from two HIDA$^-$ anions and by two oxalate ligands formed in situ; two additional oxygen atoms from two more HIDA$^-$ anions complete the ten-coordinate environment of bicapped square antiprismatic geometry. The uncoordinated nitrogen atom is protonated and involved in hydrogen bonding. Two different ligands are present in [Th(NTA)($H_2$NTA)($H_2O$)]·$H_2O$ (**2**), one of them being a $O_3$,N-chelating trianion which acts also as a bridge toward two neighboring metal ions, and the other being a bis-monodentate bridging species with an uncoordinated carboxylic arm and a central ammonium group. An aqua ligand completes the nine-coordinated, capped square antiprismatic metal environment. The EDTA$^{4-}$ anion in [Th(EDTA)($H_2O$)]·2$H_2O$ (**3**) is chelating through one oxygen atom from each carboxylate group and the two nitrogen atoms, as in a previously reported molecular complex. Two carboxylate groups are bridging, which, with the addition of an aqua ligand, gives a capped square antiprismatic coordination polyhedron. Aminopolycarboxylate ligands have been much investigated in relation with actinide decorporation and nuclear wastes management studies, and the present results add to the structural information available on their complexes with thorium(IV), which has mainly been obtained up to now by extended X-ray absorption fine structure (EXAFS) spectroscopy. In particular, the bridging (non-chelating) coordination mode of $H_2$NTA$^-$ is a novel feature in this context. All three complexes crystallize as two-dimensional assemblies and are thus novel examples of thorium–organic coordination polymers.

## Introduction

The complexation of actinide ions by chelating ligands in the aliphatic aminopolycarboxylate family has been much investigated, particularly in the context of nuclear waste processing and management, and in decorporation studies.[1−4] Most results in this field are from solution studies, such as, for example, those recently obtained by electrospray ionization-mass spectrometry (ESI-MS) on thorium(IV) speciation in the presence of nitrilotriacetic and ethylenediaminetetraacetic acids,[2] which are two complexants present in nuclear wastes that may influence thorium environmental mobility.[4] Extended X-ray absorption fine structure (EXAFS) spectroscopy is a technique of choice to gain structural information on such systems, and it has been used to characterize the complexes formed by tetravalent actinide ions with nitrilotriacetic acid in aqueous solution, in association with spectrophotometric determination of stability constants and quantum chemical calculations,[3] and also the complexes formed by thorium(IV) with ethylenediaminetetraacetic acid.[4] However, there is at present a dearth of structural data determined in the solid state since a search for crystal structures in the Cambridge Structural Database (CSD, Version 5.31)[5] gives only some examples of complexes of uranyl ions with iminodiacetic,[6] nitrilotriacetic,[7] ethylenediaminediacetic,[8] and ethylenediaminetetraacetic[9] acids, and of neptunyl

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(1) Choppin, G. R.; Thakur, P.; Mathur, J. N. *Coord. Chem. Rev.* **2006**, *250*, 936.

(2) Cartwright, A. J.; May, C. C.; Worsfold, P. J.; Keith-Roach, M. J. *Anal. Chim. Acta* **2007**, *590*, 125.

(3) (a) Bonin, L.; Guillaumont, D.; Jeanson, A.; Den Auwer, C.; Grigoriev, M.; Berthet, J. C.; Hennig, C.; Scheinost, A.; Moisy, P. *Inorg. Chem.* **2009**, *48*, 3943. (b) Jeanson, A.; Dahou, S.; Guillaumont, D.; Moisy, P.; Den Auwer, C.; Scheinost, A.; Hennig, C.; Vidaud, C.; Subra, G.; Solari, P. L. *J. Phys.: Conf. Ser.* **2009**, *190*, 012185.

(4) Xia, Y.; Felmy, A. R.; Rao, L.; Wang, Z.; Hess, N. J. *Radiochim. Acta* **2003**, *91*, 751.

(5) Allen, F. H. *Acta Crystallogr., Sect. B* **2002**, *58*, 380.

(6) (a) Bombieri, G.; Forsellini, E.; Tomat, G.; Magon, L.; Graziani, R. *Acta Crystallogr., Sect. B* **1974**, *30*, 2659. (b) Battiston, G. A.; Sbrignadello, G.; Bandoli, G.; Clemente, D. A.; Tomat, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1965. (c) Jiang, J.; Sarsfield, M. J.; Renshaw, J. C.; Livens, F. R.; Collison, D.; Charnock, J. M.; Helliwell, M.; Eccles, H. *Inorg. Chem.* **2002**, *41*, 2799.

(7) (a) Grigoriev, M. S.; Den Auwer, C.; Meyer, D.; Moisy, P. *Acta Crystallogr., Sect. C* **2006**, *62*, m163. (b) Thuéry, P. *Inorg. Chem. Commun.* **2007**, *10*, 423.

(8) Palladino, G.; Szabo, Z.; Fischer, A.; Grenthe, I. *Dalton Trans.* **2006**, 5176.

(9) Shchelokov, R. N.; Orlova, I. M.; Sergeev, A. V.; Mikhailov, Y. N.; Lobanova, G. M.; Kanishcheva, A. S. *Koord. Khim.* **1985**, *11*, 196.

ions with *N*-methyliminodiacetic acid,[10] while the only ones with tetravalent actinide ions are the uranium(IV) complexes with nitrilotriacetic[3a] and ethylenediaminetetraacetic[11] acids and the thorium(IV) complex with the latter ligand.[11a] Only one thorium(IV) complex in this family has thus been crystallographically characterized up to now, which is a molecular species with the cation bound to four oxygen and two nitrogen atoms from the aminopolycarboxylate ligand and to three fluorine atoms. Obviously, more structure determinations on actinide(IV) ions complexes with such ligands would permit a better understanding of their coordination preferences, which are not always straightforward because of the large coordination numbers of these cations. This information is of importance for the interpretation of solution experiments and the elaboration of speciation models involving the stability constants of all possible species. More particularly, the precise determination of bond lengths and angles provided by X-ray crystallography gives a model of the coordination sphere which is complementary to that resulting from EXAFS measurements, the latter giving less accurate values, but presenting the great advantage to permit the study of complexes in solution. These structural data are essential as a starting point in modeling studies. Moreover, and apart from their importance in relation with the field of nuclear contaminants, such structures are interesting in their own right since polycarboxylate ligands are particularly adapted to the building of polymeric assemblies or frameworks, which also benefit from the high coordination number of thorium(IV). Indeed, although they are less investigated than those with lanthanide or uranyl ions, several thorium−organic assemblies have been reported, with ligands as diverse as pyridine-, pyrazine- and pyrazoledicarboxylates, 1,3,5-benzenetricarboxylate, 1,3-adamantanediacetate, and 4-carboxyphenylphosphonate.[12] As further development of these two thorium(IV) chemistry fields, the synthesis and crystal structure of three novel thorium ion complexes with the three very common ligands iminodiacetic, nitrilotriacetic, and ethylenediaminetetraacetic acids (denoted $H_2IDA$, $H_3NTA$, and $H_4EDTA$, respectively), obtained under hydrothermal conditions, are reported herein.

## Experimental Section

**Synthesis.** ***Caution!*** *$^{232}$Th is a radioactive element* ($\alpha$*-emitter*) *and thorium-containing compounds must be handled with suitable care and protection.*

$Th(NO_3)_4 \cdot 5H_2O$ was provided by the CEA. Iminodiacetic acid and nitrilotriacetic acid were purchased from Fluka, and ethylenediaminetetraacetic acid disodium salt dihydrate from Sigma. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

**$[Th(HIDA)_2(C_2O_4)] \cdot H_2O$ (1).** $Th(NO_3)_4 \cdot 5H_2O$ (57 mg, 0.10 mmol), a 10-fold excess of $H_2IDA$ (133 mg, 1.00 mmol) and demineralized water (2.5 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of complex **1**, mixed with a powder which was not further characterized, were obtained in low yield within 2 weeks.

**$[Th(NTA)(H_2NTA)(H_2O)] \cdot H_2O$ (2).** $Th(NO_3)_4 \cdot 5H_2O$ (57 mg, 0.10 mmol), $H_3NTA$ (38 mg, 0.20 mmol), $NMe_4OH \cdot 5H_2O$ (36 mg, 0.20 mmol) and demineralized water (2.5 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of complex **2** were obtained within 3 days (12 mg, 19% yield). Anal. Calcd for $C_{12}H_{18}N_2O_{14}Th$: C, 22.30; H, 2.81; N, 4.33. Found: C, 22.37; H, 2.91; N, 4.36%. The same crystalline complex is obtained in the absence of tetramethylammonium hydroxide, but it is mixed with powder in this case.

**$[Th(EDTA)(H_2O)] \cdot 2H_2O$ (3).** $Th(NO_3)_4 \cdot 5H_2O$ (29 mg, 0.05 mmol), $Na_2H_2EDTA \cdot 2H_2O$ (19 mg, 0.05 mmol) and demineralized water (1.8 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of complex **3** were obtained within 5 days (13 mg, 45% yield). Anal. Calcd for $C_{10}H_{18}N_2O_{11}Th$: C, 20.91; H, 3.16; N, 4.88. Found: C, 20.95; H, 3.14; N, 4.84%.

**Crystallography.** The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[13] using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The single crystals were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames, then refined on all data. The data (combinations of $\varphi$- and $\omega$-scans giving complete data sets up to $\theta$ = 25.7° and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[14] Absorption effects were corrected empirically with the program SCALEPACK.[14] The structures were solved by direct methods with SHELXS-97, expanded by subsequent Fourier-difference synthesis, and refined by full-matrix least-squares on $F^2$ with SHELXL-97.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to the oxygen and nitrogen atoms were found on Fourier-difference maps, and the carbon-bound hydrogen atoms were introduced at calculated positions; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom.

Crystal data and structure refinement parameters are given in Table 1, selected bond lengths and angles in Table 2, and selected hydrogen bonding parameters in Table 3. The molecular plots were drawn with SHELXTL[15] and Balls & Sticks.[16] The topological analyses were performed with TOPOS.[17]

## Results and Discussion

The complex $[Th(HIDA)_2(C_2O_4)] \cdot H_2O$ (**1**) was obtained from a solution containing a 10-fold excess of $H_2IDA$ with respect to thorium nitrate, which permitted to avoid immediate precipitation of the white powder formed with larger metal concentrations and insoluble upon heating. Some powder was however mixed with the crystals, which prevented to get satisfying elemental analysis results. The oxalate ions present were formed in situ, which is a quite frequent occurrence when carboxylic acids are heated for long periods,[18] and has been reported in the particular case of

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(10) Budantseva, N. A.; Andreev, G. B.; Fedoseev, A. M.; Antipin, M. Y. *Dokl. Chem.* **2002**, *384*, 159.

(11) (a) Mikhailov, Y. N.; Lobanova, G. M.; Kanishcheva, A. S.; Sergeev, A. V.; Bolotova, G. T.; Shchelokov, R. N. *Koord. Khim.* **1985**, *11*, 545. (b) Zhuravlev, M. G.; Sergeev, A. V.; Mistriukov, V. E.; Mikhailov, Y. N.; Shchelokov, R. N. *Dokl. Akad. Nauk SSSR* **1989**, *306*, 878.

(12) See, for example: (a) Kim, J. Y.; Norquist, A. J.; O'Hare, D. *J. Am. Chem. Soc.* **2003**, *125*, 12688. (b) Ziegelgruber, K. L.; Knope, K. E.; Frisch, M.; Cahill, C. L. *J. Solid State Chem.* **2008**, *181*, 373. (c) Frisch, M.; Cahill, C. L. *Cryst. Growth Des.* **2008**, *8*, 2921. (d) Ok, K. M.; Sung, J.; Hu, G.; Jacobs, R. M. J.; O'Hare, D. *J. Am. Chem. Soc.* **2008**, *130*, 3762. (e) Ok, K. M.; O'Hare, D. *Dalton Trans.* **2008**, 5560. (f) Adelani, P. O.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **2010**, *49*, 5701.

(13) Hooft, R. W. W. *COLLECT*; Nonius BV: Delft, The Netherlands, 1998.

(14) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(15) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

(16) Ozawa, T. C.; Kang, S. J. *J. Appl. Crystallogr.* **2004**, *37*, 679.

(17) (a) Blatov, V. A.; Shevchenko, A. P.; Serezhkin, V. N. *J. Appl. Crystallogr.* **2000**, *33*, 1193. (b) Blatov, V. A.; O'Keeffe, M.; Proserpio, D. M. *CrystEngComm* **2010**, *12*, 44.

**Table 1.** Crystal Data and Structure Refinement Details

| | **1** | **2** | **3** |
|---|---|---|---|
| chemical formula | $C_{10}H_{14}N_2O_{13}Th$ | $C_{12}H_{18}N_2O_{14}Th$ | $C_{10}H_{18}N_2O_{11}Th$ |
| $M$ (g mol$^{-1}$) | 602.27 | 646.32 | 574.30 |
| cryst syst | orthorhombic | orthorhombic | monoclinic |
| space group | *Pccn* | *Pbca* | $P2_1/n$ |
| $a$ (Å) | 13.3414(9) | 6.6391(2) | 6.7301(4) |
| $b$ (Å) | 8.6998(6) | 12.1471(3) | 19.4288(14) |
| $c$ (Å) | 12.8810(5) | 42.8135(12) | 12.1668(7) |
| $\beta$ (deg) | | | 101.349(4) |
| $V$ (Å$^3$) | 1495.07(16) | 3452.73(17) | 1559.80(17) |
| $Z$ | 4 | 8 | 4 |
| $D_{calcd}$ (g cm$^{-3}$) | 2.676 | 2.487 | 2.446 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 10.056 | 8.722 | 9.623 |
| $F$(000) | 1128 | 2448 | 1080 |
| reflns collcd | 28647 | 49010 | 48627 |
| indep reflns | 1419 | 3253 | 2953 |
| obsd reflns [$I > 2\sigma(I)$] | 1156 | 2965 | 2663 |
| $R_{int}$ | 0.018 | 0.014 | 0.031 |
| params refined | 119 | 262 | 217 |
| R1[a] | 0.023 | 0.017 | 0.025 |
| wR2[b] | 0.057 | 0.034 | 0.060 |
| $S$ | 1.066 | 1.137 | 1.037 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | −1.20 | −0.73 | −1.53 |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0.87 | 0.51 | 0.78 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ ("observed" reflections). [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ (all reflections).

**Table 2.** Environment of the Thorium Atom in Compounds **1**−**3**: Selected Bond Lengths (Å) and Angles (deg)[a]

| | | | | |
|---|---|---|---|---|
| **1** | Th−O1 | 2.626(3) | O1−Th−O2 | 50.30(9) |
| | Th−O2 | 2.559(3) | O5−Th−O5′ | 65.50(12) |
| | Th−O3″ | 2.411(3) | O6#−Th−O6⁗ | 64.27(12) |
| | Th−O5 | 2.485(3) | | |
| | Th−O6# | 2.497(2) | | |
| **2** | Th−O1 | 2.467(2) | O1−Th−N1 | 63.88(7) |
| | Th−O2′ | 2.4047(19) | O3−Th−N1 | 63.19(7) |
| | Th−O3 | 2.416(2) | O5−Th−N1 | 60.12(7) |
| | Th−O4″ | 2.363(2) | O1−Th−O3 | 74.49(7) |
| | Th−O5 | 2.3976(19) | O1−Th−O5 | 84.53(7) |
| | Th−O7 | 2.4269(19) | O3−Th−O5 | 123.16(7) |
| | Th−O9′ | 2.366(2) | | |
| | Th−O13 | 2.564(2) | | |
| | Th−N1 | 2.799(2) | | |
| **3** | Th−O1 | 2.418(3) | O1−Th−N1 | 63.07(11) |
| | Th−O2′ | 2.401(3) | O3−Th−N1 | 60.64(10) |
| | Th−O3 | 2.404(3) | O1−Th−O3 | 123.63(11) |
| | Th−O5 | 2.475(3) | O5−Th−N2 | 65.19(10) |
| | Th−O6″ | 2.398(3) | O7−Th−N2 | 63.93(10) |
| | Th−O7 | 2.387(3) | O5−Th−O7 | 71.92(10) |
| | Th−O9 | 2.432(3) | N1−Th−N2 | 66.95(11) |
| | Th−N1 | 2.740(4) | | |
| | Th−N2 | 2.714(4) | | |

[a] Symmetry codes: **1**: ′ = 3/2 − *x*, 1/2 − *y*, *z*; ″ = 3/2 − *x*, −*y* − 1/2, *z*; # = *x*, 1/2 − *y*, *z* − 1/2; ⁗ = 3/2 − *x*, *y*, *z* − 1/2. **2**: ′ = 3/2 − *x*, *y* + 1/2, *z*; ″ = *x* + 1, *y*, *z*. **3**: ′ = *x* + 1, *y*, *z*; ″ = *x* + 1/2, 3/2 − *y*, *z* + 1/2.

thorium complexes.[12b] The mechanism of oxalate formation has been investigated, and it likely involves metal-mediated ligand decarboxylation.[12b] Attempts at increasing the yield by addition of oxalic acid in the solution gave no crystalline material. The asymmetric unit in **1** corresponds to half the formula unit, with the metal atom located on a 2-fold axis which also bisects the C−C bond of the oxalate anion (Figure 1). The two carboxylate groups are deprotonated in the $HIDA^-$ anion, but the uncoordinated nitrogen atom bears two protons, thus giving the ligand a zwitterionic nature. The thorium atom is chelated by one carboxylate group of $HIDA^-$ and bound in monodentate fashion by the other carboxylate from a second anion, with Th−O bond lengths of 2.59(3) Å (average) and 2.411(3) Å, respectively (Table 2). Quite surprisingly, this is only the second instance of thorium chelation by a carboxylate group, since, among the 27 structures of thorium carboxylate complexes reported in the CSD, all contain monodentate or bridging (bidentate) groups, but for the structure of the hexa-acetate complex, which is however quite old and speculative.[19] The average Th−O bond length from the CSD, 2.42(6) Å, is in good agreement with that involving the monodentate group in **1**. The thorium atom is also chelated by the bridging oxalate ligand (through one atom from each carboxylate group), so as to form a five-membered ring on each side of this ligand, and with an average Th−O bond length of 2.491(6) Å, to be compared with the average value of 2.50(5) Å in other thorium oxalate chelates.[12b,20] The metal ion is thus ten-coordinated, a usual occurrence with this large cation, and the coordination polyhedron is a bicapped square antiprism,[21] with the two square faces (related to one another by the 2-fold axis) corresponding to the two sets of atoms O2, O5, O3″, O6⁗ and O2′, O5′, O3‴, O6# [rms deviation 0.17 Å, dihedral angle 0.83(2)°] and with atoms O1 and O1′ in the capping positions. The $HIDA^-$ ligand is in an extended conformation, with all torsion angles close to anti or syn geometries, but for one gauche C−N−C−C angle, and the two coordination sites are divergent, while the central nitrogen atom is uncoordinated and protonated. The ammonium group is hydrogen bonded to the carboxylate atom O2 in a neighboring molecule and to the lattice water molecule (Table 3). This ammonium-dicarboxylate extended form of the ligand is found in many metal complexes, in particular

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(18) (a) Li, X.; Cao, R.; Sun, D.; Shi, Q.; Bi, W.; Hong, M. *Inorg. Chem. Commun.* **2003**, *6*, 815. (b) Frisch, M.; Cahill, C. L. *Dalton Trans.* **2005**, 1518. (c) Li, B.; Gu, W.; Zhang, L. Z.; Qu, J.; Ma, Z. P.; Liu, X.; Liao, D. Z. *Inorg. Chem.* **2006**, *45*, 10425. (d) Frisch, M.; Cahill, C. L. *J. Solid State Chem.* **2007**, *180*, 2597. (e) Thuéry, P. *Polyhedron* **2007**, *26*, 101. (f) Thuéry, P.; Masci, B. *Cryst. Growth Des.* **2010**, *10*, 716.

(19) Arutyunyan, E. G.; Porai-Koshits, M. A.; Molodkin, A. K.; Ivanova, O. M. *J. Struct. Chem.* **1966**, *7*, 760.

(20) Akhtar, M. N.; Smith, A. J. *Acta Crystallogr., Sect. B* **1975**, *31*, 1361.

(21) Drew, M. G. B. *Coord. Chem. Rev.* **1977**, *24*, 179.

**Table 3.** Hydrogen Bonding Geometry: Selected Distances (Å) and Angles (deg)[a]

| | | D···A | D−H | H···A | D−H···A |
|---|---|---|---|---|---|
| **1** | N1···O2′ | 2.897(4) | 0.94 | 2.08 | 146 |
| | N1···$\mathrm{O7_w}$ | 2.945(5) | 0.92 | 2.20 | 138 |
| | $\mathrm{O7_w}$···O4″ | 2.929(4) | 0.84 | 2.20 | 145 |
| **2** | N2···O7 | 2.633(3) | 0.92 | 2.19 | 109 |
| | O12···O8′ | 2.545(3) | 0.96 | 1.61 | 164 |
| | O13···O10″ | 2.828(3) | 0.89 | 2.12 | 136 |
| | O13···$\mathrm{O14_w}$ | 2.765(3) | 0.92 | 1.88 | 162 |
| | $\mathrm{O14_w}$···O6 | 2.846(3) | 0.88 | 1.98 | 164 |
| | $\mathrm{O14_w}$···O6‴ | 2.757(3) | 0.86 | 1.96 | 154 |
| **3** | O9···O10 | 2.572(4) | 0.86 | 1.76 | 157 |
| | O9···O4′ | 2.689(4) | 0.91 | 1.78 | 176 |
| | $\mathrm{O10_w}$···O8″ | 2.697(5) | 0.95 | 1.95 | 134 |
| | $\mathrm{O10_w}$···$\mathrm{O11_w}$‴ | 2.740(5) | 0.85 | 2.03 | 141 |
| | $\mathrm{O11_w}$···O1⁗ | 3.354(6) | 0.99 | 2.40 | 162 |
| | $\mathrm{O11_w}$···O8 | 2.808(5) | 0.84 | 2.04 | 151 |

[a] The oxygen atoms pertaining to solvent water molecules are indicated by a w subscript. Symmetry codes: **1**: ′ = 1 − *x*, *y* − 1/2, 1/2 − *z*; ″ = *x*, −*y* − 1/2, *z* − 1/2. **2**: ′ = 2 − *x*, *y* − 1/2, 1/2 − *z*; ″ = 3/2 − *x*, *y* + 1/2, *z*; ‴ = *x* + 1/2, 3/2 − *y*, 1 − *z*. **3**: ′ = *x* − 1/2, 3/2 − *y*, *z* − 1/2; ″ = 1/2 − *x*, *y* + 1/2, 1/2 − *z*; ‴ = *x* + 1/2, 3/2 − *y*, *z* + 1/2; ⁗ = *x* + 1/2, 3/2 − *y*, *z* − 1/2.

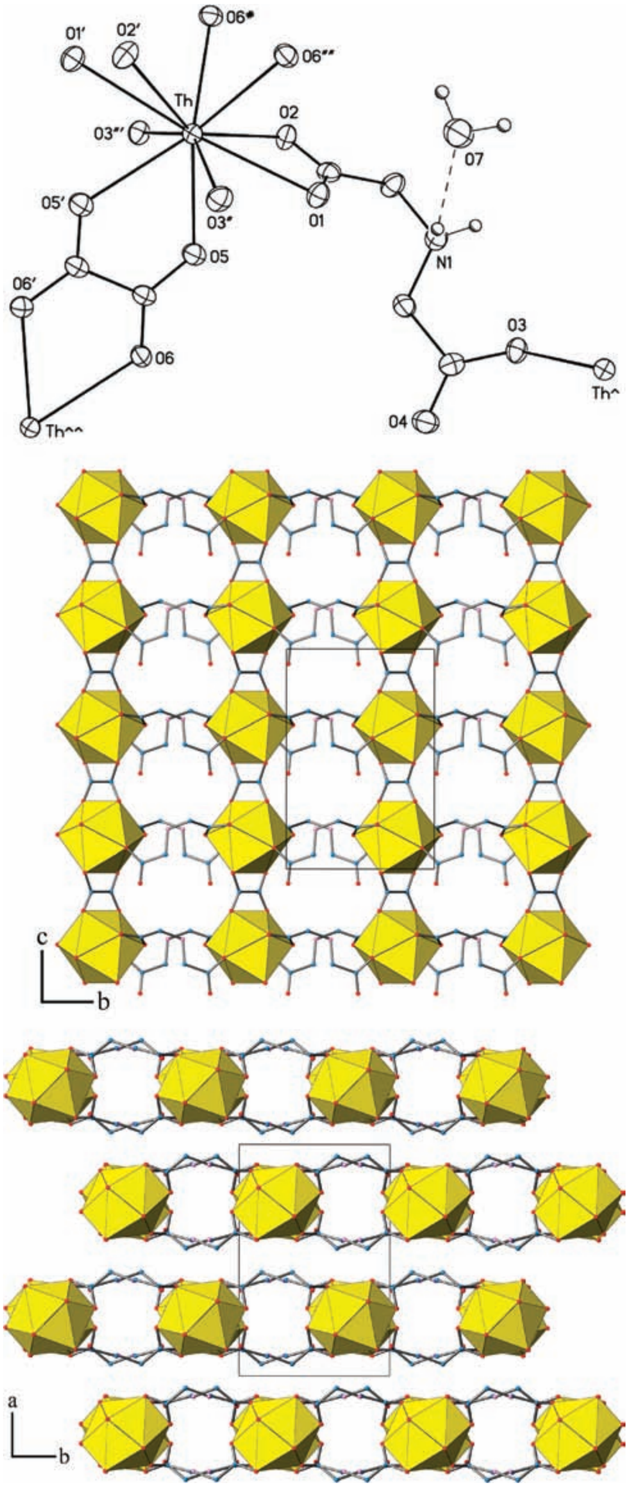

**Figure 1.** Top: View of complex **1**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted. The hydrogen bond is shown as a dashed line. Symmetry codes: ′ = 3/2 − *x*, 1/2 − *y*, *z*; ″ = 3/2 − *x*, −*y* − 1/2, *z*; ‴ = *x*, *y* + 1, *z*; ⁗ = 3/2 − *x*, *y*, *z* − 1/2; # = *x*, 1/2 − *y*, *z* − 1/2; ^ = *x*, *y* − 1, *z*; ^^ = *x*, 1/2 − *y*, *z* + 1/2. Middle: View of the two-dimensional assembly, showing the thorium coordination polyhedra. Bottom: Packing with the layers viewed edge-on. Hydrogen atoms and water molecules are excluded in the last two views.

with uranyl ions[6a] and several lanthanide ions. The uranyl ion complex displays also the unusual chelating-monodentate coordination mode, which is never found with lanthanide ions. Nitrogen coordination is generally absent with f-element ions, with the only exception of a uranyl binuclear complex;[6c] in the present case, the two oxalate ions occupying four coordination sites may contribute to exclude nitrogen bonding. This behavior is at variance with that of the related ligand oxydiacetate, in which the central oxygen atom is bound to thorium ions in the structures reported, the ligand being thus $O_3$-chelating.[22] The oxalate ligands in **1** are involved in the formation of linear chains running along the *c* axis, analogous to those found in previously reported thorium oxalate species, while chains are also formed along the *b* axis by double $HIDA^-$ bridges. These two sets of chains are orthogonal to one another, and they create a two-dimensional assembly parallel to the *bc* plane (Figure 1). The total point symbol of the trinodal network given by the TOPOS software[17] is ($4^2$, $8^8$, $12^5$)$(4)_2$(8), the three symbols corresponding to the metal center, $HIDA^-$, and oxalate ligands, respectively. A simplified representation of the network is shown in Figure 2. No other example of this topology is given in the databases associated with TOPOS. The sheets are packed with an offset along both the *b* and the *c* axes, so as to give a packing index of 0.79 (0.75 with solvent excluded).[23]

The complex $[Th(NTA)(H_2NTA)(H_2O)]\cdot H_2O$ (**2**) is represented in Figure 3. The asymmetric unit corresponds to one formula unit, which comprises two ligands in different states of protonation. The first ligand (containing N1 and O1−O6) is trianionic, and it chelates the metal ion through the nitrogen and three oxygen atoms, with two carboxylate groups being bridging bidentate, while the second (N2, O7−O12) is monoanionic, with two monodentate carboxylate groups, one uncoordinated carboxylic acid arm and a central ammonium group. The first ligand defines three Th−N−C−C−O five-membered rings, which are a usual feature of complexes with aminocarboxylate ligands comprising acetate arms.[12c] These three rings are not, however, located around a 3-fold axis of pseudo-symmetry parallel to the Th−N1 bond since they form dihedral angles of 89.25(7),

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(22) (a) Graziani, R.; Battiston, G. A.; Casellato, U.; Sbrignadello, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1. (b) Benetollo, F.; Bombieri, G.; Tomat, G.; Castellani, C. B.; Cassol, A.; Di Bernardo, P. *Inorg. Chim. Acta* **1984**, *95*, 251.

(23) (a) Kitaigorodski, A. I. In *Molecular Crystals and Molecules*; Academic Press: New York, 1973. (b) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

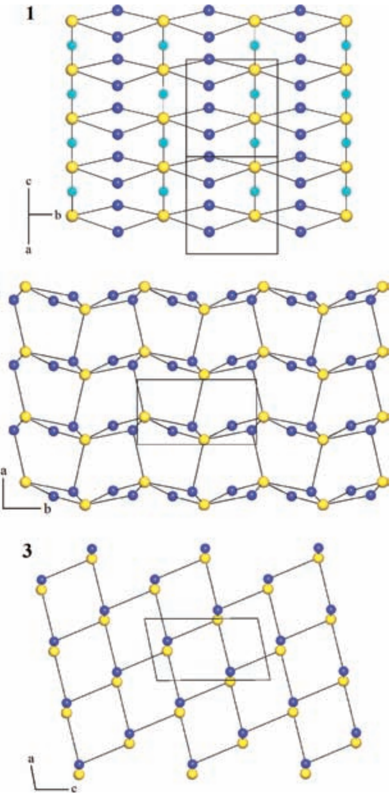

**Figure 2.** Simplified views of the networks in compounds **1**−**3**. The thorium atoms are in yellow and the centroids of the ligands in blue (water molecules excluded); the oxalate centroid in **1** is in cyan.

73.15(8), and 16.69(7)° (for rings containing O1 and O3, O1 and O5, and O3 and O5, respectively), the rings containing O3 and O5 being not far from coplanarity. The thorium atom is thus bound to seven carboxylate oxygen atoms, with an average Th−O bond length of 2.41(3) Å, in agreement with the values for monodentate carboxylates in **1** and from the CSD. The Th−N1 bond length of 2.799(2) Å is identical to the average value of 2.77(6) Å for the structures involving thorium bonding to tertiary amines reported in the CSD.[11a,24] Finally, the thorium atom is bound to an aqua ligand, with the Th−O13 bond length of 2.564(2) Å being at the upper end of the range determined from the CSD [2.40−2.58 Å, average 2.49(4) Å]. The metal coordination number is thus nine and the environment geometry is capped square antiprismatic, with the two square faces corresponding to the two sets of atoms O1, O3, O2′, O5 and O4″, O7, O9′, O13 [rms deviations 0.06 and 0.09 Å, dihedral angle 2.87(11)°] and with atom N1 in the capping position. The two ligands connect either three or two metal atoms, and their conformations are different. The chelating one displays a tripodal shape with the plane defined by the three coordinating oxygen atoms and that of the three uncoordinated ones being roughly parallel, with a dihedral angle of 4.50(10)°, and the atom N1 being located at 1.656(3) and 0.161(3) Å from these two planes, respectively. The three arms of the second ligand are divergent, and an intramolecular hydrogen bond links the ammonium group to atom O7 (Table 3). In the two-dimensional assembly formed, with sheets parallel to the *ab* plane (Figure 3), the chelating ligand connects all the metal ions and the second ligand does not play an essential structural role, since it bridges metal ions already connected to one another by the first ligand; in this respect, it can be viewed as a decorating

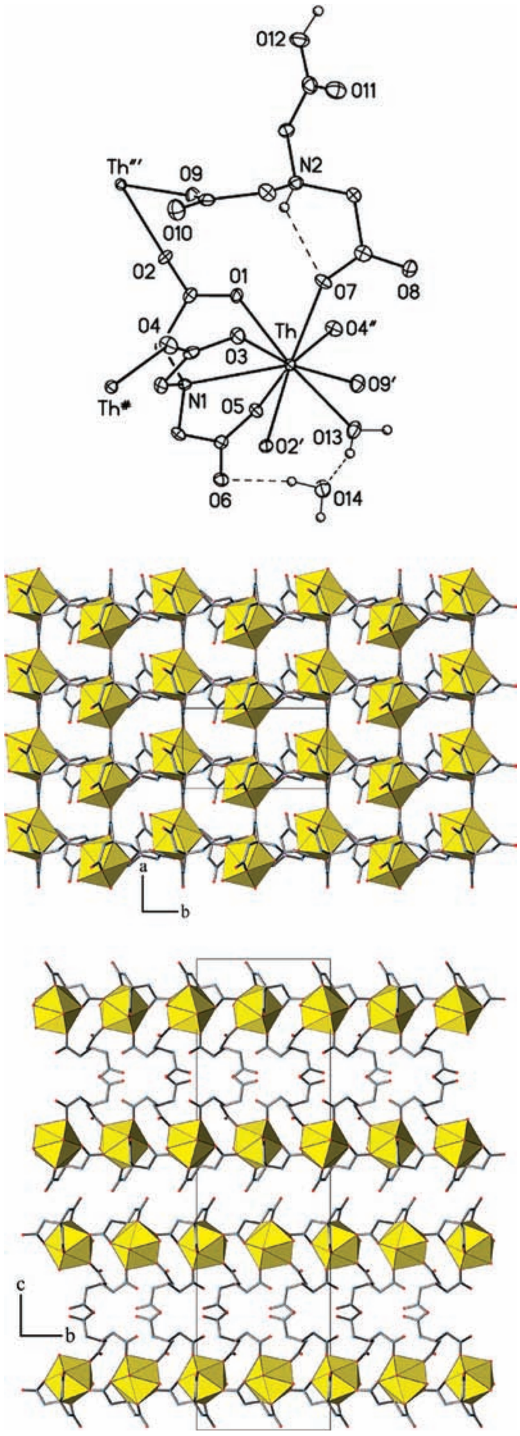

**Figure 3.** Top: View of complex **2**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dashed lines. Symmetry codes: ′ = 3/2 − *x*, *y* + 1/2, *z*; ″ = *x* + 1, *y*, *z*; ‴ = 3/2 − *x*, *y* − 1/2, *z*; # = *x* − 1, *y*, *z*. Middle: view of the two-dimensional assembly. Bottom: Packing with the layers viewed edge-on. Hydrogen atoms and solvent water molecules are excluded in the last two views.

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[24] (a) Drew, M. G. B.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1984**, 727. (b) Scott, P.; Hitchcock, P. B. *Chem.Commun.* **1995**, 579. (c) Barnhart, D. M.; Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1995**, *34*, 5416. (d) Rabinovich, D.; Schimek, G. L.; Pennington, W. T.; Nielsen, J. B.; Abney, K. D. *Acta Crystallogr., Sect. C* **1997**, *53*, 191. (e) Andrea, T.; Barnea, E.; Botoshansky, M.; Kapon, M.; Genizi, E.; Goldschmidt, Z.; Eisen, M. S. *J. Organomet. Chem.* **2007**, *692*, 1074.

species. The total point symbol of the trinodal network is $(4, 6^2)(4^2, 6^5, 8^3)(4)$, with the three symbols corresponding to the first ligand, metal ion, and second ligand, respectively. A view of the simplified net is shown in Figure 2, in which rows of doubly bridged metal centers (four-membered rings) parallel to the *b* axis are apparent, these rows being further linked to one another by the additional bonds involving atom O4 in the first ligand. All the uncoordinated carboxylic groups are located on the same side of the sheets, the uncoordinated carboxylate atoms (O6) pointing on the other side. The sheets face each other through similar faces, and hydrogen bonds are formed either between the carboxylic atom O12 and the carboxylate atom O8 of the analogous ligand in the next sheet, or between water molecules located between the sheets (O14) and the O6 atoms pertaining to neighboring sheets (Table 3). The stacking is quite tight, with a packing index of 0.78 (0.75 with solvent excluded), and no significant free space is present.

The third compound, $[Th(EDTA)(H_2O)]\cdot 2H_2O$ (**3**), is the second example of a thorium(IV) complex of EDTA to be crystallographically characterized, the other one being a trianionic molecular species containing also three fluorine atoms as ligands.[11a] The asymmetric unit in **3** corresponds to one formula unit, with the metal atom chelated by four oxygen and two nitrogen atoms of the $EDTA^{4-}$ anion (Figure 4), as in the previously reported complex. Two carboxylate oxygen atoms from neighboring molecules and an aqua ligand complete the coordination sphere, which has a capped square antiprismatic geometry with the two square faces corresponding to the two sets of atoms O1, N2, O3, O6″ and O2′, O5, O7, O9 [rms deviations 0.11 and 0.06 Å, dihedral angle 4.86(15)°], and with atom N1 in the capping position. Five Th−N−C−C−O or Th−N−C−C−N five-membered rings are present and, as in compound **2**, the arrangement of these rings around the Th−N bonds are far from pseudo-trigonal, with dihedral angles between the rings in the range 7.2(2)−88.38(11)°. The average Th−O and Th−N bond lengths, 2.41(3) and 2.727(13) Å, respectively, as well as the Th−O(aqua) bond length, are unexceptional. The metal centers are thus bound to three different $EDTA^{4-}$ ligands, each of the latter in its turn being bound to three metal ions. The resulting two-dimensional, slightly corrugated assembly parallel to the *ac* plane is uninodal, with the total point symbol $(6^3)$, and it corresponds to the topological type hcb (Shubnikov hexagonal plane net), as illustrated in Figure 2. In this case also, there is no available free space, and the packing index amounts to 0.75 (0.67 with solvent excluded). The water molecules of solvation are located in the interlayer spaces, and they ensure the connection between sheets through hydrogen bonding (Table 3).

The behavior toward thorium(IV) ions of the NTA and EDTA ligands, which are particularly relevant in actinide decorporation and nuclear wastes management studies, has been investigated through several solution and solid state techniques, with structural information in particular being derived from EXAFS measurements.[3,4] About NTA complexation more generally, it has been noted that tetravalent cations are prone to form eight-coordinate $M(NTA)_2$ 1:2 complexes, where the two ligands are $O_3$,N-chelating, while trivalent ones can be eight- or nine-coordinated, an aqua ligand completing the coordination sphere in the latter case.[3a] Mainly, the lanthanide ion complexes with NTA reported in the CSD are either molecular 1:2 chelate species, with or without an additional aqua ligand, or polymeric 1:1 species with additional carboxylate bridging involving two to four other metal centers. An interesting case is that which associates in a polymeric network both the 1:1 form and an unusual one in which each of the three carboxylate groups is O,O-chelating, the nitrogen atom being uncoordinated;[25] in this $\mu_3$-complexing mode, NTA acts as a trigonal node, as in its uranyl ion complex.[7] The 1:2 coordination mode with

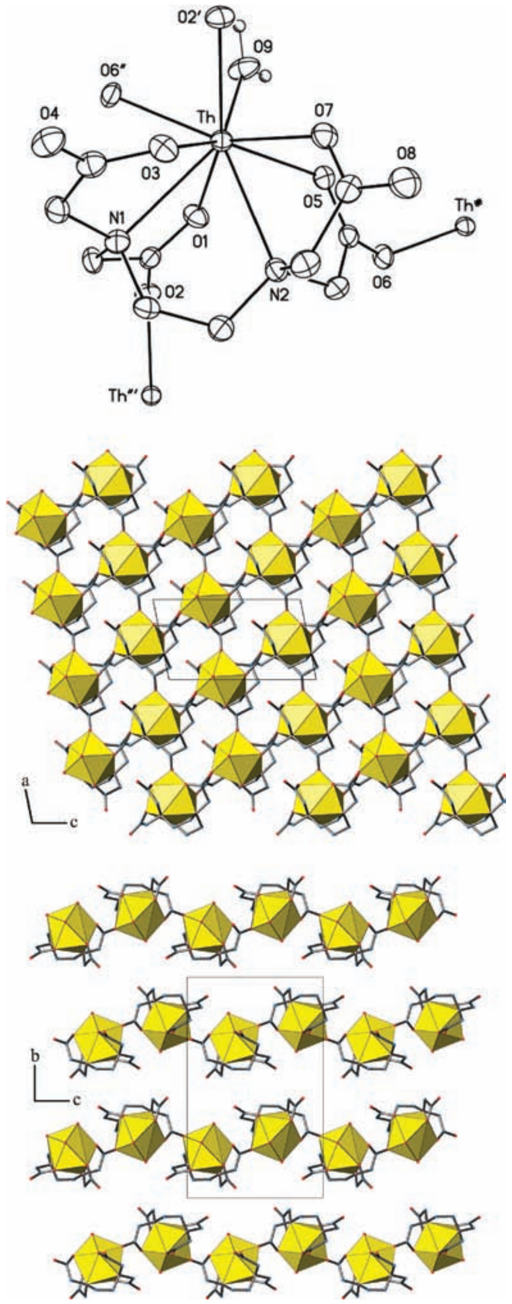

**Figure 4.** Top: View of complex **3**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms and solvent water molecules are omitted. Symmetry codes: ′ = $x + 1, y, z$; ″ = $x + 1/2, 3/2 - y, z + 1/2$; ‴ = $x - 1, y, z$; # = $x - 1/2, 3/2 - y, z - 1/2$. Middle: view of the two-dimensional assembly. Bottom: Packing with the layers viewed edge-on. Hydrogen atoms and solvent water molecules are excluded in the last two views.

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(25) Wang, J.; Gao, G.; Wang, X.; Zhang, X.; Liu, X. *J. Coord. Chem.* **2008**, *61*, 220.

an extra bridging carboxylate (nine-coordination), giving a zigzag one-dimensional polymer, is found in the crystal structure of the uranium(IV) complex $(Hpy)_2[U(NTA)_2]\cdot H_2O$, obtained at 130 °C in pyridine.[3a] ESI-MS has shown the formation of either the 1:1 or the 1:2 thorium(IV) complexes in solution, depending on the pH range,[2] while the EXAFS results on the 1:2 complex evidence the presence of a first shell containing six atoms at 2.39 Å from the metal, the nitrogen atoms being unresolved (although some improvement results from their inclusion in a multishell fit).[3a] In the same study, quantum chemistry calculations gave Th$-$O bond lengths of 2.40$-$2.41 Å, and Th$-$N bond lengths larger by 0.3$-$0.4 Å,[3a] these values matching quite perfectly those determined in complex **2** (and also those in complex **3**). It can be noted that the average U$-$O and U$-$N bond lengths in the uranium(IV) complex, 2.37(3) and 2.69(2) Å, respectively, are 0.04 and 0.11 Å shorter than their counterparts with thorium(IV), while the ionic radius difference between these two ions in nine-coordinated environments is 0.04 Å;[26] the variation in the M$-$O bond length matches exactly the difference in radii, but that in the M$-$N bond length is nearly three times as large, the latter, weaker bonds being possibly more sensitive to geometric variations, as suggested by quantum chemistry calculations.[3a] In all of the cases of f-element complexation reported thus far, at least one oxygen atom from each carboxylic group is bound to a metal center. However, the structure of the 1:2 complex **2** shows that this cannot be considered as a general rule and that NTA is a more versatile ligand than usually thought, since it can behave as a bidentate, bridging ligand through two carboxylate groups only, the uncoordinated carboxylic arm and ammonium group being available as hydrogen bond donors. As in the europium and uranyl ion complexes cited above, NTA adopts in this case a geometry different from that in the chelate complexes, and it behaves as a node of different topology in metal$-$organic networks. Obviously, the nature of the complexes formed is likely to be strongly dependent upon the experimental conditions, but it should be noted that the hydrothermal conditions used in the present study are not necessarily widely different from those prevailing in the nuclear wastes storage sites, but may on the contrary be more comparable to these conditions than room temperature ones.[27]

Both EXAFS[4] and ESI-MS[2] give evidence of the 1:1 stoichiometry of the thorium(IV) complex with EDTA, in agreement with the crystal structure of the molecular species $[Th(EDTA)F_3]^{3-}$ (as well as that of the isomorphous uranium(IV) complex).[11a] However, in contrast with these cases, the metal coordination sphere in **3** includes a donor from another molecule, giving a coordination polymer, which is a situation frequently encountered in the lanthanide complexes of EDTA reported in the CSD. The mixed ligand thorium complex including both NTA and EDTA has been detected experimentally,[2] but, under the present conditions, reaction of thorium nitrate with an equimolar mixture of the two acids gives the EDTA complex **3** as sole product. Unfortunately, it has been impossible up to now to grow crystals of the thorium complex with diethylenetriaminepentaacetate (DETPA), which, as EDTA, is a candidate ligand for actinide decorporation [more generally, the syntheses of thorium complexes with carboxylates are often hampered by precipitation of amorphous powders, possibly because of the formation of polynuclear or colloidal thorium oxyhydroxide hydrates of general formula $ThO_n(OH)_{4-2n}\cdot xH_2O$ ($0 \leq n \leq 2$)[28]].

## Conclusion

The crystal structures of three thorium(IV) complexes with aminopolycarboxylates have been determined, which are the only ones to be known, apart from that of the trianionic molecular complex with EDTA and fluorine ligands. All three compounds have been obtained under hydrothermal conditions and are two-dimensional coordination polymers with 1:2 (IDA, NTA) or 1:1 (EDTA) stoichiometries, the complex with IDA comprising also oxalate ligands formed in situ. The nitrogen atom is uncoordinated in the IDA complex **1** and in one molecule of the NTA complex **2**, in which cases it is protonated and involved in hydrogen bonding, while the other ligand in **2** and the EDTA ligand in **3** are both chelating through the nitrogen atoms and one oxygen atom from each carboxylate group; bridging carboxylate groups are present in **2** and **3**. The actinide-complexing properties of aminopolycarboxylate ligands are much investigated in relation with decorporation and nuclear wastes management studies, and the present results add to the quite scarce structural information already available, most of which was provided by EXAFS spectroscopy experiments. In particular, the bridging coordination mode of one ligand in the NTA complex has no precedent in previous studies. These three compounds are also novel examples of thorium$-$organic assemblies, a field much less developed than those of lanthanide- or uranyl-based architectures.

**Supporting Information Available:** Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(27) Zanonato, P. L.; Di Bernardo, P.; Bismondo, A.; Rao, L.; Choppin, G. R. *J. Solution Chem.* **2001**, *30*, 1.

(28) Rothe, J.; Denecke, M. A.; Neck, V.; Müller, R.; Kim, J. I. *Inorg. Chem.* **2002**, *41*, 249.