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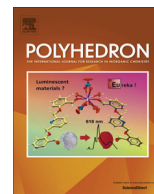


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Synthesis, spectroscopic characterization and crystal structures of thorium(IV) mononuclear lactato and hexanuclear formate complexes

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ABSTRACT

Two thorium(Th) complexes with lactate or formate have been synthesized and characterized. Th(C₃H₅O₃)₄(H₂O)₂ (**1**) [C₃H₅O₃H = lactic acid] has a mononuclear structure with ten-fold coordinated Th polyhedron in deformed bicapped square antiprism by four chelating lactate ligands via both carboxylate O and the alcohol O atoms in addition to two coordinated water molecules. The lactate ligands are enantiomer with equal proportion of *R*- and *S*-isomers. [Th₆(O)₄(OH)₄(HCO₂)₁₂(H₂O)₆]·5H₂O (**2**) [HCO₂H = formic acid] is a hexanuclear Th nanocluster constructed by four oxo-, four hydroxyl, twelve μ₂-bridging formate ligands and six water molecules. The calculated bond valence sums are in good agreement with the presence of equal numbers of oxo- and hydroxyl groups in the cluster. Thermal studies confirmed that both complexes lost water molecules first followed by the decomposition of the organic ligands to form ThO₂ as the final product. The presence of bridging OH-groups in both complexes has been proven by Raman spectroscopy.

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1. Introduction

Lanthanide (Ln) complexes with carboxylate ligands have been extensively studied and many of them have been found practical applications in biological and clinical areas as well as in advanced functional materials, e.g. nonlinear optical, organic light emitting diode, metal organic frameworks and single molecule magnets [1–3]. In contrary, the structural chemistry of actinide (An) ions with carboxylate ligands is relatively less studied and mainly focussed on uranyl ion [U(VI)] [4]. For An ions in lower valence states, only oxalato complexes have been extensively studied [5] due to the widely use of oxalic acid as a precipitation agent for the separation of minor An in the current nuclear fuel cycle [6].

There has been renewed interest in the thorium(Th) fuel cycle in recent years, driven by the potential for an alternative fuel cycle to reduce proliferation concerns, waste management challenges associated with the uranium fuel cycle and vast cheap thorium resources available to the market [7]. Consequently, there is a growing international interest in thorium structural chemistry with carboxylate ligands. In addition, from the pure structural

chemistry point of view, it is of interest to explore the rich structural diversity of Th(IV) ion with variety of carboxylate ligands, subsequently to study the relationship between structures and properties leading to their potential applications.

As the simplest monocarboxylic acid, formic acid can form several types of complexes with Ln ions through both chelating and bridging coordination modes [8]. The formation of hexanuclear complexes for An(IV) ions with formic acid have been reported [9]. The hexanuclear Th species has been proven to be present as a minor speciation in very acidic aqueous solutions [9,10] and generally the hexanuclear complexes can be prepared from the mixture of An(IV) nitrate and formic acid in aqueous solutions at low pH (~1) conditions. However, the reaction of An(IV) with formate in near neutral pH aqueous solutions has not been addressed properly. In addition, single and double Ln complexes with lactate have been established [11]. As for An ions, only a U(VI) lactate structure was reported [12]. It has a two-dimensional (2D) layered structure built with pentagonal bipyramidal uranyl centres linked through two types of bridging lactate ligands. There is no Th(IV) lactate structure being reported so far. It is of our interest to reveal the structures of Th(IV) with lactate ligand as well as with formate but prepared in near neutral pH conditions, subsequently, examine their spectroscopic and thermal properties. Herein we report the synthesis, spectroscopic and thermal studies, and structures of a

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mononuclear complex $\text{Th}(\text{C}_3\text{H}_5\text{O}_3)_4(\text{H}_2\text{O})_2$ (**1**) and a hexanuclear complex $[\text{Th}_6(\text{O})_4(\text{OH})_4(\text{HCO}_2)_{12}(\text{H}_2\text{O})_6] \cdot 5\text{H}_2\text{O}$ (**2**).

2. Results and discussion

2.1. Structure description and discussion

The crystal data and refinement details for **1** and **2** are summarized in Table 1. The asymmetric unit of **1** consists of a Th atom, two coordinated lactate ligands and one coordinated water molecule. The expansion by symmetry operations suggests that the Th atom is ten-fold coordinated with four lactate ligands all chelating through one carboxylate O atom and the alcohol O atom as well as two coordinated water molecules (Fig. 1a and b). The Th atom has a slightly distorted bicapped square antiprismatic polyhedron (Fig. 1c). The polyhedral packing view (Fig. 1d) highlights the packing of the monomeric complex in the crystal lattice. The Th–O bond lengths are from 2.432(7) Å to 2.447(6) Å for the carboxylate O atoms, 2.480(5) Å to 2.581(4) Å for the alcohol O atoms and 2.540(5) Å for water molecules. Note the four lactate ligands all have chiral carbon atoms with two ligands in *R*- and two in *S*-isomers. The coordinated water molecules and the alcohol O atoms are involved in hydrogen bonding with the carboxylate O atoms from the nearby Th centres leading the monomeric structure into three dimensions.

Complex **1** is the first reported crystal structure of Th(IV) with lactate ligand. For other An ions, a lactate complex of uranyl ion was previously reported [12]. It has a 2D layered structure built with pentagonal bipyramidal uranyl centres linked through two types of bridging lactate ligands. Since the coordination environment of uranyl ion is quite different from those of the An(IV) ions as the coordination of former only limits to the equatorial planes, it is of more interest to compare the coordination environment of **1** with the published structures of Ln ions incorporating lactate

Table 1

Crystal data and refinement details for **1** and **2**.

Complex	1	2
Formula	$\text{C}_{12}\text{H}_{18}\text{O}_{14}\text{Th}$	$\text{C}_{12}\text{H}_{24}\text{O}_{48}\text{Th}_6$
Formula weight	618.30	2328.55
Crystal system	orthorhombic	cubic
Space group	<i>Fdd2</i>	<i>P2_13</i>
<i>a</i> (Å)	15.719(3)	18.457(2)
<i>b</i> (Å)	16.155(3)	18.457(2)
<i>c</i> (Å)	14.115(3)	18.457(2)
<i>V</i> (Å ³)	3584.3(12)	6288 (2)
<i>Z</i>	8	4
μ (mm ^{−1})	8.393	15.202
Minimum/Maximum θ (°)	3.617/27.891	2.532/24.983
<i>D</i> _{calcd} (g cm ^{−3})	2.292	2.460
Goodness-of-fit (GOF)	0.63	1.560
Final <i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0216	0.0352
Final <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0642	0.0994

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

ligands. The coordination environments of **1** and two types of lactate complexes with Ln ions are summarized in Table 2. Some interesting results can be obtained from the comparison. First, the relatively larger cation size of Th(IV) allows the coordination number (CN) of 10 compared to CN of 8 for Ln ions. Second, the average M–O bond lengths decrease from 2.419(1) Å for Sm–O to 2.406(2) for Eu–O and 2.371(2) Å for Tb, consistent with the Ln contraction theory. In contrast, complex **1** has a longer average Th–O bond length of 2.496(6) Å, due to the relatively bigger ionic radius and higher CN of Th(IV) ion.

The asymmetric unit of **2** contains two Th atoms linked through an oxo-, a hydroxyl and a bridging formate ligand; each Th atom also coordinated by a water molecule and half formate ligands with some lattice water molecules. The expansion by symmetry suggests that **2** is a hexanuclear Th cluster (Fig. 2a and b)

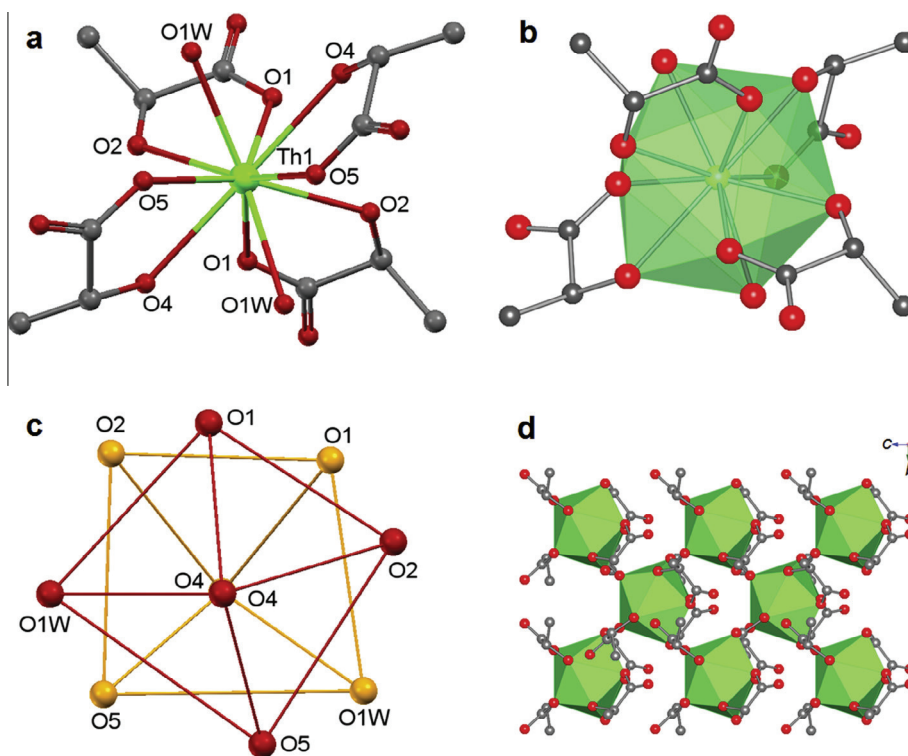
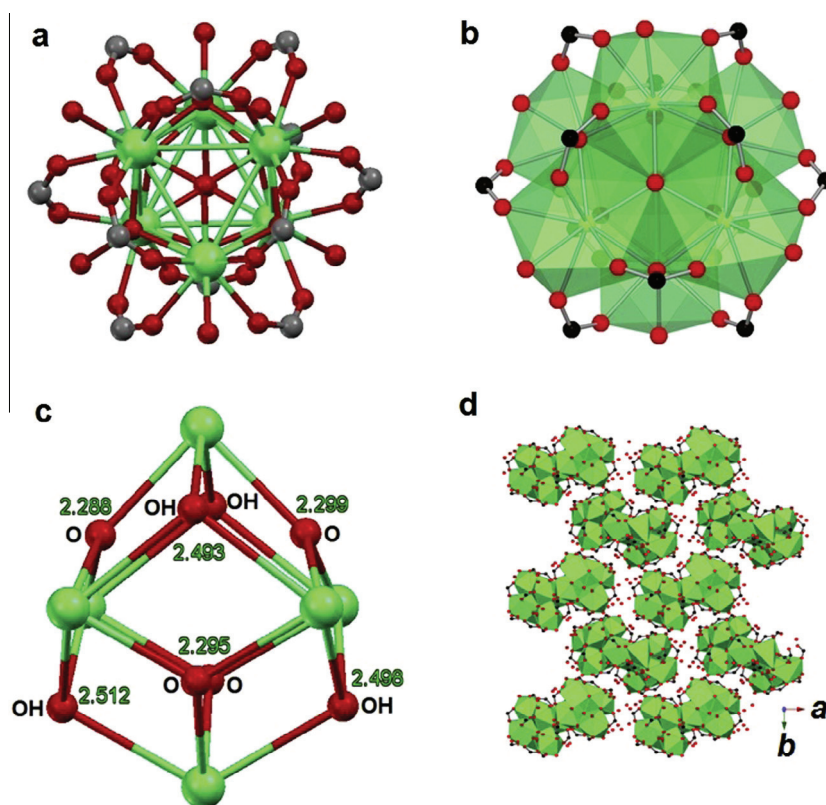


Fig. 1. The structure of **1**: ball-stick (a) and polyhedral (b) views of the Th coordination environment (Th green, O red, C grey), a slightly distorted bicapped square antiprismatic Th polyhedron (c) and Th polyhedral packing view along the *a*-axis (d). (Colour online.)

Table 2Comparison of coordination environments of **1** and Ln lactate complexes [11].

	Complex 1	NaSm(C ₃ H ₅ O ₃) ₄ ·2H ₂ O	NaEu(C ₃ H ₅ O ₃) ₄ ·2H ₂ O	Tb(C ₃ H ₅ O ₃) ₂ (H ₂ O) ₂ (ClO ₄)
Coordination number	10	8	8	8
M–O (COO [−])	2.432(7)(2X); 2.447(6)(2X)	2.350(1)(2X); 2.408(1)(2X)	2.340(2)(2X); 2.397(2)(2X)	2.300(2)(3X)
M–O (OH–C)	2.480(5)(2X); 2.581(4)(2X)	2.415(1)(2X); 2.503(1)(2X)	2.399(2)(2X); 2.490(2)(2X)	2.443(2)(3X)
M–O (OH ₂)	2.540(5)(2X)			2.370(2)(2X)
Average M–O	2.496(6)	2.419(1)	2.406(2)	2.371(2)

**Fig. 2.** The structure of **2**: ball-stick (a) and polyhedral (b) views of the Th(IV) cluster (Th green, O red, C grey/black), distorted Th atom arrangements in the cluster with equal numbers of μ_3 -bridging oxo- (O) and hydroxyl (OH) groups (c) and Th polyhedral packing view along the *c*-axis (d). (Colour online.)

containing 4 oxo-, 4 hydroxyl, 12 μ_2 -bridging formate ligands and 6 water molecules. Each Th atom is surrounded by 4 O atoms from μ_2 -HCOO[−], 4 O atoms from μ_3 -oxygen, and 1 O atom of the terminal water molecule with CN of 9 for Th. Th atoms are bridged by μ_2 -HCOO[−] through a *syn-syn* coordination mode. The arrangements of Th atoms in the cluster are distorted (Fig. 2c). Subsequent bond valence sum (BVS) calculations [13] suggest that equal numbers of μ_3 -oxo- (with calculated BVS values of 2.13 and 2.16) and μ_3 -hydroxyl (with calculated BVS values of 1.21 and 1.23) groups are present in the cluster (Fig. 2c). The diameter of the cluster measured via the two opposite coordinated water molecules is about 10.854(8) Å. The clusters are packed in crystal lattice (Fig. 2d) and the extensive hydrogen bonding between carboxylate O atoms and coordinated water molecules from nearby clusters leads the hexanuclear clusters into three dimensions (Fig. S3).

A similar compound with additional NaClO₄ and HClO₄ in the crystal lattice and slightly smaller cell was reported recently [9]. The compound was prepared from an aqueous solution containing 0.05 M Th(IV) and 1.0 M HCOOH at pH 1.0 after slow evaporation of the solvent, with a low yield (~20%). Solution speciation study also confirmed that the hexanuclear Th specie exists in fairly acidic solutions (pH 1–3) as a minor speciation [9,10]. However, in the current work, the similar phase has been prepared from an

aqueous solution with a relatively high pH value (~5.0) and a much higher yield (~80%). The fast crystallization kinetics is believed to be the driving force to move the solution speciation equilibrium towards the hexanuclear Th specie.

2.2. Thermal property

The thermogravimetric and differential thermal analysis (TG/DTA) results for **1** and **2** are shown in Fig. 3. On the DTA curve of **1** (Fig. 3a), there are a medium endotherm at ~190 °C, three small endotherms at ~265, ~685 and ~755 °C, and one large exotherm at ~395 °C. The endotherm at ~190 °C with a weight loss of ~8.0% corresponds to the loss of two coordinated water molecules (calc. 5.77%). The inconsistency between observed and calculated weight loss suggests that the loss of water process overlaps with the following decomposition process. The endotherm at ~265 °C and the exotherm at ~395 °C correspond to the decomposition of coordinated lactate ligands in several continuous steps. The two small endotherms at ~685 and ~755 °C with essentially little weight loss correspond to the formation of ThO₂ (residue: 42.9%; calc. 42.3%).

On the DTA curve of **2** (Fig. 3b), there are three endotherms at ~88, ~218 and ~265 °C, respectively. The small endotherm at

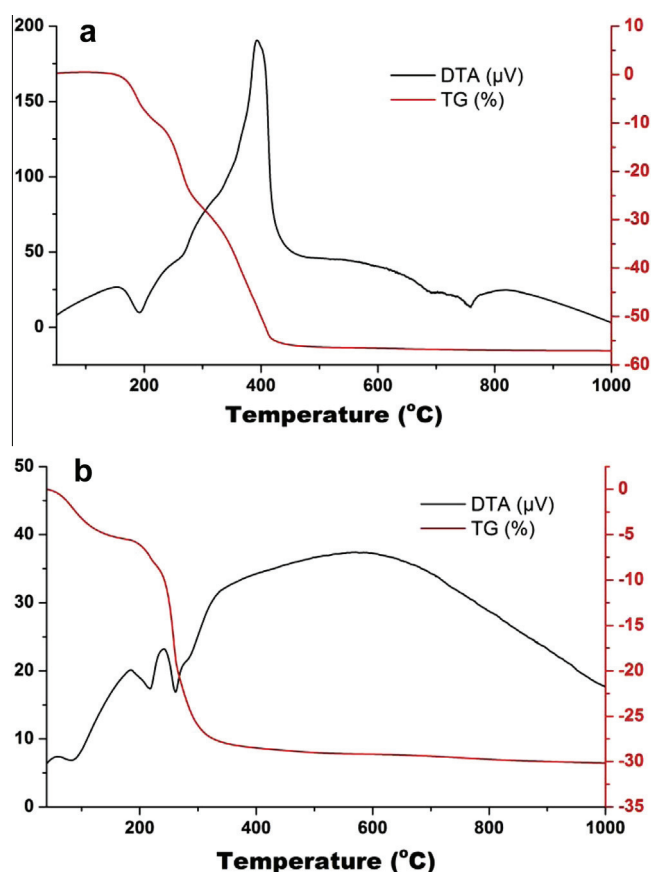


Fig. 3. Thermogravimetric and differential thermal analysis for 1 (a) and 2 (b).

~88 °C with a weight loss of ~4.9% corresponds to the loss of the five lattice and one coordinated water molecules (calc. 4.77%) whilst the two endotherms at ~218 and ~265 °C correspond to the further loss of the coordinated water molecules overlapped with the decomposition of formate ligands to form the final product of ThO₂ (residue: 69.8%; calc. 70.0%).

2.3. Raman spectroscopy

Raman spectroscopy has been used to further study the vibrational modes of the two complexes (Fig. 4). Detailed band assignments are based on some relevant Ref. [14] and summarized in Table 3. Note for both complexes, the bands below 250 cm⁻¹ are due to the lattice modes.

Complex 1: Two Raman bands at 1631 and 1585 cm⁻¹ with medium intensity have been assigned to asymmetric stretching modes of the deprotonated carboxylate groups (COO⁻). The corresponding symmetric stretching vibrations are found at 1375 and 1331 cm⁻¹. Two bands at 1450 and 1417 cm⁻¹ with nearly equal intensity have been attributed to asymmetric bending modes of CH₃ with weak CH₃ symmetric deformation bands located at 1288 and 1260 cm⁻¹. The band at 1122 cm⁻¹ with a shoulder at 1132 cm⁻¹ is a combination of C–O stretch and CH₃ rocking vibrations. Another band due to the rocking vibrations of CH₃ is found at 937 cm⁻¹ together with the OH-bending vibration where the alcohol group forms a bridge between Th and C atoms. The alkane C–C skeletal vibrations produced several Raman bands, including the C–CH₃ stretching vibrations at 1058–1045 cm⁻¹ and a very strong C–COO stretch band at 865 cm⁻¹. Raman bands at 776 and 552 cm⁻¹ are predominantly due to various δ(COO⁻) deformation vibrations, with the rocking vibrations of carboxylate groups at

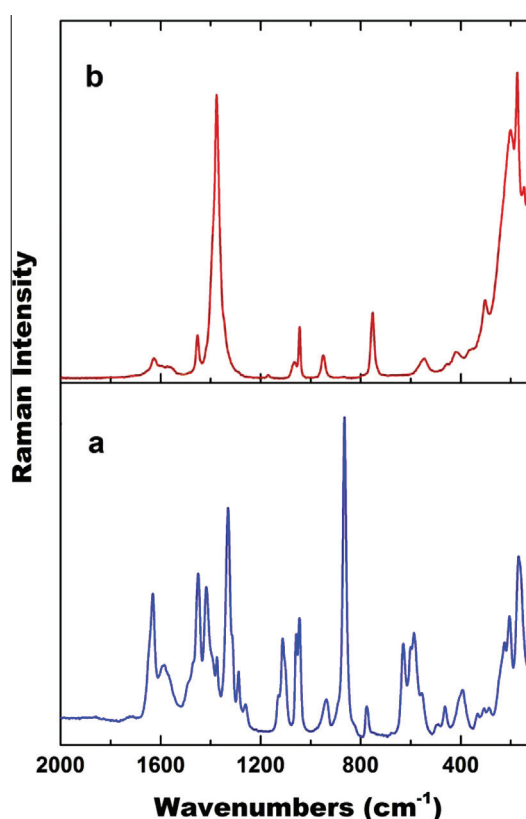


Fig. 4. Raman spectra of 1 (a) and 2 (b) in the 2000–100 cm⁻¹ region.

Table 3

Raman bands and assignments for 1 and 2.

Raman band position, cm ⁻¹	Proposed band assignment
Complex 1	
1631 and 1585 m	ν _{as} (COO ⁻) – coordinated carboxylate groups
1450 and 1417 m	δ _{as} (CH ₃)
1374 and 1331 s	ν _s (COO ⁻)
1288 m and 1260 w	δ _s (CH ₃)
1131 sh and 1112 m	ν (C–O) and δ (CH ₃) rocking vib.
1058 and 1045 m	ν (C–CH ₃)
937 m	δ (CH ₃) rocking vib. and δ (OH) bridging
865 vs	ν (C–COO ⁻)
775 w	δ (OCO) in-plane bending vib.
629, 587, 552 m	δ (C–COH), δ (OCO) out-of-plane deform., δ (HOH)
462 w	δ (OCO) rocking
394 m	δ (CCC) and ν (Th–O _{ligand})
297 m	δ (CCC)
Complex 2	
1626 and 1550 vw	ν _{as} (COO ⁻) – coordinated carboxylate groups
1452 m	δ (C–H), in-plane bending vib.
1376 s	ν _s (COO ⁻)
1065 w and 1044 m	δ (CH) out-of-plane bending vib.
950 w	δ (OH) hydroxyl bridges
752 m	δ (OCO) in-plane bending vib. δ (HOH)
545 w	δ (OCO) out-of-plane deform.
420 w, br and 302 m	ν (Th–O _{ligand})

463 cm⁻¹. Multiple bands in the region 630–552 cm⁻¹ have been assigned to various deformation vibrations, including δ (C–COH), δ (OCO) out-of-plane deformation, and δ (HOH) of coordinated water molecules. Two bands at 393 and 287 cm⁻¹ with medium to weak intensities have been assigned to the C–C–C deformation vibrations; the former should also have a contribution from the stretch ν (Th–O_{ligand}).

Complex 2: A weak band at 1626 cm^{-1} and a shoulder on a lower frequency side at $\sim 1550\text{ cm}^{-1}$ are due to asymmetric stretching modes of carboxylate groups (COO^-) coordinated to Th atoms. The strong band at 1376 cm^{-1} and a shoulder on a lower frequency side have been assigned to the corresponding symmetric stretching modes. The CH in-plane and out-of-plane bending vibrations are located at 1452 and $1065\text{--}1044\text{ cm}^{-1}$, respectively. The band at 950 cm^{-1} is due to hydroxyl (OH) bending vibrations in the complex where the OH group forms a bridge. Bands at 752 and 545 cm^{-1} are due to various $\delta(\text{COO}^-)$ deformation vibrations whilst the bands at 420 and 302 cm^{-1} are due to the stretch $\nu(\text{Th-O}_{\text{ligand}})$.

Previously a Raman spectrum of a powdered sample with a similar hexanuclear Th cluster was reported [10b]. It is in a broad agreement with the Raman spectrum reported here. However, the spectrum reported in this paper was collected on the surface of a large single crystal, which allows additional structural information being revealed: $\delta(\text{OH})$ hydroxyl-bridging between metal centres at 950 cm^{-1} . It is the first Raman observation and clearly spectroscopic evidence that hydroxyl bridging modes are present in the hexanuclear Th(IV) complexes.

3. Conclusions

A mononuclear Th(IV) lactato complex has been prepared at ambient temperature by either dissolving the freshly precipitated $\text{Th}(\text{OH})_4$ with lactic acid or by the direct reaction of Th nitrate with tetramethylammonium lactate. $\text{Th}(\text{C}_3\text{H}_5\text{O}_3)_4(\text{H}_2\text{O})_2$ (**1**) has a monomeric structure with 10-fold coordinated Th polyhedron made up of four lactate ligands and two water molecules. All four coordinated lactate ligands have chiral carbon atoms and are in equal ratio of *R*- and *S*-isomers. Thermal analysis confirmed that **1** lost coordinated water molecules at $\sim 190^\circ\text{C}$ followed by a two-step decomposition of lactate ligands to form ThO_2 . A hexanuclear Th(IV) formate complex has been prepared by the reaction of Th nitrate with ethylenediammonium formate at pH ~ 5 at ambient temperature with high yield in pure single crystal form. $[\text{Th}_6(\text{O})_4(\text{OH})_4(\text{HCO}_2)_{12}(\text{H}_2\text{O})_6]\cdot 5\text{H}_2\text{O}$ (**2**) is a hexanuclear nanocluster constructed with oxo-, hydroxyl, water molecules and bridging formate ligands. Bond valence sum calculations confirmed the presence of both oxo- and hydroxyl groups in equal proportion in the cluster. Thermal analysis confirmed that **2** lost lattice and coordinated water molecules at around 100°C followed by the decomposition of formate ligands to form the final product of ThO_2 . The presence of bridging OH-groups [$\delta(\text{OH})$ at 937 and 950 cm^{-1}] in both complexes has been confirmed by Raman spectroscopy.

4. Experimental

4.1. Materials

4.1.1. $\text{Th}(\text{C}_3\text{H}_5\text{O}_3)_4(\text{H}_2\text{O})_2$ (**1**)

1.0 mL of thorium nitrate solution (0.5 M) was precipitated with 1.0 mL of concentrated ammonium hydroxide. The fresh precipitate was washed three times with deionized (DI) water and centrifuged to remove the ammonia residue. The precipitate was then dissolved with 1.0 mL of lactic acid ($\sim 85\%$, ACS) and 5.0 mL of DI water. Colourless thin plate crystals formed in two weeks with $\sim 70\%$ yield based on thorium content. *Anal. Calc.* for **1**, $\text{C}_{12}\text{H}_{24}\text{O}_{14}\text{Th}$ (FW = 624.30 ; %): C, 23.08 ; H, 3.87 . Found: C, 23.15 ; H, 3.92% . Compound **1** was also prepared by the direct reaction of Th nitrate with tetramethylammonium lactate but with lower yield ($\sim 50\%$).

4.1.2. $[\text{Th}_6(\text{O})_4(\text{OH})_4(\text{HCO}_2)_{12}(\text{H}_2\text{O})_6]\cdot 5\text{H}_2\text{O}$ (**2**)

2.0 mmol of HCOOH ($\sim 98\%$, Fluka), 1.0 mmol of ethylenediamine (Fluka), 0.5 mmol of thorium nitrate solution and 10 mL DI water were added to a 20 mL glass vial with measured pH ~ 5.0 . Colourless prismatic crystals were formed within a week with $\sim 80\%$ yield based on thorium content. *Anal. Calc.* for **2**, $\text{C}_{12}\text{H}_{38}\text{O}_{43}\text{Th}_6$ (FW = 2262.63 ; %): C, 6.37 ; H, 1.69 . Found: C, 6.45 ; H, 1.74% .

4.2. Characterization

4.2.1. Elemental analyses

Elemental analyses were carried out using a Perkin-Elmer 2400 CHN elemental analyzer.

4.2.2. Scanning Electron Microscope/Energy Disperse Spectroscopy (SEM/EDS)

A Zeiss Ultra Plus SEM (Carl Zeiss NTS GmbH, Oberkochen, Germany) operating under an accelerating voltage of 20 kV and equipped with an electron disperse spectroscopy (EDS) was used to confirm the presence of Th in both compounds. Secondary SEM images and EDS spectra for both complexes are shown in Figs. S1 and S2.

4.2.3. Powder X-ray diffraction (PXRD)

PXRD patterns were collected to confirm the crystal structure using a PANalytical X'Pert Pro diffractometer (Almelo, the Netherlands) using $\text{Cu K}\alpha$ radiation (1.54187 \AA) at 45 kV and 40 mA . The data were recorded over an angular range of $10\text{--}80^\circ$ (2θ) with a step size of 0.03° and an acquisition time of 2 s per step. The measured and calculated PXRD patterns are in good agreement for both complexes and are shown in Fig. S4.

4.2.4. Thermogravimetric and differential thermal analysis (TG/DTA)

The thermogravimetric and differential thermal analysis were made on a SEIKO 6300 Thermal Analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ and an air flow rate of $300\text{ cm}^3\text{ min}^{-1}$.

4.2.5. Raman spectroscopy

The Raman spectra were recorded on a Renishaw inVia spectrometer equipped with a 514 nm excitation Ar laser. The spectra were collected in the range $2000\text{--}100\text{ cm}^{-1}$ with a spectral resolution of $\sim 1.7\text{ cm}^{-1}$ and calibrated using the 520.5 cm^{-1} line of a silicon wafer.

4.2.6. Single crystal X-ray diffraction

Single-crystal X-ray data for **1** and **2** were collected at $100(2)\text{ K}$ on MX1 beamline at the Australian Synchrotron with Silicon Double Crystal radiation ($\lambda = 0.7225\text{ \AA}$). The data were collected using BlueIce software [15]. Cell refinements and data reductions were carried out using XDS software [16]. The structure was solved by direct methods and the full-matrix least-squares refinements were carried out using SHELX suite of programs [17]. Structural refinements were straightforward with all non-hydrogen atoms located and refined anisotropically except for some lattice water molecules with half occupancies which were refined isotropically. Hydrogen atoms were added in the calculated positions without restraints.

Acknowledgements

The crystallographic data for **1** and **2** were collected on MX1 beamline at the Australian Synchrotron, Victoria, Australia.

Appendix A. Supplementary data

CCDC 1030247 and 1030248 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2014.12.006>.

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