

catena-Poly[thorium(IV)-tetrakis(μ_2 -3-carboxyadamantane-1-carboxylato)]: a quadruple helical strand driven by a synergy of coordination and hydrogen bonding

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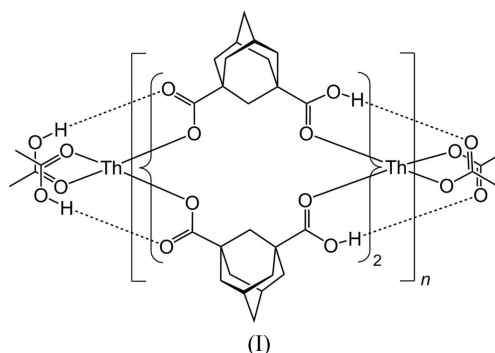
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The title compound, $[\text{Th}(\text{C}_{12}\text{H}_{15}\text{O}_4)_4]_n$, is the first homoleptic thorium–carboxylate coordination polymer. It has a one-dimensional structure supported by the bidentate bridging coordination of the singly charged 3-carboxyadamantane-1-carboxylate (HADC^-) anions. The metal ion is situated on a fourfold axis (site symmetry 4) and possesses a square-antiprismatic ThO_8 coordination, including four bonds to anionic carboxylate groups [$\text{Th}—\text{O} = 2.359$ (2) Å] and four to neutral carboxyl groups [$\text{Th}—\text{O} = 2.426$ (2) Å], while a strong hydrogen bond between these two kinds of O-atom donor [$\text{O} \cdots \text{O} = 2.494$ (3) Å] affords planar pseudo-chelated $\text{Th}\{\text{CO}_2 \cdots \text{HO}_2\text{C}\}$ cycles. This combination of coordination and hydrogen bonding is responsible for the generation of quadruple helical strands of HADC^- ligands, which are wrapped around a linear chain of Th^{IV} ions [$\text{Th} \cdots \text{Th} = 7.5240$ (4) Å] defining the helical axis.

Comment

A particular issue of supramolecular chemistry is spontaneous self-assembly of chiral metal–organic architectures involving helical elements (Seeber *et al.*, 2006). In recent years, different types of discrete helicates and infinite helices have been developed under an elegant approach utilizing polychelating ligands related to the oligopyridine family (Albrecht, 2001). In such systems, the preferred coordination geometry at the metal ion determines the helical twist and thus provides a necessary chiral prerequisite. This leads to the generation of single or multiple ligand strands wrapped around a set of metal ions, which define the helical axis (Lehn *et al.*, 1987). Double-stranded helicates are common for tetrahedral Cu^{I} and Ag^{I} ions, and in the same fashion tris-chelate coordination

of octahedral metal ions may be applied for the generation of triple-stranded helical arrays (Albrecht, 2001). In the present contribution, we report how a quadruple-stranded helical architecture can be designed without the need for complicated polychelating ligands, utilizing the typical eightfold coordination of Th^{IV} ions accompanied by strong interligand hydrogen-bonding interactions. In this context, we have prepared the title compound, $\text{Th}^{4+}(\text{HADC}^-)_4$, (I), and describe its structure here. The bifunctional ADC^{2-} ligand (ADC^{2-} is the adamantane-1,3-dicarboxylate dianion) has been the subject of growing interest as a geometrically rigid angular connector to sustain the structures of metal–organic polymers, such as Zn^{2+} (Nielsen *et al.*, 2008), Co^{2+} (Tang *et al.*, 2009), Eu^{3+} (Millange *et al.*, 2004) and UO_2^{2+} (Rusanova *et al.*, 2010) complexes, whereas the particular supramolecular potential of the singly charged 3-carboxyadamantane-1-carboxylate (HADC^-) anion does not appear to have been considered.



Compound (I) is the first homoleptic thorium–carboxylate coordination polymer. A few examples of carboxylate/fluoride and carboxylate/aqua thorium compounds involving isophthalate (Kim *et al.*, 2003), trimesate (Ok *et al.*, 2008), adamantane-1,3-diacetate anions (Ok & O'Hare, 2008) and some heteroaryl dicarboxylate anions (Frisch & Cahill, 2008; Ziegelgruber

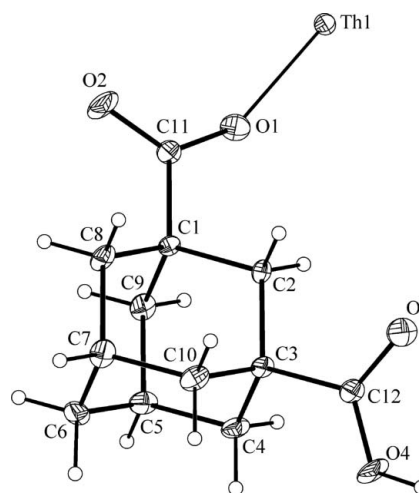


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

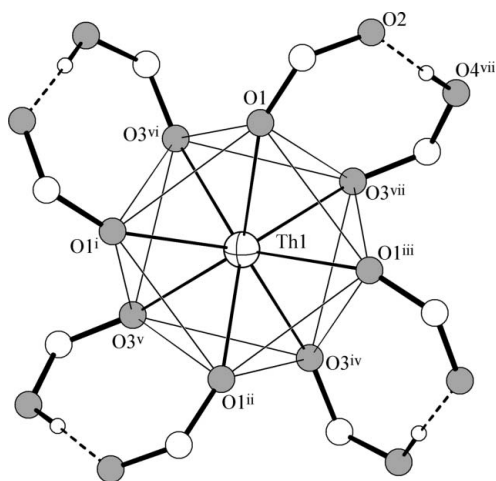


Figure 2
The square-antiprismatic coordination polyhedron of the Th^{IV} ion of (I), showing the strong hydrogen bonding between the coordinated $-\text{CO}_2^-$ and $-\text{CO}_2\text{H}$ groups and the formation of pseudo-chelated cycles. [Symmetry codes: (i) $-y, x, z$; (ii) $-x, -y, z$; (iii) $y, -x, z$; (iv) $-x, -y, z - 1$; (v) $-y, x, z - 1$; (vi) $x, y, z - 1$; (vii) $y, -x, z - 1$.]

et al., 2008) have been characterized in the context of porous metal-organic framework materials.

The asymmetric unit of (I) contains an HADC⁻ anion and a Th⁴⁺ cation (Fig. 1), which is situated on a fourfold axis (site symmetry 4). The metal ion is eight-coordinated, *viz.* ThO₈, and adopts a slightly distorted square-antiprismatic geometry, with the angle of twist between the upper and lower square faces [40.0 (3)°] approaching the value of 45° for an ideal square antiprism (Fig. 2). There are two different kinds of singly coordinated O-atom donor: four anionic carboxylate groups, $-\text{COO}^-$, and four neutral carboxyl groups, $-\text{COOH}$, constituting two square faces of the coordination polyhedron. Although the anionic groups adopt slightly shorter Th–O bond lengths [Th1–O1 = 2.359 (2) Å *versus* Th1–O3^{vi} = 2.426 (2) Å; symmetry code: (vi) $x, y, z - 1$] (Table 1), all the coordination interactions are rather uniform.

A salient feature of the alignment of the eight donors originates in a strong hydrogen bond between the coordinated $-\text{COO}^-$ and $-\text{COOH}$ groups: O4 \cdots O2^{vii} = 2.494 (3) Å, H1 \cdots O2^{vii} = 1.64 Å, O4–H1 \cdots O2^{vii} = 178° [symmetry code: (vii) $-y, x, 1 + z$]. In this way, four pairs of anionic and neutral donor groups, which are related by a fourfold axis, yield four planar pseudo-chelated Th{CO₂H \cdots O₂C} fragments (Fig. 2), and therefore the coordination around the Th^{IV} ion may be directly related to the simpler square-antiprismatic molecular tetrakis-chelates, for example, thorium–malonate complexes, with a very similar distribution of Th–O bond lengths [2.337 (2)–2.450 (2) Å; Zhang *et al.*, 2000].

Such an interplay of coordination and hydrogen-bonding interactions has a pronounced impact on the helical supramolecular structure of (I) and it could be considered as a design tool. This kind of supramolecular synthon is well known for molecular carboxylates. It is particularly important for the structure of hydrogen pivalate complexes, for example, [Fe(BuCO₂)₃(BuCO₂H)₃] (Kiskin *et al.*, 2006) and [Y₂(BuCO₂)₆(BuCO₂H)₆] (Kiseleva *et al.*, 2006), since the bulky *tert*-butyl groups provide effective shielding of the complex unit and contribute to the stabilization of the coordination core involving such relatively poor donors as neutral carboxylic acid. This is exactly the case in the present dicarboxylate, featuring two tertiary donor groups installed on the bulky adamantane platform.

The organic ligands of (I) connect pairs of Th^{IV} ions at a distance of 7.5240 (4) Å [parameter *c* of the unit cell; symmetry code: (viii) $x, y, 1 + z$], giving a one-dimensional polymeric array along the *c* direction in which successive metal ions are linked by quadruple HADC⁻ bridges (Fig. 3). This motif may also be regarded as a chain of the above-mentioned tetrakis-pseudo-chelates interconnected by rigid angular adamantane-1,3-diyl spacers, similar to the discrete dinuclear lanthanide complexes with the angular 1,3-phenylene bis-diketonate ligand (Bassett *et al.*, 2004). The resulting architecture is a quadruple-stranded hydrogen-bonded helix, with a

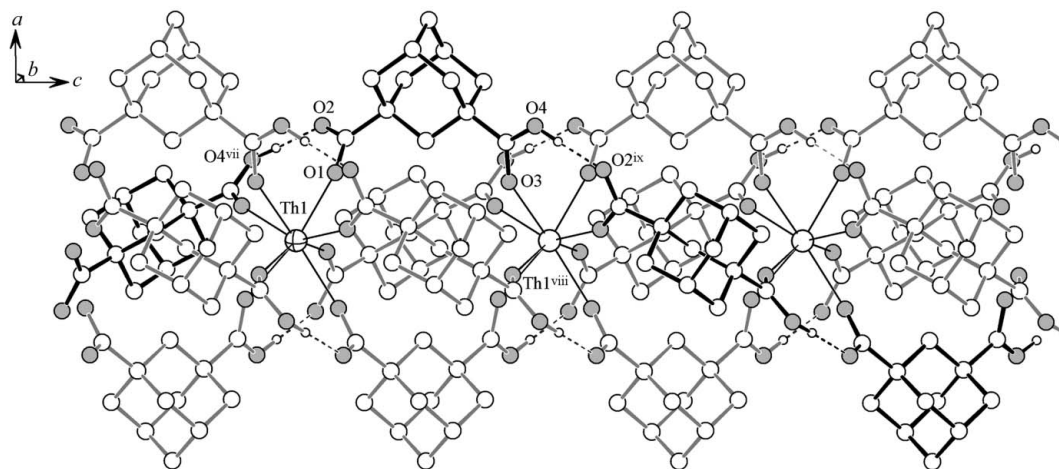
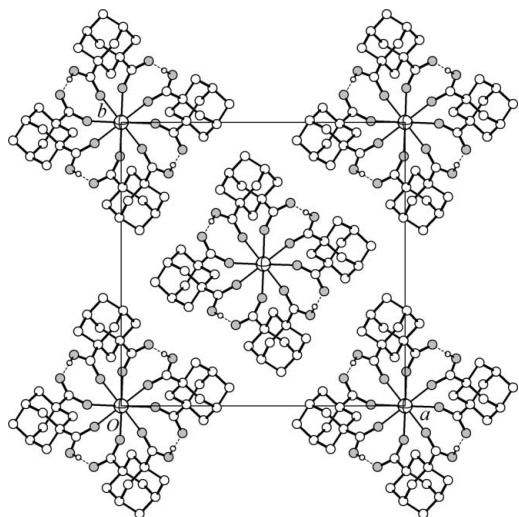


Figure 3
A fragment of the one-dimensional coordination polymer of (I), depicting the quadruple-stranded helical arrangement of the HADC⁻ ligands along the chain of Th^{IV} ions, which define the helical axis. A single ligand strand is shown with black bonds. [Symmetry codes: (vii) $y, -x, z - 1$; (viii) $x, y, 1 + z$; (ix) $-y, x, 1 + z$.]


Figure 4

A projection of the structure of (I) on the *ab* plane, showing the packing of the coordination chains. C—H...O hydrogen bonds have been omitted for clarity.

pitch of $3c = 22.57 \text{ \AA}$, wrapped around the infinite chain of Th^{IV} ions (Fig. 4). Thus, the chiral information is clearly embedded in the square-antiprismatic coordination geometry of the central atom and the angular configuration of the dicarboxylate linker. All the helical chains possess the same chirality. They are packed in a parallel fashion along the *c* direction (Fig. 4), with the shortest interchain contact observed between the methylene and carbonyl groups [$\text{C4} \cdots \text{O2}^x = 3.308 (3) \text{ \AA}$ and $\text{C4} - \text{H} \cdots \text{O2}^x = 131^\circ$; symmetry code: (x) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} + z$], which possibly indicates a very weak hydrogen bond. It is worth noting that, unlike the simpler double- and triple-stranded helical patterns constructed with polychelating ligands, quadruple helices are relatively uncommon. Recently, Xu & Raymond (2006) reported using thorium tetrakis-chelate coordination with bifunctional 4-acyl-2-pyrazolin-5-one ligands for the assembly of discrete quadruple-stranded helicates.

In brief, our findings suggest new possibilities for the generation of multiple-stranded helical arrays while utilizing very simple and general ligand systems and synergy between coordination and hydrogen-bonding interactions.

Experimental

Adamantane-1,3-dicarboxylic acid (H_2ADC) was synthesized by Koch–Haaf carboxylation of adamantane-1,3-diol (Stetter & Wulff, 1960). Crystals of the title compound were grown in a silica-gel medium. The gelling solution, prepared by neutralization of a 1:10 sodium silicate solution (density 1.39 Mg m^{-3}) with 0.055 M HClO_4 to pH 5, was placed in a U-shaped tube and left for 2 d. Solutions of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (5.5 mg, 0.01 mmol) in water (3 ml) and H_2ADC (9.0 mg, 0.04 mmol) in 0.05 M aqueous ammonia (3 ml) were then placed in two separate parts of the tube over the bottom gel layer. Small colourless prisms of the product, (I), grew in the gel as the initial solutions interdiffused over a period of three months. The crystals were separated from the gel by repeated slurring in water followed by decantation (yield 7.3 mg, 65%).

Table 1

Selected geometric parameters (\AA , $^\circ$).

Th1—O1	2.359 (2)	Th1—O3 ⁱ	2.426 (2)
O1 ⁱⁱ —Th1—O1	74.71 (6)	O1—Th1—O3 ⁱ	75.16 (9)
O1 ⁱⁱⁱ —Th1—O1	118.20 (13)	O3 ^v —Th1—O3 ⁱ	71.67 (6)
O1—Th1—O3 ^{iv}	146.32 (8)	O1—Th1—O3 ^{vi}	80.28 (8)
O1—Th1—O3 ^v	138.14 (8)	O3 ⁱ —Th1—O3 ^{vi}	71.67 (6)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-y, x, z$; (iii) $-x, -y, z$; (iv) $-x, -y, z - 1$; (v) $-y, x, z - 1$; (vi) $y, -x, z - 1$.

Crystal data

$[\text{Th}(\text{C}_{12}\text{H}_{15}\text{O}_4)_4]$	$Z = 2$
$M_r = 1125.00$	Mo $K\alpha$ radiation
Tetragonal, $I4$	$\mu = 3.58 \text{ mm}^{-1}$
$a = 16.8182 (9) \text{ \AA}$	$T = 294 \text{ K}$
$c = 7.5240 (4) \text{ \AA}$	$0.11 \times 0.06 \times 0.06 \text{ mm}$
$V = 2128.2 (2) \text{ \AA}^3$	

Data collection

Stoe IPDS diffractometer	6302 measured reflections
Absorption correction: numerical	2498 independent reflections
$[X\text{-RED}$ (Stoe & Cie, 2001) and	2472 reflections with $I > 2\sigma(I)$
$X\text{-SHAPE}$ (Stoe & Cie, 1999)]	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.694, T_{\text{max}} = 0.814$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$	H-atom parameters constrained
$wR(F^2) = 0.036$	$\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
$S = 0.96$	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
2498 reflections	Absolute structure: Flack (1983),
148 parameters	with 1103 Friedel pairs
1 restraint	Flack parameter: $-0.020 (6)$

All H atoms were located in difference maps, then geometrically idealized and refined as riding, with O—H = 0.85 \AA , C—H = 0.97 and 0.98 \AA for CH_2 and CH groups, respectively, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$.

Data collection: *IPDS Software* (Stoe & Cie, 2000); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3060). Services for accessing these data are described at the back of the journal.

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