

Poly[[diaquacerium(III)]- μ_5 -propane-1,2,3-tricarboxylato]Jennifer A. Armstrong and
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Key indicators

Single-crystal X-ray study

T = 150 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

R factor = 0.026

wR factor = 0.064

Data-to-parameter ratio = 14.1

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Crystals of polymeric cerium(III) 1,2,3-propanetricarboxylate dihydrate, $[\text{Ce}(\text{C}_6\text{H}_5\text{O}_6)(\text{H}_2\text{O})_2]_n$, were grown under hydrothermal conditions. The nine-coordinate Ce atoms occur as centrosymmetric pairs. Two bidentate and three monodentate carboxylate groups, each from a different anion, and two water molecules are coordinated to each cerium ion. Ce—O distances range from 2.390 (3) to 2.637 (2) Å. Each anion is joined to five cerium ions, forming a three-dimensional network.

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Comment

Metal salts of polycarboxylic acids can often be prepared only as powders by precipitation from aqueous solution. The very low solubilities of these powders frequently defeat attempts to grow single crystals from solution. For example, in spite of many attempts in this laboratory, only one metal salt of tetrahydrofuran tetracarboxylic acid has been obtained with crystals adequate for structure determination (Barnes & Paton, 1982). The exploitation of hydrothermal recrystallization by Yaghi *et al.* (1996) and Plater *et al.* (1997) offers a new route to these crystals. These workers have used the relatively rigid 1,3,5-benzenetricarboxylate anion in attempts to stabilize open-network structures. In the present work, we report the hydrothermal recrystallization and structure of a cerium(III) salt, (I), of the very flexible 1,3,5-propanetricarboxylate anion (tca).

Barnes & Paton (1988) reported the crystal structure of 1,2,3-propanetricarboxylic acid (H_3tca) at 298 K. A redetermination at 150 K, using better crystals, shows that no phase changes occur over this temperature range (Barnes, 2004).

Gupta & Powel (1963, 1964) prepared powdered samples of lanthanide–tca salts by precipitation from solutions at pH 4–5. They reported that, at room temperature, lanthanum formed $\text{La}(\text{tca})\cdot 5\text{H}_2\text{O}$, but all other lanthanides studied gave $\text{Ln}(\text{tca})\cdot 4\text{H}_2\text{O}$. From thermogravimetric analysis (TGA) measurements, they concluded that $\text{Ln}(\text{tca})\cdot n\text{H}_2\text{O}$ lost water by several different sequences to give anhydrous $\text{Ln}(\text{tca})$ between 423 and 473 K.

Solution studies by Barnes & Bristow (1969) showed the existence of LnHtca^+ and Lntca in the pH range 2–5. Almost quantitative precipitation occurs above pH 5.0.

In the present work, hydrothermal recrystallization of $\text{Ce}(\text{tca})\cdot 4\text{H}_2\text{O}$ powder gave crystals shown by thermogravimetry and structural analysis to be $\text{Ce}(\text{tca})\cdot 2\text{H}_2\text{O}$, (I). Data were collected at 150 and 298 K using different crystals. There were no significant structural differences but the room-temperature crystal proved to be of much better quality; *R* is 0.028 compared with 0.055 for the low-temperature crystal.

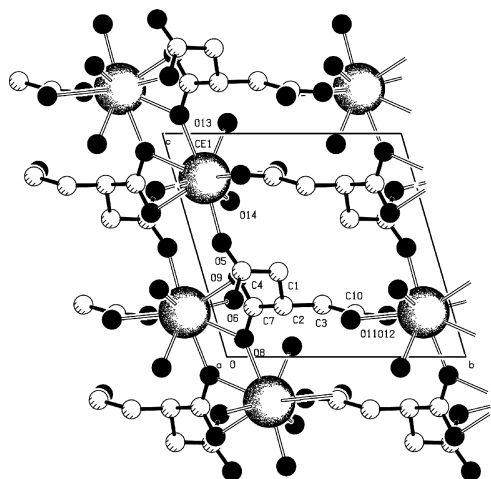


Figure 1
The structure of Ce(tca)·2H₂O, viewed down *a*.

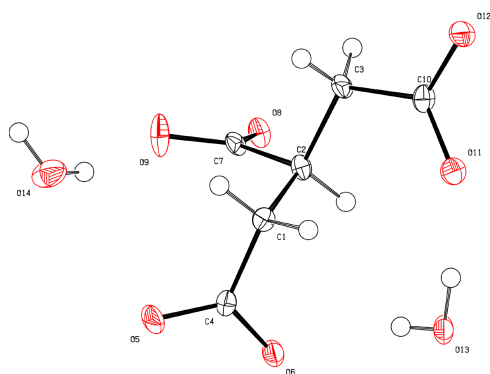


Figure 2
The tca anion and the water molecules, showing 50% probability displacement ellipsoids.

The low-temperature cell has $a = 6.840$ (6) Å, $b = 8.687$ (11) Å, $c = 8.819$ (14) Å, $\alpha = 99.72$ (17)°, $\beta = 110.25$ (7)° and $\gamma = 110.25$ (7)°.

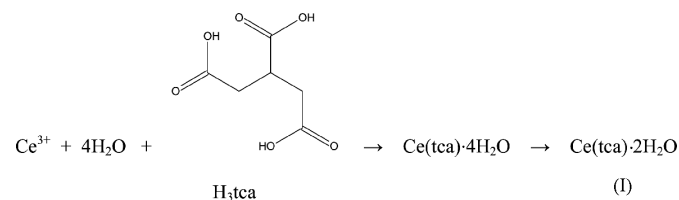


Fig. 1 shows that the Ce atoms occur as centrosymmetric pairs, bridged by the O8 atoms of two bidentate carboxylate groups. The nine-coordinate Ce³⁺ ion has an unusual 2–5–2 geometry, with *trans* bidentate carboxylate groups (C7/O8/O9 and C10/O11/O12) from different ligands. The angle between these carboxylate planes is 89.3 (4)°. Atoms O5, O6 and O8 from three more ligands and two water molecules O13 and O14 make up a pentagonal median plane (r.m.s. deviation = 0.344 Å) at 88.4 (3)° to the plane Ce/O11/O12. (A more familiar but less precise visualization is a monocapped square antiprism with O9 as the cap.) Ce–O distances are in the ranges 2.390 (3)–2.489 (2) Å (monodentate), 2.505 (3)–2.516 (2) Å (water) and 2.544 (2)–2.637 (2) Å (bidentate carboxylate groups).

The tca anion is shown in Fig. 2, with torsion angles in Table 1. Each anion is joined to five Ce atoms to form a three-dimensional network. This flexible anion allows the formation of a framework with no significant volumes of free space, unlike the open-network structures reported by Plater *et al.* (1997) for complexes of the rigid 1,3,5-benzenetricarboxylate anion.

The coordinated water molecules contribute to the network by inter-unit hydrogen bonding (Table 2).

X-ray powder diffraction showed that the powder sample of Ce(tca)·2H₂O prepared at room temperature is identical to the observations of Ce(tca)·2H₂O crystals. TGA studies on Ce(tca)·4H₂O confirmed the observation of Gupta & Powel (1963, 1964) that Ce(tca)·2H₂O is not formed by dehydration of Ce(tca)·4H₂O at atmospheric pressure. In the present work, highly crystalline Ce(tca)·4H₂O was converted at 423 K into the monohydrate which had not been observed by Gupta & Powel. This Ce(tca)·H₂O is of very low crystallinity. Ce(tca)·2H₂O was thermally stable to 400 K, forming crystalline anhydrous Ce(tca) by 430 K.

Experimental

Two samples of hydrated Ce(tca) salts were prepared by mixing aqueous CeCl₃ and H₃tca solutions (0.01 mol) at room temperature and adjusting the pH to 5.5 with NaOH. The resulting fine precipitates were collected after stirring for 1 h. Analysis showed that one sample was Ce(tca)·4H₂O and the other Ce(tca)·2H₂O, in spite of no intentional differences in preparation.

Analytical data for Ce(tca)·4H₂O: Ce found by edta titration: 37.92%; required: 38.14%. Thermogravimetry: weight loss to 423 K = 14.53%, required for Ce(tca)·H₂O = 14.72%; weight loss to 1200 K = 51.68%, required for CeO₂ = 52.05%

Analytical data for Ce(tca)·2H₂O: Ce found by edta titration 39.83%, required = 40.11%. Thermogravimetry: weight loss to 430 K = 10.42%, required for Ce(tca) = 10.31%, weight loss to 1200 K = 49.83%, required for CeO₂ = 49.58%.

Using a Parr model 4745 bomb with a PTFE liner, 0.5 g of Ce(tca)·4H₂O and 15 ml of water were heated to 423 K for 16 h, cooled at 7.5 K h^{−1} to 363 K and then allowed to cool naturally to room temperature. Colourless poorly shaped crystals were obtained.

Crystal data

[Ce(C₆H₃O₆)(H₂O)₂]
 $M_r = 349.25$
 Triclinic, $P\bar{1}$
 $a = 6.9084$ (2) Å
 $b = 8.7738$ (4) Å
 $c = 8.8162$ (4) Å
 $\alpha = 99.552$ (2)°
 $\beta = 110.209$ (2)°
 $\gamma = 104.461$ (2)°
 $V = 466.51$ (3) Å³

$Z = 2$
 $D_x = 2.486$ Mg m^{−3}
 Mo $K\alpha$ radiation
 Cell parameters from 5965 reflections
 $\theta = 2.6$ – 27.5 °
 $\mu = 4.90$ mm^{−1}
 $T = 150$ (2) K
 Block, colourless
 0.30 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.353$, $T_{\max} = 0.613$
 5965 measured reflections

2091 independent reflections
 2046 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 27.5$ °
 $h = -8 \rightarrow 8$
 $k = -11 \rightarrow 9$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.064$
 $S = 1.13$
 2091 reflections
 148 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.7556P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.018$
 $\Delta\rho_{\max} = 1.05 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -2.89 \text{ e } \text{\AA}^{-3}$

Table 1

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

Ce1—O5 ⁱ	2.390 (3)	C1—C2	1.539 (4)
Ce1—O6	2.489 (2)	C2—C7	1.517 (5)
Ce1—O14	2.505 (3)	C2—C3	1.537 (5)
Ce1—O13	2.518 (2)	C3—C10	1.513 (5)
Ce1—O12 ⁱⁱ	2.544 (2)	C4—O5	1.237 (4)
Ce1—O8 ⁱⁱⁱ	2.572 (2)	C4—O6	1.267 (4)
Ce1—O9 ^{iv}	2.611 (2)	C7—O9	1.251 (4)
Ce1—O8 ^{iv}	2.619 (2)	C7—O8	1.272 (4)
Ce1—O11 ⁱⁱ	2.637 (2)	C10—O12	1.257 (4)
C1—C4	1.510 (4)	C10—O11	1.270 (4)
O5—C4—C1—C2	−126.3 (3)	O5—C4—C1—C2	−126.3 (3)
C4—C1—C2—C3	−176.7 (3)	C4—C1—C2—C7	61.7 (4)
C1—C2—C3—C10	72.6 (4)	C1—C2—C7—O8	−151.6 (3)
C2—C3—C10—O11	−4.9 (5)		

Symmetry codes: (i) $-x, 2-y, 1-z$; (ii) $x, y-1, z$; (iii) $-1-x, 2-y, -z$; (iv) $1+x, y, z$.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O13—H131 ^v ···O11 ^v	0.86 (5)	1.95 (5)	2.810 (3)	174 (5)
O13—H132 ^v ···O6 ^v	0.79 (5)	1.99 (3)	2.741 (4)	160 (5)
O14—H141 ⁱ ···O9 ⁱ	0.89 (5)	1.96 (5)	2.830 (4)	165 (5)
O14—H142 ^{vi} ···O12 ^{vi}	0.83 (5)	1.91 (5)	2.718 (4)	165 (5)

Symmetry codes: (i) $-x, 2-y, 1-z$; (v) $-x, 2-y, -z$; (vi) $1+x, y-1, z$.

H atoms of the tricarballylate anion were placed in calculated positions with U_{iso} values set at 1.3 times the U_{eq} value of the parent atom and the C—H distance set at 0.97 \AA . H atoms of water were located in a difference synthesis and the coordinates were refined with U_{iso} values set at 1.3 times the U_{eq} value of the parent atom; the O—H distances were not constrained. The highest difference map peak was 0.83 \AA from Ce1 and the deepest hole was 0.86 \AA from Ce1.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

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