

Triaquabenzotocalcium(II) mono- benzoate: coordination polymer chains linked into a two-dimensional framework by hydrogen bonds

Irena Senkovska^{a*} and Ulf Thewalt^b

^aDresden University of Technology, Institute of Inorganic Chemistry I, Mommsenstraße 13, 01069 Dresden, Germany, and ^bSector of X-ray and Electron Diffraction, University of Ulm, D-89069 Ulm, Germany
 Correspondence e-mail: irena.senkovska@chemie.tu-dresden.de

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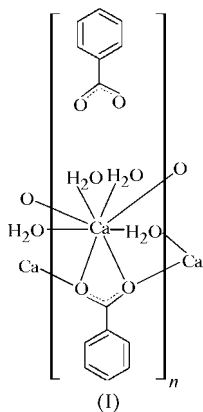
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In the title complex, *catena*-poly[[[diaquacalcium(I)]- μ_2 -aqua- μ_3 -benzoato- $\kappa^4 O:O,O':O'$] benzoate], $\{[\text{Ca}(\text{C}_6\text{H}_5\text{O}_2)(\text{H}_2\text{O})_3]-(\text{C}_6\text{H}_5\text{O}_2)\}_n$, obtained by the reaction of CaCl_2 and potassium benzoate in water, the Ca atom is eight-coordinated by four carboxylate O atoms and four water molecules. The structure consists of polymeric $\{[\text{Ca}(\text{C}_6\text{H}_5\text{COO})(\text{H}_2\text{O})_3]^+\}_\infty$ chains alternating with layers of uncoordinated $\text{C}_6\text{H}_5\text{COO}^-$ anions. The nearly planar anions are linked to the chain by short hydrogen bonds to form a two-dimensional network.

Comment

This study is part of a systematic structural investigation of complexes of aromatic carboxylic acids and alkaline earth metals (Ca, Sr and Ba) in aqueous solution. A wide variety of coordination modes, polymeric arrangements and molecular topologies have been observed, depending on the metal, pH and other synthetic conditions. For calcium with the



benzoate anion, three compounds have been reported, namely $[\text{Ca}(\text{C}_6\text{H}_5\text{COO})_2]\cdot 3\text{H}_2\text{O}$ (from neutral solution), $[\text{Ca}(\text{C}_6\text{H}_5\text{COO})_2](\text{C}_6\text{H}_5\text{COO})_{0.5}\cdot 2\text{H}_2\text{O}$ (from acid solution;

Cherkezova *et al.*, 1987) and $[\text{Ca}(\text{C}_6\text{H}_5\text{COO})_2]$ (hydrothermal conditions; Zhang *et al.*, 1999).

In spite of the wide-ranging applications of calcium benzoate (for example, as a preservative in the food industry), the crystal structure of this compound has been poorly investigated. Cherkezova *et al.* (1987) studied the syntheses and thermal stabilities of Mg, Ca, Sr and Ba benzoates and determined only the space group and cell parameters of $[\text{Ca}(\text{C}_6\text{H}_5\text{COO})_2]\cdot 3\text{H}_2\text{O}$. We describe here the crystal structure of triaquabenzotocalcium(II) monobenzoate, (I).

The asymmetric unit of (I) consists of one Ca centre, two benzoate anions and three water molecules. The Ca atom is coordinated in a distorted square-antiprismatic geometry by two monodentate carboxylate groups of different benzoate moieties, one bidentate carboxylate group and four water molecules. Indeed, the atoms that form square faces $[\text{O}2/\text{O}7\text{A}^i/\text{O}3/\text{O}7\text{B}^{ii}]$ and $[\text{O}1/\text{O}1^i/\text{O}7\text{B}/\text{O}7\text{A}]$; symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z$] deviate from a square-planar geometry and the coordination polyhedra could alternatively be described as an irregular trigonal dodecahedron. The coordination geometry around the Ca atom cannot be assigned unequivocally to one of these ideal structures due to strong distortion (Fig. 1). The Ca–O bond lengths vary from 2.338 (1) to 2.616 (1) Å (Table 1).

The independent benzoate entities play distinct structural roles. One type (atoms C1–C7/O7A/O7B) acts as a bridging ligand between three Ca atoms, giving polymeric $\{[\text{Ca}(\text{C}_6\text{H}_5\text{COO})(\text{H}_2\text{O})_3]^+\}_\infty$ chains running parallel to the *c* axis and generated by the *c*-glide plane at $y = 0.75$ (Fig. 1). The carboxylate group (O7A/C7/O7B) of these anions is almost coplanar with the phenyl ring [dihedral angle = $6.64(6)^\circ$].

The second type of benzoate anion (atoms C11–C17/O17A/O17B) is present in an isolated form and is not linked to the chain by covalent bonds (Figs. 1 and 2). These anions are linked to the chain by strong hydrogen bonds between the

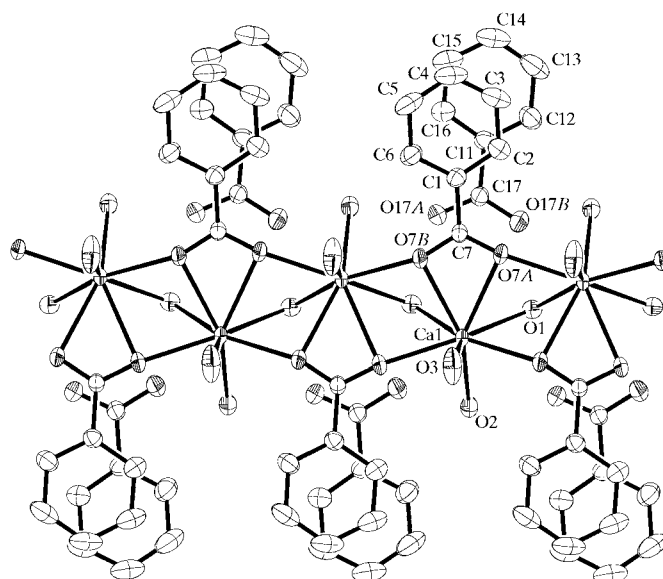


Figure 1
 Part of the $\{[\text{Ca}(\text{C}_6\text{H}_5\text{COO})(\text{H}_2\text{O})_3]^+\}_\infty$ chain. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.

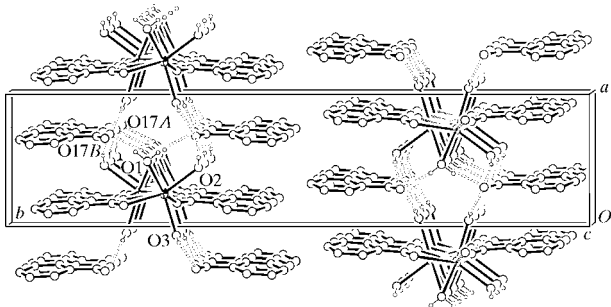


Figure 2
A view of the two-dimensional networks in (I), which are assembled by hydrogen bonds, π - π stacking interactions and Ca—O bonds, shown approximately down the crystallographic [001] direction. The H atoms of the phenyl rings have been omitted for clarity.

carboxyl group (O17A/C17/O17B) and water molecules (Table 2). All aqua ligands act as hydrogen-bond donors, and atoms O17A and O17B of the carboxylate group are hydrogen-bond acceptors.

Neighbouring phenyl groups are stacked nearly parallel along the *a* axis. The interplanar distance between phenyl rings C1–C6 and C11–C16 is 3.593 (4) Å. The dihedral angle is 0.99 (6)° and the shortest atom-to-atom distance between these two rings is 3.596 (1) Å. This distance lies in the normal range of 3.3–3.8 Å (Janiak, 2000), indicative of π - π interaction.

The combination of these hydrogen bonds, π - π stacking interactions and Ca—O bonds leads to the formation of a two-dimensional network running parallel to the *ac* plane (Fig. 2).

Experimental

Single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation at room temperature of an aqueous solution containing CaCl₂ and potassium benzoate.

Crystal data

[Ca(C ₇ H ₅ O ₂)(H ₂ O) ₃](C ₇ H ₅ O ₂)	$D_x = 1.452 \text{ Mg m}^{-3}$
$M_r = 336.35$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 11074 reflections
$a = 7.3004 (10) \text{ \AA}$	$\theta = 2.5\text{--}25.9^\circ$
$b = 32.252 (4) \text{ \AA}$	$\mu = 0.44 \text{ mm}^{-1}$
$c = 6.5364 (7) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 91.145 (15)^\circ$	Needle, colourless
$V = 1538.7 (3) \text{ \AA}^3$	$0.38 \times 0.15 \times 0.04 \text{ mm}$
$Z = 4$	

Data collection

Stoe IPDS diffractometer	$R_{\text{int}} = 0.038$
φ scans	$\theta_{\text{max}} = 25.9^\circ$
12022 measured reflections	$h = -8 \rightarrow 8$
2838 independent reflections	$k = -39 \rightarrow 39$
2256 reflections with $I > 2\sigma(I)$	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.027$	$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$
$wR(F^2) = 0.063$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{\text{max}} = 0.002$
2838 reflections	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
223 parameters	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Ca1—O7A ⁱ	2.3383 (11)	Ca1—O7B	2.5481 (11)
Ca1—O7B ⁱⁱ	2.3516 (11)	Ca1—O1 ⁱ	2.6158 (12)
Ca1—O2	2.3855 (12)	C7—O7B	1.2523 (18)
Ca1—O3	2.4129 (14)	C7—O7A	1.2598 (18)
Ca1—O7A	2.4985 (10)	C17—O17B	1.2543 (19)
Ca1—O1	2.5275 (12)	C17—O17A	1.2619 (19)
O7A ⁱ —Ca1—O7B ⁱⁱ	137.96 (4)	O7A—Ca1—O1	68.25 (4)
O7A ⁱ —Ca1—O2	85.28 (4)	O7A ⁱ —Ca1—O7B	78.79 (4)
O7B ⁱⁱ —Ca1—O2	82.98 (4)	O7B ⁱⁱ —Ca1—O7B	130.41 (4)
O7A ⁱ —Ca1—O3	72.17 (5)	O2—Ca1—O7B	142.48 (4)
O7B ⁱⁱ —Ca1—O3	74.43 (5)	O3—Ca1—O7B	96.94 (5)
O2—Ca1—O3	110.21 (5)	O7A—Ca1—O7B	51.26 (3)
O7A ⁱ —Ca1—O7A	124.63 (4)	O1—Ca1—O7B	94.09 (4)
O7B ⁱⁱ —Ca1—O7A	79.56 (4)	O7A ⁱ —Ca1—O1 ⁱ	69.12 (4)
O2—Ca1—O7A	148.70 (4)	O7B ⁱⁱ —Ca1—O1 ⁱ	144.93 (4)
O3—Ca1—O7A	89.85 (5)	O2—Ca1—O1 ⁱ	77.30 (4)
O7A ⁱ —Ca1—O1	147.38 (4)	O3—Ca1—O1 ⁱ	139.76 (5)
O7B ⁱⁱ —Ca1—O1	69.57 (4)	O7A—Ca1—O1 ⁱ	103.13 (4)
O2—Ca1—O1	81.39 (4)	O1—Ca1—O1 ⁱ	78.93 (3)
O3—Ca1—O1	140.44 (5)	O7B—Ca1—O1 ⁱ	65.32 (3)

Symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1—H1A \cdots O17B	0.86 (2)	1.89 (2)	2.7370 (15)	166 (2)
O1—H1B \cdots O17A ⁱⁱ	0.82 (2)	1.95 (2)	2.7445 (15)	166 (2)
O2—H2B \cdots O17A ⁱⁱ	0.84 (3)	1.98 (3)	2.7939 (19)	163 (2)
O2—H2A \cdots O17B ⁱⁱ	0.81 (2)	1.97 (2)	2.7705 (18)	166 (2)
O3—H3A \cdots O17A ⁱⁱⁱ	0.79 (3)	2.10 (3)	2.875 (2)	166 (3)
O3—H3B \cdots O17B ^{iv}	0.79 (3)	2.32 (3)	3.083 (2)	164 (3)

Symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x - 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $x - 1, -y + \frac{3}{2}, z - \frac{1}{2}$.

All H atoms were found in ΔF maps, but those connected to C atoms were placed in calculated positions and refined using a riding model, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$. Water H atoms were refined isotropically.

Data collection: *IPDS* (Stoe & Cie, 1996); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Johnson & Burnett, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1149). Services for accessing these data are described at the back of the journal.

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