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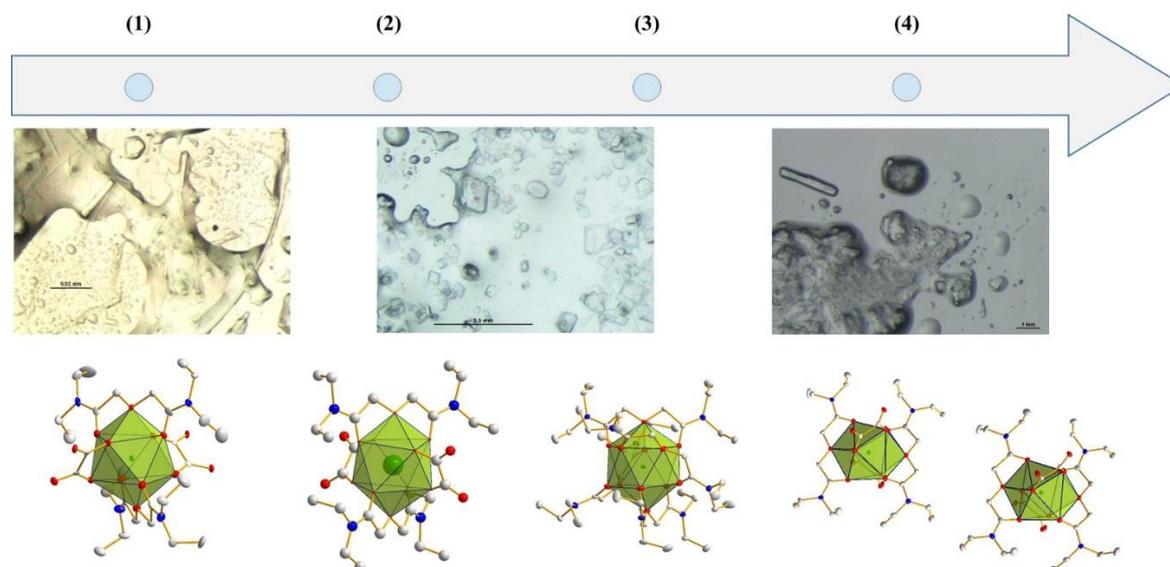
Single-Crystal to Single-Crystal Transformation in the Thorium-TEDGA-Oxalate-Nitrate System: Description and Comparison of the Main Structural Features

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TOC



Keywords: thorium, oxalate, tetraethyldiglycolamide, mixed ligands, nitrate, crystal structure, spectroscopic data, single-crystal to single-crystal phase transitions, oxalic acid geometry

Abstract

This paper reports the synthesis and the characterization of four new compounds based on thorium and tetraethyldiglycolamide (TEDGA), $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)][\text{NO}_3]_2[\text{H}_2\text{C}_2\text{O}_4] \cdot 6\text{H}_2\text{O}$ (**1**), $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)_2][\text{H}_2\text{C}_2\text{O}_4]_2 \cdot 2\text{H}_2\text{O}$ (**2**), $[\text{Th}(\text{TEDGA})_4][\text{NO}_3]_4 \cdot 4\text{H}_2\text{O}$ (**3**) and $[\text{Th}_2(\text{C}_2\text{O}_4)_3(\text{TEDGA})_4][\text{NO}_3][\text{HC}_2\text{O}_4][\text{H}_2\text{C}_2\text{O}_4]_4 \cdot 7\text{H}_2\text{O}$ (**4**). All of them are obtained by successive single crystal to single crystal phase transformation from a unique synthesis medium containing thorium nitrate and TEDGA, in presence of oxalic acid. Compound (**1**)

($a=b=18.7140(12)\text{\AA}$, $c=12.9212(9)\text{\AA}$, S.G. $P4_22_12$) is obtained at first. This solid undergoes two successive transformations which lead to a mixture of **(2)** ($a=12.246(2)\text{\AA}$, $b=32.253(5)\text{\AA}$, $c=12.256(2)\text{\AA}$, $\beta=106.741(12)^\circ$, S.G. $P2_1/n$) and **(3)** ($a=26.5966(13)\text{\AA}$, $b=15.4489(7)\text{\AA}$, $c=18.5582(9)\text{\AA}$, $\beta=116.528(1)^\circ$, S.G. $C2/c$) then to a mixture of **(1)** and **(4)** ($a=15.6611(7)\text{\AA}$, $b=17.9082(9)\text{\AA}$, $c=18.1814(7)\text{\AA}$, $\alpha=89.896(2)^\circ$, $\beta=65.549(2)^\circ$, $\gamma=87.623(2)^\circ$, S.G. $P-1$). Solving the crystal structure by single crystal diffraction reveals that the TEDGA is always coordinated to the thorium atom through its three oxygen atoms. In the mixed-ligands compounds **(1)**, **(2)** and **(4)**, the actinide atom is surrounded by two oxalate ligands and two TEDGA, leading to a 10-fold coordination. The dimensionality of the networks changes from linear chains (1D) **(1)** to isolated entities (0D) **(2)** or dimeric units (0D) **(4)**. Compound **(3)** is formed by the assembly of 12-fold coordinated monomeric entities (0D) in which the thorium cation is surrounded by four TEDGA. This compound is the first example of such a coordination number without nitrate anion included in the coordination sphere of Th.

Introduction

In the nuclear industry, the long term radiotoxicity of the spent fuel is mainly due to plutonium and minor actinides.¹ So, in order to reduce the radiotoxicity of ultimate wastes, researches for new generations of nuclear plants focus on the recycling of plutonium and minor actinides with the aim, on one hand, to fabricate new Pu and U-based mixed oxides nuclear fuel pellets (MOX), on the other hand, to synthesize Minor Actinides-based transmutation targets. In the current industrial PUREX process, uranium(VI) and plutonium(IV) are recovered from a nitric solution containing the fission products and minor actinides by liquid-liquid phase extraction thanks to the use of tributylphosphate (TBP) in dodecane.^{2,3} The extracting molecules have to meet various specifications such as (i) good extraction of actinides from a highly concentrated nitric solution to the organic diluent (ii) stability in aliphatic diluents *ie* resistance to radiolytic and hydrolytic degradation (iii) ease of synthesis (iv) low environmental impact. The use of tributylphosphate as an extracting agent may induce the presence of residual phosphate groups in the wastes which explain that new extracting molecules containing only C, H, O and N elements, fully incinerable, has been the subject of intense researches these last years.^{4,5} The amide family containing a carbonyl group and a nitrogen atom in alpha-position has shown promising results for the complexation of actinides and liquid-liquid extraction.⁶ Within this family of compounds, the diglycolamide molecules (DGA) of general formula $(R_2N(CO)(CH_2)O(CH_2)(CO)NR_2)$ are promising An(IV) complexing agents due to their large number of electronegative sites. The solubility of DGA molecules and their complexing properties strongly depends on their substituent groups, R. By example, tetraoctyldiglycolamide (TODGA) is deemed to be a very good extractant of transuranic elements in dodecane^{1,7,8} while tetraethyldiglycolamide (TEDGA) shows good abilities for precipitating actinides and other metals in acidic conditions.⁹ Despite the possible use of DGA as extracting and/or complexing agents of f-elements, few structural studies have been conducted in the DGA-lanthanides or -actinides systems. The crystal structures of lanthanides complexes coordinated by DGA ligands, L, have been reported for lanthanum $[La(pic)_3(L_2)]$ with L containing $RR' = Et$ and Ph ;¹⁰ $(LaL_3)(La(NO_3)_6)$ with L substituted by $R = i-Pr$ or by $i-Bu$], for cerium and ytterbium $[(CeL)(Ce(NO_3)_6)(CH_3OH)(C_4H_{10}O)$,

(YbL)(NO₃)₃ where L is a tris-DGA ligand and (YbL₃)(NO₃)₄ with L holding R = i-Pr]¹¹ and for the heavy lanthanides series (Ln = Tb, Dy, Ho, Er, Tm, Yb, and Lu) [(LnL₃)(NO₃)₃.4H₂O with L substituted by R = Et].¹² Main of the crystal structures of the actinides-DGA complexes were reported for An-yl salts with a DGA:actinyle ratio of 1:1 [(UO₂L)X₂ with L carrying R = i-Pr or R = i-Bu and X = Cl⁻ or NO₃⁻]¹³ or 1:2 [(UO₂L₂)(X)₂]^{13,14}, (PuO₂L₂)(X)₂¹⁵ and (NpO₂L₂)(X)₂¹⁶ with R = Me and X = ClO₄⁻]. But, to the best of our knowledge, the crystal structures reported in the An(IV)-DGA system have remained limited to (Pu^{IV}L₃)(NO₃)₃.MCN and (Pu^{IV}L₃)(NO₃)₃.ETOH with R = Me attached to L.¹⁷

This paper reports the influence of tetraethyldiglycolamide (TEDGA) on the crystallization process in the An(IV)-oxalate system, where Th(IV) was used as an analog of Pu(IV). Under evaporation, the presence of TEDGA leads to the crystal growth of four new compounds hereafter named **(1)**, **(2)**, **(3)** and **(4)** which crystal structures were determined by single-crystal X-Ray Diffraction. This paper aims to describe and compare the structural arrangement of these compounds and to report the spectroscopic study of compound **(3)**, obtained as a pure phase.

Experimental section

Synthesis *Caution! Thorium nitrate (Th(NO₃)₄.4H₂O) is a radioactive and chemically toxic reactant, so precautions with suitable care and protection for handling such substances have been followed.*

Reactants

(NO₃)₄.4H₂O was purchased from Prolabo (99%), oxalic acid from Alfa Aesar (98%) and TEDGA from Pharmasynthèse SA (>99%).

*Synthesis of [Th(TEDGA)₂(C₂O₄)] [NO₃]₂[H₂C₂O₄].6H₂O **(1)**, [Th(TEDGA)₂(C₂O₄)₂][H₂C₂O₄]₂.2H₂O **(2)**, [Th(TEDGA)₄][NO₃]₄.4H₂O **(3)** and [Th₂(C₂O₄)₃(TEDGA)₄][NO₃][HC₂O₄][H₂C₂O₄]₄.7H₂O **(4)***

Thorium nitrate (0.2 mmol) and TEDGA (1.4 mmol) were added in 10 mL of deionized water. The solution was heated at 50°C for 2h then a solution of oxalic acid (1.4 mmol in 10 mL of deionized water) was added within 2h. The colorless solution obtained after adding all reactants was left under the hood for slow evaporation. After ten days, a viscous solution containing crystals of **(1)** was obtained. The crystals of **(1)** had to be retained into their solution otherwise a rapid degradation was observed.

The solution was sealed to prevent further evaporation which leads to the massive crystallization of oxalic acid. The compound **(1)** was initially retained into the viscous solution but after five weeks it was transformed into a mixture of **(2)** and **(3)**. Four months later the mixture has turned into a new mixture, containing crystals of **(1)** and **(4)**. It has to be noted that the single-crystal to single-crystal transformation is reproducible except for the formation of **(2)** which has occurred just at once and couldn't be reproduced. Several trials were conducted in order to obtain the compound **(2)** from **(1)**. In particular, the effect of the

temperature on the transformation was studied. Despite a careful monitoring on the solutions at different temperatures, the compound (2) was not obtained.

These transformations are accompanied by a morphological change of the crystals (Figure 1). Indeed, the compound (1) displays a rod-like shape (Figure 1a) while intermediate compounds (2) and (3) have a platelet shape (Figure 1b), the smallest single crystals being typical of compound (2) and the biggest corresponding to (3). In the final mixture, the rod-like single-crystals of (1) appear again whereas compound (4) displays a block type morphology (Figure 1c).

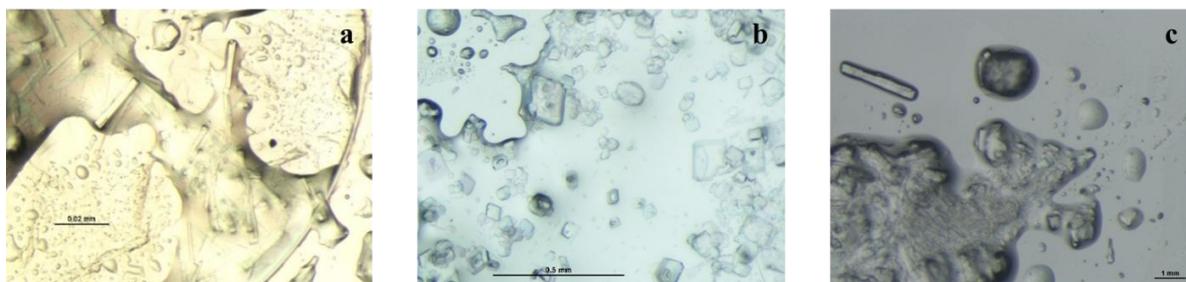


Figure 1: Micrographs of the single-crystals of compound (1) (a); the mixture of (2) and (3) (b) and the mixture of rods like crystals (1) and blocks (4) (c).

Synthesis of pure $[Th(TEDGA)_4(NO_3)_4 \cdot 4H_2O]$ (3)

Compound (3) was obtained as a pure phase by adding thorium nitrate (0.2 mmol), TEDGA (0.8 mmol) and oxalic acid (50 mg) to 10 mL of deionized water, at room temperature. Solid oxalic acid was used in place of oxalic acid solution to favor slow diffusion and then achieve a better crystal growth. The colorless solution obtained after adding all the reactants was left under the hood. After ten days, a precipitate matching the X-Ray powder diffraction pattern of compound (3) was obtained (Figure S2) with a yield of 25%. This pure powder was afterward used to perform further chemical analysis.

Single crystal diffraction

Except for (2), the collections of the diffraction data were performed at 100K, on a Bruker DUO-APEX2 CCD area detector diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) with an Incoatec microsource. The data reduction was accomplished using SAINT V7.53a.¹⁸ The substantial redundancy in data allowed a semi empirical absorption correction (SADABS V2.10) to be applied, on the basis of multiple measurements of equivalent reflections. Due to the low stability of (1), data were collected with 5s frame exposure while data for (2), (3) and (4) were recorded with 20s frame exposure. The structures were solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F^2 data using OLEX2 and SHELXL program software.^{19,20} Hydrogen atoms of the TEDGA were included in calculated positions and allowed to ride on their parent atoms. Hydrogen atoms of water molecules and oxalic acid parts were found on Fourier-difference maps. The low quality of the data for the compound (2) has led to consider several C-O distance constrains for free oxalic part.

Selected crystallographic data are reported Table 1. The CIF files of compounds 1-4 are provided as supplementary materials under the CCDC numbers xxx for (1) etc.

Table 1: Crystallographic data for compounds 1-4.

Compound	1	2	3	4
Chemical formula	C28 H60 N6 O26 Th	C32 H48 N4 O24 Th	C48 H104 N12 O28 Th	C64 H117 N9 O54 Th2
M (g.mol ⁻¹)	1128.86	1104.78	1529.47	2340.74
Temperature (K)	100	293	100	100
Symmetry	tetragonal	monoclinic	monoclinic	triclinic
Space group	P 4 ₂ 2 ₁ 2	P 2 ₁ /n	C 2/c	P -1
a (Å)	18.7140(12)	12.246(2)	26.5966(13)	15.6611(7)
b (Å)	18.7140(12)	32.253(5)	15.4489(7)	17.9082(9)
c (Å)	12.9212(9)	12.256(2)	18.5582(9)	18.1814(7)
α (°)	90	90	90	89.896(2)
β (°)	90	106.741(12)	116.528(1)	65.549(2)
γ (°)	90	90	90	87.623(2)
V Å ³	4525.2(7)	4635.6(13)	6822.5(6)	4637.2(4)
Z	4	4	4	2
Density calc. (g.cm ⁻³)	1.657	1.583	1.489	1.676
μ (mm ⁻¹)	3.387	3.301	2.273	3.310
θ range	1.539 – 26.393	1.846 – 22.002	1.527 – 30.511	1.449 – 26.351
Limiting indices	-23 ≤ h ≤ 18 -16 ≤ k ≤ 22 -12 ≤ l ≤ 16	-12 ≤ h ≤ 12 -33 ≤ k ≤ 33 -12 ≤ l ≤ 12	-37 ≤ h ≤ 37 -22 ≤ k ≤ 22 -26 ≤ l ≤ 26	-19 ≤ h ≤ 19 -22 ≤ k ≤ 22 -22 ≤ l ≤ 22
Collected reflections	21750	39816	51745	61346
Unique reflections	4652	5668	10367	18660
R(int)	0.0739	0.0879	0.0287	0.0338
Parameters	289	575	416	1206
Goodness of fit	1.026	1.015	1.070	1.020
Final R indices [I > 2σ(I)]	R1 = 0.0352 wR2 = 0.0651	R1 = 0.0432 wR2 = 0.0844	R1 = 0.0173 wR2 = 0.0416	R1 = 0.0253 wR2 = 0.0515
R indices (all data)	R1 = 0.0766 wR2 = 0.0787	R1 = 0.0788 wR2 = 0.0972	R1 = 0.0234 wR2 = 0.0442	R1 = 0.0394 wR2 = 0.0562
Flack parameter	-0.002(13)			
Largest diff. peak and hole (e.Å ⁻³)	0.851 ; -0.634	0.527 ; -0.631	1.396 ; -0.320	1.075 ; -0.522

Powder diffraction

X-ray powder diffraction was performed on Bruker D8 Advance diffractometer (LynxEye detector) in a Bragg-Brentano θ - θ mode using Cu-K α radiation. Each powder pattern was recorded within an angular range of 5-70° in 2 θ , with steps of 0.02° and counting time of 0.5s per step.

Infrared spectroscopy

Infrared spectroscopy was performed with a PerkinElmer Spectrum Two spectrometer equipped with a single reflection attenuated total reflectance (ATR), between 4000-400 cm^{-1} with a 1 cm^{-1} resolution.

Thermal analysis

Thorium based compounds, thermal analysis was performed on a thermoanalyser 92 SETARAM TGA up to 900 $^{\circ}\text{C}$ under air condition with a heating rate of 5 $^{\circ}\text{C}\cdot\text{min}^{-1}$.

Results and discussion

Structural description

Crystal structure of (1)

Compound (1) $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)][\text{NO}_3]_2[\text{H}_2\text{C}_2\text{O}_4]\cdot 6\text{H}_2\text{O}$ crystallizes in the tetragonal non-centrosymmetric space group $\text{P}4_22_12$ ($n^{\circ}94$) with $a = b = 18.7140(12)$ \AA and $c = 12.9212(9)$ \AA . The thorium (IV) ions are surrounded by ten oxygen atoms which form a bicapped square antiprism (Figure 2a). Six oxygen atoms are provided by the coordination of two tridentate TEDGA ligands and four oxygen atoms come from two bidentate oxalate ligands leading to structural building units (SBU) of formula $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)_2]$. The TEDGA ligands are planar and possess two ethyl groups in a syn-syn conformation and two ethyl groups in a syn-anti conformation (Figure 2b). The Th-O distances range between 2.421(6) and 2.648(6) \AA . The longest Th-O distances are representative of the Th-O_{ether} bonds while the shortest lengths are attributed to the Th-O_{carbonyl} ones. The Th-O_{oxalate} distances have intermediate values close to the Th-O_{carbonyl} (Table 2). Due to symmetry consideration (4-fold axis) the oxalate ligands are twisted of 90 $^{\circ}$ on both sides of the SBU.

The SBU share their bis-bidentate oxalate ligands, $\mu_2\text{-}\eta^2\text{:}\eta^2$, to form cationic chains, $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)]^{2+}_{\infty}$, running along the c axis (Figures 2c and 2d). The distance Th-Th through the oxalate ligands is equal to 6.490 \AA and is similar to the one encountered in the literature for most of the ten-fold coordinated Thorium(IV) compounds connected by a bis-bidentate μ_2 -oxalate.^{21,22} In (1), the $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)]^{2+}_{\infty}$ chains are linear with successive Th-Th-Th atoms forming an angle equal to 180 $^{\circ}$, close to the one found in $(\text{NH}_4)_4\text{Th}(\text{C}_2\text{O}_4)_4\cdot 4\text{H}_2\text{O}$,²³ while in compounds $\text{M}_4[\text{An}(\text{C}_2\text{O}_4)_4]\cdot n\text{H}_2\text{O}$ ($\text{An} = \text{Th}, \text{M}=\text{K}, \text{N}_2\text{H}_5, n=4$; $\text{M}=\text{C}(\text{NH}_3)_2, n=2$; $\text{M}=\text{Na}, n=5.5$ – $\text{An} = \text{U}$,²² $\text{M}=\text{K}, n=4$; $\text{M}=\text{C}(\text{NH}_3)_2, n=2$ and $\text{An}=\text{Np}, \text{Pu}, \text{M}=\text{C}(\text{NH}_3)_2, n=2$) the $[\text{An}(\text{C}_2\text{O}_4)_4]^{4+}_{\infty}$ chains are corrugated with a An-An-An angle close to 158 $^{\circ}$.²³⁻²⁶

Four nitrates, found along the (110) and (-110) directions, are found in the environment of one out of two $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)_2]$ SBU. These nitrate anions are involved in a H-bonding network along with the oxalic acid molecules, found on the 2 fold axes parallel to c axis, and the water molecules. Only the water molecules bond the $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)]^{2+}_{\infty}$ chains, which could explain the low stability of compound (1) in air (Figure 2d).

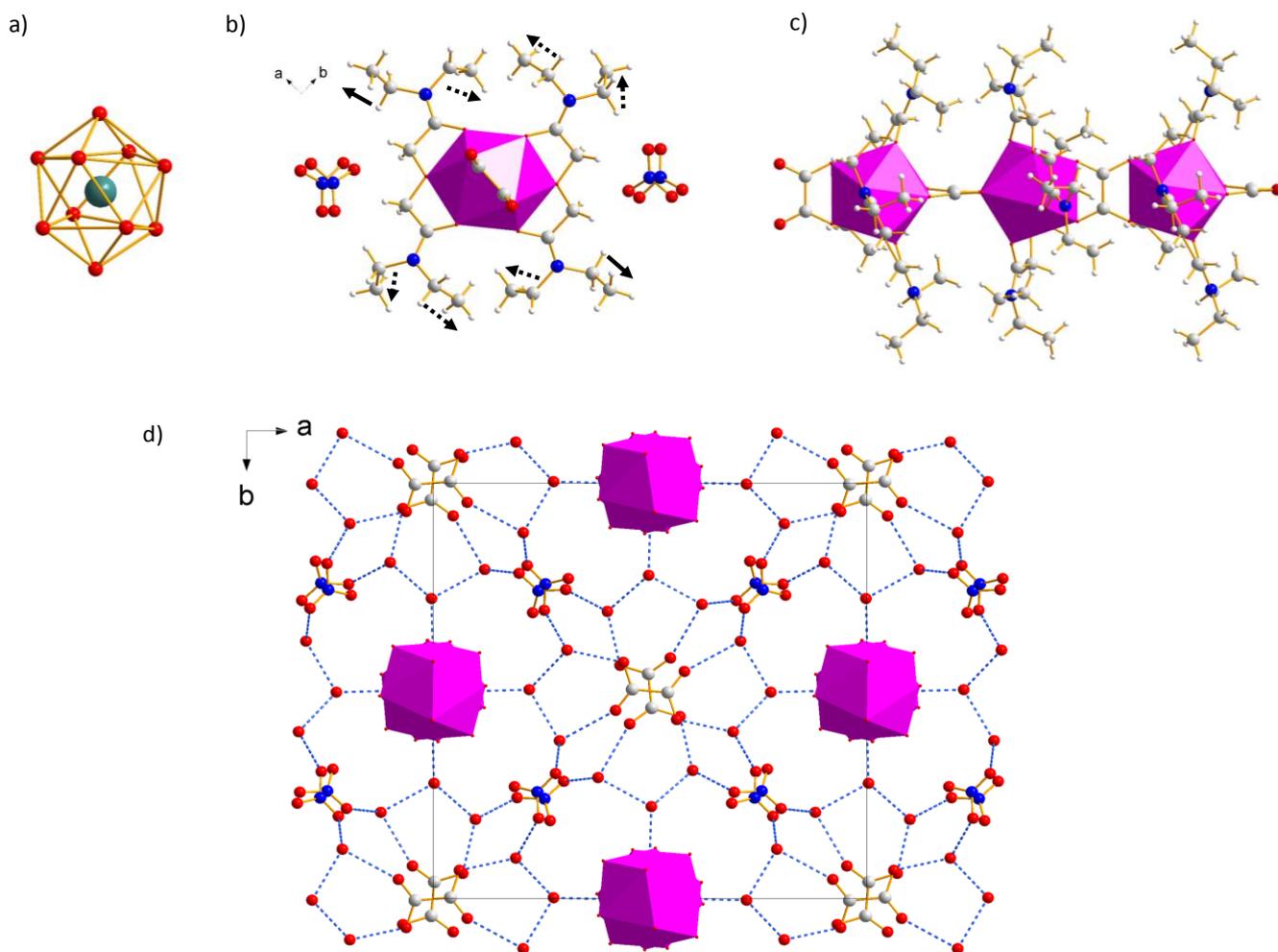


Figure 2: Crystal structure of $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)][\text{NO}_3]_2[\text{H}_2\text{C}_2\text{O}_4] \cdot 6\text{H}_2\text{O}$ (**1**). The ten-fold coordination sphere around Th forms a bicapped square antiprism (a) which summits are occupied by oxygen atoms coming from two bidentate oxalates and two tridentate TEDGA molecules. Two ethyl-groups of the TEDGA ligands have a syn-syn conformation while the other two have a syn-anti conformation (b). One out of two structural building units $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)_2]$ is surrounded by four nitrate groups (b). The $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)_2]$ share their oxalate ligands and form $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)]^{2+}_\infty$ chains (c) running along the c axis (d). The chains are maintained in a three-dimensional arrangement by means of a H-bond network (blue dotted lines) involving the nitrate anions, oxalic acid and water molecules (d). Legend: Th^{4+} are in green, C in grey, O in red and N in blue. The black arrows show the orientation of the ethyl groups over the plane defined by N-C-C atoms: full line: up, dotted line: down. The TEDGA molecules were removed for clarity in the H-network representation.

Crystal structure of (2)

Compound (**2**), $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)_2][\text{H}_2\text{C}_2\text{O}_4]_2 \cdot 2\text{H}_2\text{O}$, crystallizes in the monoclinic space group $P2_1/n$ ($n^\circ 14$) with the unit cell parameters: $a = 12.246(2) \text{ \AA}$, $b = 32.253(5) \text{ \AA}$, $c = 12.256(2) \text{ \AA}$ and $\beta = 106.741(1)^\circ$. The ten oxygen atoms surrounding Th^{4+} form a bicapped square antiprism polyhedron (Figure 3a). The 10-fold coordination involves six oxygen atoms coming from two tridentate TEDGA ligands and four oxygen atoms provided by two bidentate oxalate ligands, leading to structural building units (SBU) with the same formula as observed in (**1**), $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)_2]$ (Figure 3b). The Th-O distances range between

2.422(6) and 2.721(6) Å, the longest Th-O distances being representative of the Th-O_{ether} bonds (2.7Å) and the shortest of the Th-O_{carbonyl} and Th-O_{oxalate} ones (2.4Å) (Table 2).

The two TEDGA ligands show, both, a planar geometry. In TEDGA 1, the ethyl groups are in a syn-anti conformation. In TEDGA 2 the two conformations, syn-anti and syn-syn, are found since the C3 atoms half occupy two crystallographic positions leading to two orientations of the C3-C4 ethyl groups (Figure 3b).

The oxalate ligands are in a bis-monodentate coordination mode leading to a 0D compound. The neutral SBU are assembled by hydrogen bonds which involve two oxalic acid uncoordinated to Th⁴⁺ and two water molecules (Figure 3c). The hydrogen bonds network between H₂C₂O₄, H₂O and [Th(TEDGA)₂(C₂O₄)₂] forms [Th(TEDGA)₂(C₂O₄)₂][H₂C₂O₄]₂.2H₂O layers laying in the *aoc* plane (Figure 3c). The layers are stacked in *b* direction thanks to Van der Waals interaction between the TEDGA molecules (Figure 3d). The absence of strong bonding interaction between the [Th(TEDGA)₂(C₂O₄)₂][H₂C₂O₄]₂.2H₂O layers most probably explain the lack of stability of compound (2) and the difficulties in reproducing its synthesis. It has also to be noted that it is the only compound of the series with no nitrate included in the crystal structure.

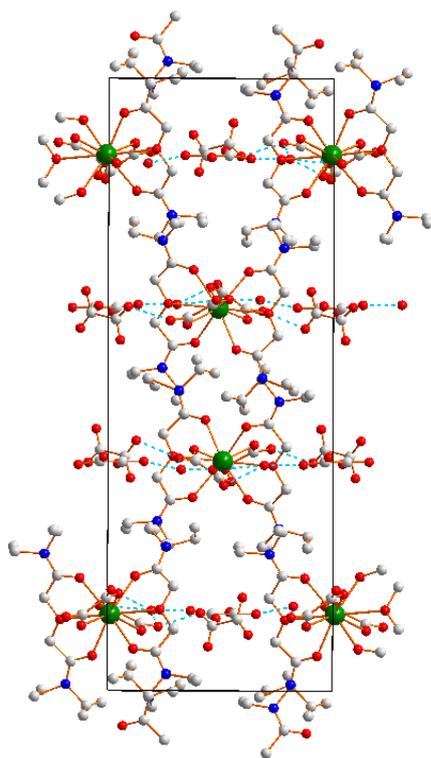


Figure 3: Crystal structure of [Th(TEDGA)₂(C₂O₄)₂][H₂C₂O₄]₂.2H₂O (**2**). The ten-fold coordination sphere around Th forms a bicapped square antiprism (a) which summits are occupied by oxygen atoms coming from two bidentate oxalates and two tridentate TEDGA molecules. Two ethyl-groups of the TEDGA ligands have a syn-syn conformation while the other two have either a syn-anti or a syn-syn conformation (b). The [Th(TEDGA)₂(C₂O₄)₂] SBU are maintained in a two-dimensional arrangement by means of a H-bond network (blue dotted lines) involving two oxalic acid and two water molecules (c). Legend: Th⁴⁺ are in green, C in grey, O in red and N in blue. The black arrows show the orientation of the ethyl groups over the plane defined by N-C-C atoms: full line: up, dotted line: down. The TEDGA molecules were removed for clarity in the H-network representation.

Crystal structure of (3)

Compound (3), $[\text{Th}(\text{TEDGA})_4][\text{NO}_3]_4 \cdot 4\text{H}_2\text{O}$, crystallizes in the monoclinic space group $C2/c$ ($n^\circ 15$) with $a = 26.5966(13) \text{ \AA}$, $b = 15.4489(7) \text{ \AA}$, $c = 18.5582(9) \text{ \AA}$ and $\beta = 116.528(1)^\circ$. Th^{4+} is coordinated by four tridentate TEDGA leading to an uncommon coordination number of 12 (Figure 4a) instead of the 8 to 10-fold oxygen coordination usually reported.²⁷ The Th-O distances, between $2.500(1) \text{ \AA}$ and $2.681(1) \text{ \AA}$ (table 2), are much shorter than the Th-O distances calculated for a 12-fold coordination (2.87 \AA).²⁸ Indeed, the Th-O distances are equivalent to those calculated for $\text{Th}(\text{DGA})_3$ ²⁸ which shows the strong interaction existing between the Th^{4+} cations and TEDGA molecules in compound (3).

The dihedral angles between the planes including the amide functions of each TEDGA are close to 140° which indicates a strong constrain of the TEDGA ligands. Moreover, the ethyl groups are in a syn-anti conformation, most probably in order to reduce the steric hindrance (Figure 4b).

Four nitrate anions surround the isolated entities $[\text{Th}(\text{TEDGA})]^{4+}$ (Figure 4c). They contribute to stabilize the overall structure by electrostatic interaction involving $[\text{Th}(\text{TEDGA})]^{4+}$ and hydrogen bonds involving water molecules and forming $(\text{NO}_3)_4(\text{H}_2\text{O})_4$ clusters (figure 4d).

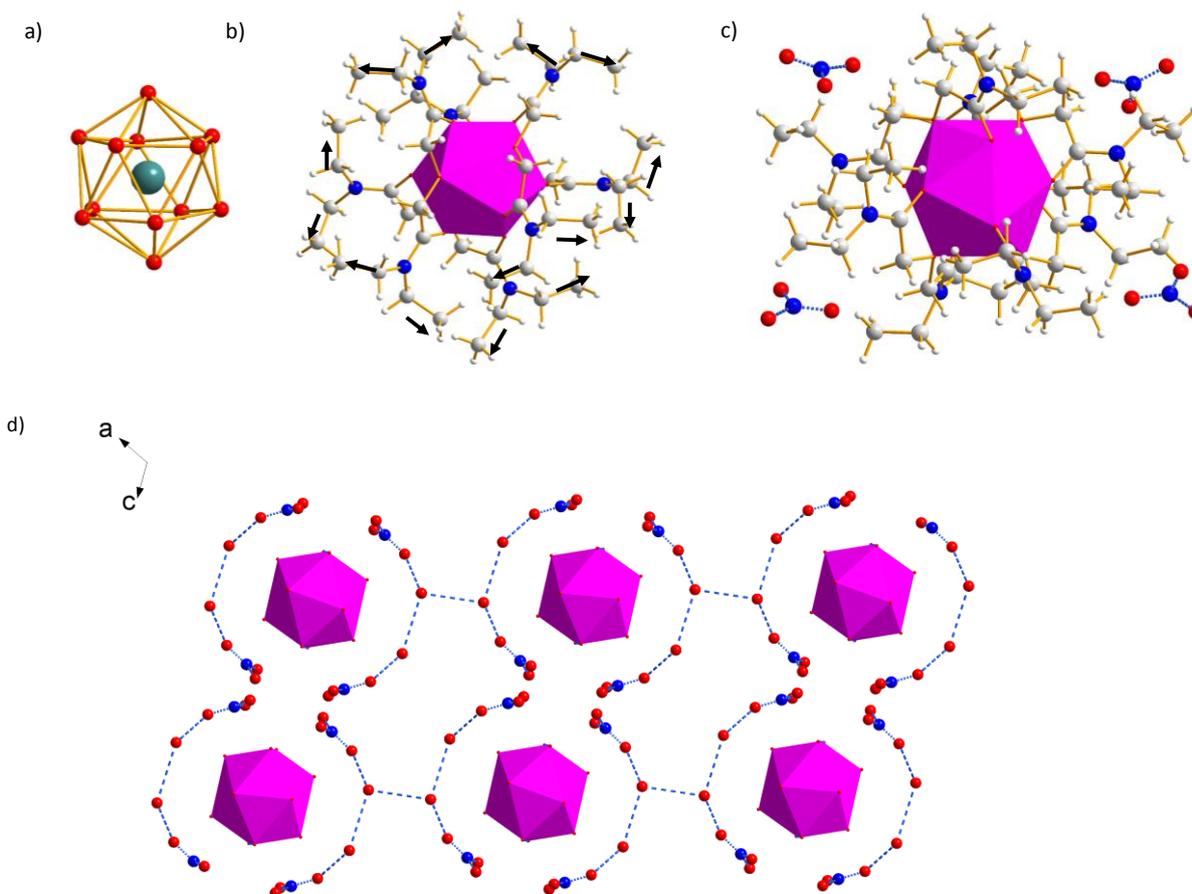


Figure 4: Crystal structure of $[\text{Th}(\text{TEDGA})_4][\text{NO}_3]_4 \cdot 4\text{H}_2\text{O}$ (3). Each of oxygen atoms of the twelve-fold coordinated Th (a) belongs to a tridentate TEDGA molecules. The ethyl-groups of the four TEDGA ligands have

a syn-anti conformation (b). The $[\text{Th}(\text{TEDGA})_4]^{4+}$, surrounded by four nitrate anions (c, d), are maintained in a three-dimensional arrangement thanks to the electrostatic interactions and the H-bond network (blue dotted lines) between the nitrate anions and the water molecules (d). Legend: Th^{4+} are in green, C in grey, O in red and N in blue. The black arrows show the unique syn-anti orientation of the ethyl groups. The TEDGA molecules were removed for clarity in the H-network representation.

Crystal structure of (4)

Compound **(4)**, $[\text{Th}_2(\text{C}_2\text{O}_4)_3(\text{TEDGA})_4][\text{NO}_3][\text{HC}_2\text{O}_4][\text{H}_2\text{C}_2\text{O}_4] \cdot 4.7\text{H}_2\text{O}$, crystallizes in a triclinic P-1 space group with $a = 15.6611(7) \text{ \AA}$, $b = 17.9082(9) \text{ \AA}$, $c = 18.1814(7) \text{ \AA}$, $\alpha = 89.896(2)^\circ$, $\beta = 65.549(2)^\circ$ and $\gamma = 87.623(2)^\circ$. The cationic environment is similar for the two independent thorium which are surrounded by ten oxygen atoms, forming a bicapped square antiprism (Figure 5a). As observed in compounds **(1)** and **(2)**, six oxygen atoms come from the TEDGA ligands and four come from two oxalate ligands (Figure 5b). The $\text{Th}-\text{O}_{\text{oxalate}}$ distances belong to $2.416(2) \text{ \AA} - 2.509(2) \text{ \AA}$. The longest $\text{Th}-\text{O}_{\text{oxalate}}$ distances come from the bridging oxalate (O7, O8 and O19, O20; $d_{\text{mean}} = 2.500 \text{ \AA}$) and the shortest come from the terminal oxalate (O9, O10 and O21, O22; $d_{\text{mean}} = 2.422 \text{ \AA}$). The $\text{Th}-\text{O}_{\text{carbonyl}}$ distances have values close to the $\text{Th}-\text{O}_{\text{oxalate}}$ distances ($d_{\text{mean}} = 2.463 \text{ \AA}$) while the $\text{Th}-\text{O}_{\text{ether}}$ bond-lengths are longer ($d_{\text{mean}} = 2.657 \text{ \AA}$) (Table 2).

The oxalates, Ox1, coordinate the thorium cations in a bidentate mode η^2 while the oxalates, Ox2, are in a bridging bis-bidentate mode $\mu_2-\eta^2:\eta^2$ which leads to the formation of dimeric units $[\text{Th}_2(\text{C}_2\text{O}_4)_3(\text{TEDGA})_4]^{2+}$ (Figures 5c, 5d). One out of two dimeric units $[\text{Th}_2(\text{C}_2\text{O}_4)_3(\text{TEDGA})_4]^{2+}$ is surrounded by two nitrate anions.

The terminal oxalates, Ox1a and Ox1b, part form the hydrogen-bond network with water molecules and oxalic acids (Figure 5d). In order to respect the global neutral charge of the network, among the different oxalate acids, one must be partially deprotonated. According to the crystal structure determination (H positioning and Wickoff positions), the planar oxalate Ox3 is this peculiar one. Finally, seven water molecules are located in the interstices, two of them (O30 and O32) are involved in the hydrogen bonding with the terminal oxalate of the dimeric units (Ox1a and Ox1b), and the other five are involved in the hydrogen bonding with the uncoordinated oxalic parts, the nitrate anions and the bridging oxalate, Ox2a and Ox2b, thereby ensuring the stability of the network.

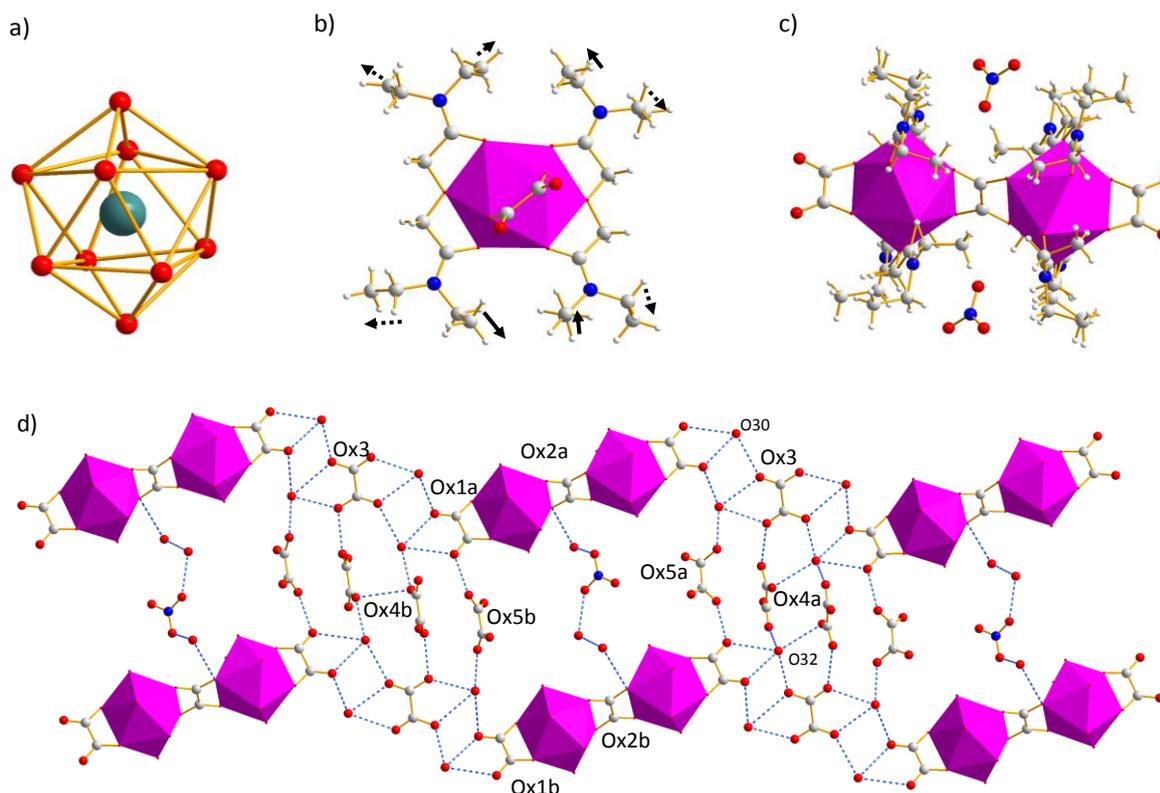


Figure 5: Crystal structure of $[\text{Th}_2(\text{C}_2\text{O}_4)_3(\text{TEDGA})_4][\text{NO}_3][\text{HC}_2\text{O}_4][\text{H}_2\text{C}_2\text{O}_4]_4 \cdot 7\text{H}_2\text{O}$ (4). The ten-fold coordination sphere around Th forms a bicapped square antiprism (a) which summits are occupied by four oxygen atoms coming from two bidentate oxalates and by 6 oxygen atoms originating from two tridentate TEDGA molecules. One ethyl-group of the TEDGA ligands has a syn-syn conformation while the other three have a syn-anti conformation (b). One out of two dimeric units $[\text{Th}_2(\text{Ox})_3(\text{TEDGA})_4]^{2+}$ is surrounded by two nitrate which are included in the second coordination sphere (c). The dimeric units are maintained in a three-dimensional arrangement by means of a H-bond network (blue dotted lines) between the nitrate anions, oxalic acid and water molecules (d). **Legend:** Th⁴⁺ are in green, C in grey, O in red and N in blue. The black arrows show the orientation of the ethyl groups over the plane defined by N-C-C atoms: full line: up, dotted line: down. The TEDGA molecules were removed for clarity in the H-network representation.

Thorium coordination

Although the connectivity of the networks differs between (1), (2) and (4), the first coordination sphere of the thorium cation remains equivalent in these three compounds. The actinide is located at the center of a bicapped square antiprism (CN: 10) whose summits of the square faces are made of two carbonyl oxygen atoms from one TEDGA and two oxygen atoms coming from two different oxalate groups. The two ether oxygen atoms of the TEDGA ligands occupy the capping positions. Unlike in (1), (2) and (4), the actinide in compound (3) presents a 12-fold coordination forming an icosahedron whose summits are composed by the oxygen atoms of TEDGA parts, without oxalate's bonding. An overview of the literature indicates that 12-coordinated thorium atoms are found in thorium nitrate compounds $[\text{Th}(\text{NO}_3)_6][\text{L}]$ with L = bipyridinium,^{29–31} oxadiazole,³² phosphonium,³³ oxonium,³⁴ or $[\text{Th}(\text{NO}_3)_{3-5}][\text{M}]$ with M = phosphate,³⁵ sulfoxide³⁶ and phosphine³⁷ but remain rarely encountered (only 26 results in the conquest database). To the best of our knowledge, it is the first compound presenting such coordination number without any nitrate anion belonging to the coordination sphere. The presence of TEDGA in the coordination sphere of each of the

compounds shows the great complexing behavior and stability of Th(TEDGA)_x complexes despite the presence of oxalic acid which is known to form insoluble and stable thorium oxalate Th(C₂O₄)₂·nH₂O.^{38,39}

The Th-O_{ether} mean distances (2.648 to 2.719Å) are almost equivalent through the series despite the 4-fold TEDGA coordination of Th(IV) in (3) and the higher ionic radius expected for a twelve-fold coordinated Th(IV) compared to a ten-fold one (1.21Å vs 1.13Å). These Th-O_{ether} bond values are higher than the mean Th-O_{oxalate} and Th-O_{carbonyl} distances (Table 2), while the Th-O_{oxalate} distances, between 2.423(7) and 2.509(2)Å, are similar to those encountered in the literature for μ₂-η²:η² and μ₂-η² bridging oxalate ligands.^{22,40} The Th-O_{carbonyl} bond values are close for compounds (1), (2) and (4). Their values, between 2.421(6) and 2.532(1)Å, lie within the same range than previously described for carbonyl derivative based compounds^{41,42} however the Th-O_{carbonyl} bond seems affected by the ionic radius variation of Th(IV) since compound (3) presents a larger Th-O_{carbonyl} mean distance (2.516Å) than compounds (1), (2) and (4) (2.427, 2.461 and 2.463Å, respectively). These values remain consistent with the Th-O_{carbonyl} distances determined by the calculation.²⁸ So far, only two compounds based on An(IV) have been described in the literature: (Pu^{IV}(TMDGA)₃)(NO₃)₃.MCN (TMDGA = tetramethyldiglycolamide ; MCN = acetonitrile) and (Pu^{IV}(TMDGA)₃)(NO₃)₃.ETOH.¹⁷ In these examples, the Pu(IV) cations are surrounded by nine oxygen atoms coming from the three TMDGA which form a twisted tricapped trigonal prism. The ether oxygen atoms occupy the capping position while the oxygen atoms belonging to the carbonyl function form the summits of the trigonal faces. The Pu-O distances show the same trend than observed in the present study in that the Pu-O_{ether} distances are longer than the Pu-O_{carbonyl} distances (~0.18Å difference). The Pu-O distance are, on average, *ca.* 0.15-0.19Å shorter than the Th-O distances which may account for the larger ionic radius of Th(IV) than Pu(IV) together with the higher coordination numbers of Th(IV) in the present compounds than the one of Pu(IV) in the previously reported Pu^{IV}(TMDGA)₃(NO₃)₃ solvates. The presence of an additional TEDGA around the thorium cation in (3) may also be related to the larger ionic radius of Th(IV) than Pu(IV) (~0.09Å difference for a same coordination number), thereby allowing a higher coordination number. The DFT calculations performed by Gong *et al*²⁸ on the Thorium-tetramethyldiglycolamide (TMDGA) system showed that the structure of Th(TMDGA)₄ is less stable than the one of Th(TMDGA)₃ due to larger Th-O distances. One may note that the experimental Th-O distances, more specifically the Th-O_{ether} distances experimentally determined in the present study, are shorter than the calculated distances.

In (1) the angle formed by two oxalate parts coordinating Th is of 90° while it is lower in (2) and (4) with a mean value of about 71° and 80°, respectively (Table S6). The opposite TEDGA ligands coordinating Th in compounds (1), (2), (3) and (4) are turned by an angle varying from 31° to 69° (Table S7). No relationships could be established between the torsion angle of the TEDGA molecules and the dihedral angle formed by their mean planes (Table S8).

Table 2: Minimal, maximal and mean Th-O distances in (1), (2), (3) and (4).

	Th-O (min – max)					Th-O (mean)				
	1	2	3	4		1	2	3	4	ref
Th-O _{ether} (Å)	2.648 (6)	2.717(6)	2.666(1)	2.622(2)	Th-O _{ether} (Å)	2.648	2.719	2.674	2.657	2.697 ⁴¹ 2.623 ^{43,44}
Th-O _{carbonyl} (Å)	2.421(6)	2.450(7)	2.500(1)	2.434(2)	Th-O _{carbonyl} (Å)	2.427	2.461	2.516	2.463	2.458 ²⁵ 2.411 ⁴¹
Th-O _{oxalate} (Å)	2.487(5)	2.423(7)	–	2.416(2)	Th-O _{oxalate} (Å)	2.490	2.447	–	2.461	2.491 ⁴⁰ 2.485 ²⁵
	2.492(5)	2.468(6)	–	2.509(2)						

Nitrate positioning

In all the compounds reported herein, the nitrate anions are found in the interstices, as for instance in $(Ln(TEDGA)_3)(NO_3)_3 \cdot 4H_2O$ with $Ln = Tb, Dy, Ho, Er, Tm, Yb, \text{ and } Lu$ ¹², $(Yb(\text{tris-DGA}))(\text{NO}_3)_3$, $(Yb(i\text{-PrDGA})_3)(\text{NO}_3)_4$,¹¹ $(Pu^{IV}(TMDGA)_3)(\text{NO}_3)_3 \cdot \text{MCN}$ and $(Pu^{IV}(TMDGA)_3)(\text{NO}_3)_3 \cdot \text{EtOH}$.¹⁷ One may note that no solid compounds containing simultaneously nitrate and DGA ligands in the same coordination of the f-element was reported up to date and that the only mixed ligands compounds including DGA (L) are found only with the lightest lanthanides, La and Ce. These compounds are heteroleptic which means that $Ln(\text{NO}_3)_6$ polyhedra coexist in the crystal structure besides the $Ln(\text{DGA})_n$ entities leading to $(LaL_3)(La(\text{NO}_3)_6)$ and $(CeL)(Ce(\text{NO}_3)_6)(\text{CH}_3\text{OH})(\text{C}_4\text{H}_{10}\text{O})$ formula. In the present study, the nitrate anions remain close to the thorium cations, but do not integrate the coordination sphere. They occupy either the free spaces between the two arms of TEDGA ligands in compounds (1) and (3) (Figures 2b and 4c) or the free spaces between the TEDGA ligands in compound (4) (Figure 5c). According to these structural results and to the crystal structure previously reported, one can assume that the presence of DGA ligands in the coordination sphere of the f-cations preclude the integration of nitrate in the same environment.

Geometry of the free di- and mono-protonated oxalic acids in (1), (2) and (4)

The oxalate ligands coordinating Th(IV) in compounds (1), (2) and (4) are nearly planar (Table S4). In these oxalate ligands, the C-O distances are slightly different in accordance with the bridging mode of the oxalate groups. In the $\mu_2\text{-}\eta^2\text{:}\eta^2$ oxalates, all the C-O distances are equivalent to 2.24-2.26 Å while in the $\mu_2\text{-}\eta^2$ terminal oxalates the C-O distances with O atoms in the coordination sphere of Th(IV) tend to be slightly longer (1.25-1.28 Å) than the C-O distances with free oxygen atoms (1.22-1.26 Å). The oxalic acid molecules can be planar⁴⁵, as the oxalate groups, but their carboxylate plans can also display a twisted angle up to 90°. ^{45,46} In the present compounds the free di- and mono-protonated oxalic acids exhibit a twisted angle varying from 7 to 88° which shows that the oxalic acid can adopt different geometries (Figure 6, Table S9). The nomenclature introduced by Nieminen et al. uses the

lower case letters c (cis) and t (trans) to describe the relative orientation of the O-H and C-C bonds and the upper letters C (Cis) or T (Trans) to define the relative orientations of the C=O bond.⁴⁷ In compound (1) the oxalic acid has a conformation tTt and exhibit a torsion angle, τ , equal to 19° . In compound (2) the two oxalic acids with the same conformations tTt, Ox2 and Ox3, shows torsion angles of about 7 - 8° . In compound (4) different conformations of oxalic acid coexist: the tCt conformation with torsion angles equal to 7 , 19 and 88° for the oxalates ox4a, ox4b and ox5a, respectively, and the tTt conformation for the oxalate ox5b (τ equal to 39°) (Figure 6). On the basis of these results, it is impossible to establish a relation between the torsion angle and the oxalic acid conformation. However, a careful examination of the C-O distances in compounds (2) and (4), which crystal structure was solved at 100K , reveal undoubtedly that the C-O distances around 1.2\AA can be attributed to the C=O bonds while the C-O distances around 1.3\AA are related to the C-OH bonds. The 1.3\AA distance characteristic of C-OH is also found in the monoprotonated oxalate ox3 of compound (4).

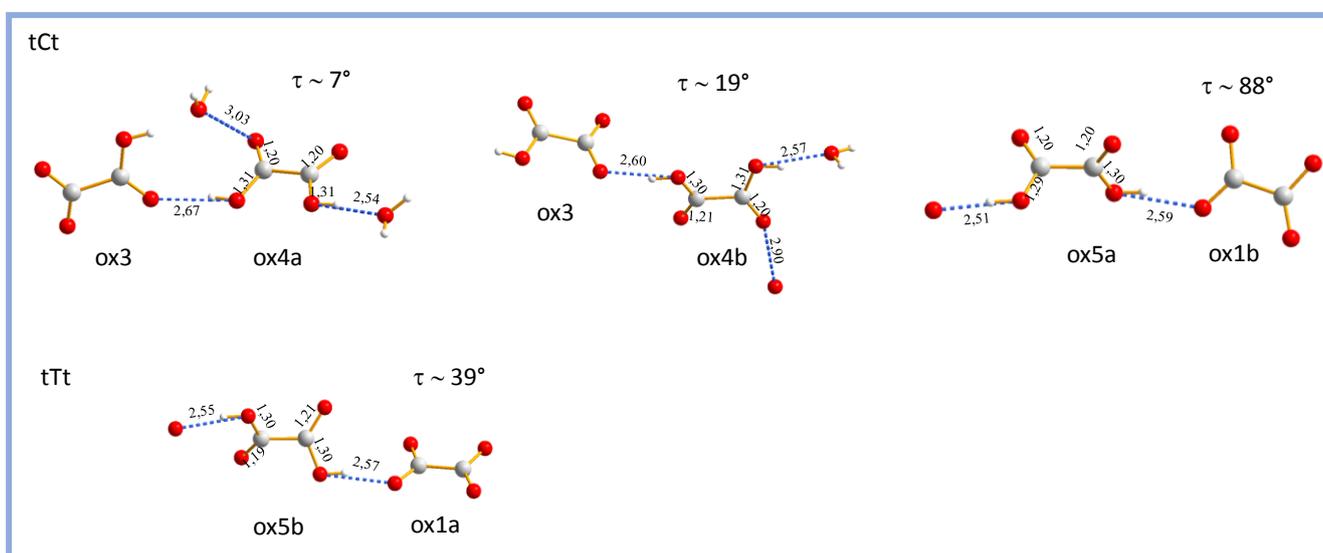


Figure 6: Oxalic acids in the crystal structure of $[\text{Th}_2(\text{C}_2\text{O}_4)_3(\text{TEDGA})_4][\text{NO}_3][\text{HC}_2\text{O}_4][\text{H}_2\text{C}_2\text{O}_4]_4 \cdot 7\text{H}_2\text{O}$ (4).

Comparison of the spectroscopic data for TEDGA, (1), and (3)

We were able to obtain the compound (1) and (3) as pure powders, the last by modifying the temperature of synthesis. The X-ray diffraction pattern and thermal decomposition of compounds (1) and (3) are shown in Figures S2 and S5, while IR spectra are presented in Figure 7. Between 4000 cm^{-1} and 2000 cm^{-1} , the spectra show the three bands characteristic of the $\nu_{\text{C-H}}$ stretching of the methylene and methyl groups. One can also notice the presence of a large band between 3600 cm^{-1} and 3400 cm^{-1} due to the presence of water molecules in the structures. In the region between 2000 cm^{-1} and 400 cm^{-1} , the peak at 1639 cm^{-1} corresponding to the carbonyl stretching of the TEDGA is shifted at 1612 cm^{-1} and 1607 cm^{-1} in (1) and (3) spectra, respectively, because of the coordination of the TEDGA to the actinide.^{12,48} The C-O-C of the TEDGA exhibits two vibrational bands at 1125 cm^{-1} (ν_{as}) and 1039 cm^{-1} (ν_{s}) for the free ligands.⁵⁰ Those bands are slightly shifted due to the coordination

of the ether oxygen atom. The bands at 826, 1282 and 1385 cm^{-1} correspond to the vibrational bands of uncoordinated nitrate anions.^{49–51} The compound (1) spectrum displays one additional band at 1730 cm^{-1} due to the presence of oxalic acid molecules in the crystal structure. For this compound, the band at 1607 cm^{-1} might be attributed to the combination of the carbonyl stretching arising from the TEDGA part or to the asymmetric stretching of the oxalate part.^{25,52,53} The symmetric stretching bands are observed in 1300–1350 cm^{-1} range.^{25,52}

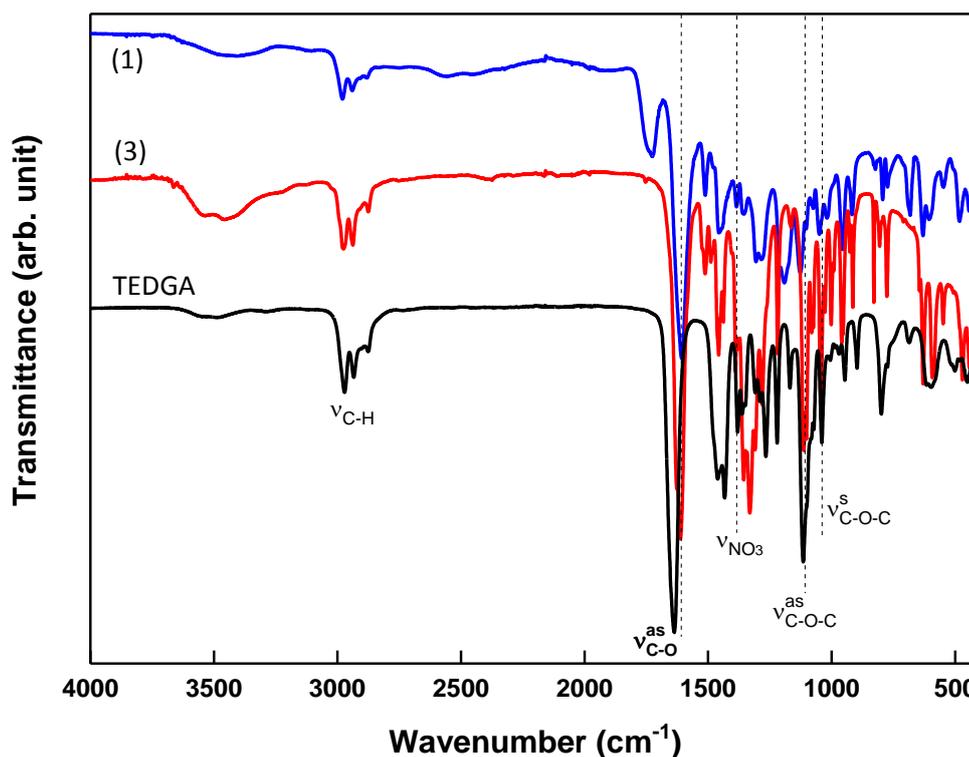


Figure 7: Infrared spectra of TEDGA (in black), $[\text{Th}(\text{TEDGA})_2(\text{C}_2\text{O}_4)][\text{NO}_3]_2[\text{H}_2\text{C}_2\text{O}_4] \cdot 6\text{H}_2\text{O}$ (1) (in blue) and $[\text{Th}(\text{TEDGA})_4[\text{NO}_3]_4 \cdot 4\text{H}_2\text{O}$ (3) (in red).

Conclusions

Even if the use of diglycolamide molecules for the nuclear waste treatment has been studied for long time, the ability of these organic compounds for complexing the lanthanides or the renewable elements, plutonium or uranium, is still a hot topic and the knowledge of the different possible phases able to be formed during a process, a very crucial point. The pre-complexation of the water soluble TEDGA and thorium(IV), followed by an addition of oxalic acid, has allowed to isolate and characterize four new compounds containing Th(IV) and TEDGA, by successive single-crystal to single-crystal phase transformations. Three of them are homoleptic mixed ligands compounds containing two TEDGA and two oxalate in the coordination sphere of Th(IV) while the fourth compound exhibits four TEDGA in the cation environment leading then to an uncommon coordination number of 12. Although the

mixed oxalate-TEDGA ligands compounds present the same coordination sphere, the dimensionality of the networks varies from linear chains to isolated entities or dimeric units. The TEDGA molecule shows then a great ability to complex the actinide cation (thorium in the present case) despite the presence of oxalic acid. The influence that TEDGA might have on the structural and microstructural properties of the precipitate during the next step of the industrial process, *i.e.* the oxalic precipitation, is under study by carrying out oxalic precipitation and crystal growth of $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ in presence of TEDGA.

Supporting information

Comparison between simulated and experimental powder pattern for **(1)**, **(3)** and the mixtures **(2) + (3)** and **(1) + (4)** can be found on figure S1-S4 in supporting information. The figure S5 contains the thermal analysis of **(3)**.

The crystallographic data of (1), (2), (3) and (4) are available in CIF format.

Acknowledgements

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