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Tetraaquabis(2,3-dihydro-1,4-benzodioxine-2-carboxylato)calcium(II)

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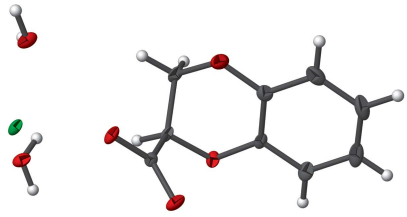
Keywords: crystal structure; 1,4-benzodioxane; calcium atom; carboxylate groups; hydrogen bonding.

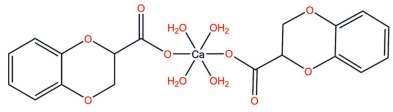
Structural data: full structural data are available from iucrdata.iucr.org

The acid–base reaction of 1,4-benzodioxane 2-carboxylic acid with calcium carbonate furnished the centrosymmetric title compound, $[Ca(C_9H_7O_4)_2(H_2O)_4]$, in which the metal ion is octahedrally coordinated by two monodentate 1,4-benzodioxane 2-carboxylate ligands and four water molecules. In the crystal, O—H···O and C—H···O hydrogen bonds link the molecules into a three-dimensional network.

3D view



Chemical scheme



Structure description

1,4-Benzodioxanes are components of some therapeutic agents used in cardiovascular treatments, acting as α- and β-adrenergic antagonists (Nelson *et al.*, 1977, 1979; Pigini *et al.*, 1988). For the latter application, the enantiopure derivatives of chiral 2-substituted 1,4-benzodioxanes lend affinity and selectivity, mainly those derived from 1,4-benzodioxane 2-carboxylic acid (Ennis & Old, 1992; Antus *et al.*, 1993; Khouili *et al.*, 1999; Jasinski *et al.*, 2009). Naturally ocurring compounds with a similar structure to these heterocyclic scaffolds are known as 1,4-benzodioxane lignans, which also exhibit a wide array of biological activities (*e.g.*, anticancer, antioxidant; Pilkington & Barker, 2015).

In this work, we report the synthesis and the structure of the coordination properties of 1,4-benzodioxane 2-carboxylic acid toward calcium carbonate to afford the title compound $Ca(C_9H_7O_4)_2(H_2O)_4$.

The crystal structure of the title compound has monoclinic symmetry with half a molecule in the asymmetric unit, the other half being generated by a crystallographic inversion center. The calcium ion is bonded to four aqua ligands and two 1,4-benzodioxane 2-carboxylate ligands, whose carboxylate groups link to the central atom in

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O1^{i}	0.84 (2)	1.96 (2)	2.800 (3)	178 (4)
O5—H5B···O4^{ii}	0.84 (3)	2.07 (3)	2.828 (3)	149 (4)
O6—H6A···O2^{iii}	0.83 (3)	1.93 (2)	2.707 (3)	155 (3)
O6—H6B···O2^{i}	0.84 (3)	1.88 (4)	2.715 (3)	176 (3)
C2—H2···O2^{i}	1.00	2.53	3.379 (4)	143
C6—H6···O3^{iv}	0.95	2.54	3.357 (4)	145

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

monodentate mode (Fig. 1). The Ca1—O1, Ca1—O5, and Ca1—O6 bond lengths are 2.304 (2), 2.358 (2) and 2.317 (2) Å, respectively. The dioxane ring adopts a half-chair conformation with the pendant carboxylate group in an axial orientation. In the arbitrarily chosen asymmetric unit, C2 has an *R* configuration but crystal symmetry generates a racemic mixture.

In the crystal, O—H···O hydrogen bonds link the molecules into (010) sheets with the acceptor O atoms being parts of carboxylate groups (O1 and O2) and the dioxane ring (O4) and the packing is consolidated by weak C—H···O interactions (Fig. 2, Table 1).

Synthesis and crystallization

In a 100 mL two-necked flask, anhydrous $CaCO_3$ (0.0100 g, 0.100 mmol) was dissolved in deionized water (20 mL) by heating to 338 K, and a solution of 1,4-benzodioxane-2-carboxylic acid (0.0560 g, 0.200 mmol) dissolved in distilled water (10 mL) was added dropwise at 353 K. The reaction mixture was refluxed for 2 h and then concentrated under vacuum to 10 mL. The precipitate obtained upon cooling overnight was filtered off and washed with cold distilled water. Colorless crystals suitable for X-ray analysis were grown from a warm water–methanol mixed solvent mixture (1:1) at room temperature. Yield: 0.0362 g (55%), m.p. 501–505 K. FTIR data (KBr, cm^{-1}): 3600 and 3000 (*br*, *m*); 3568 (*m*); 1330 (*m*); 879 (*m*); 833 (*s*); 767 (*s*); 752 (*s*); 654 (*m*); 569 (*m*); 545 (*w*); 476 (*m*). ^{1}H NMR (400 MHz, mix 1:1 D_2O: CD_4O, 298 K): δ 6.87–6.99 (*s*, 4H), 4.82 (*dd*, 1H), 4.35 p.p.m. (*qd*, 2H). ^{13}C NMR (400 MHz, 1:1 mix D_2O: CD_4O, 298 K): δ 176, 143, 142, 123, 122, 117, 115, 73.5, 66 p.p.m. The ^{1}H NMR and ^{13}C NMR spectra for the title compound are included in the supporting information.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ca(C_9H_7O_4)_2(H_2O)_4]$
M_r	470.44
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	5.3477 (4), 26.6084 (18), 7.7367 (5)
β (°)	106.715 (2)
V (Å^3)	1054.37 (13)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.36
Crystal size (mm)	0.35 × 0.25 × 0.15
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.661, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32373, 2384, 2242
R_{int}	0.036
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.647
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.057, 0.133, 1.39
No. of reflections	2384
No. of parameters	158
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.42, −0.43

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

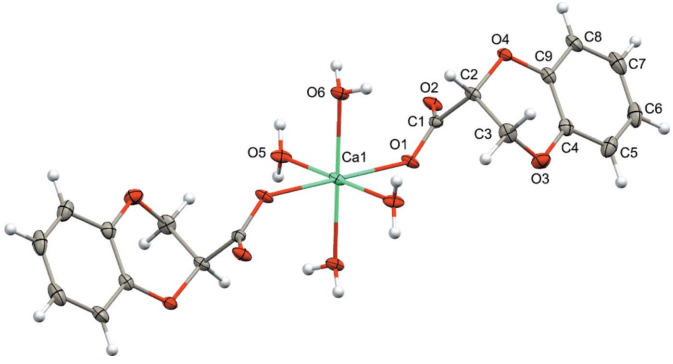


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Unlabeled atoms are generated by the symmetry operation $1-x, 1-y, 2-z$.

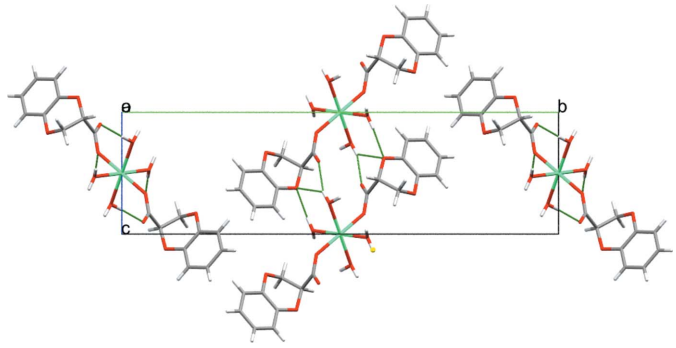


Figure 2
Packing of the molecules of the title compound. O—H···O and C—H···O hydrogen bonds are shown as green dashed lines.

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full crystallographic data

IUCrData (2020). **5**, x201092 [https://doi.org/10.1107/S2414314620010925]

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Crystal data

$[Ca(C_9H_7O_4)_2(H_2O)_4]$
M_r = 470.44
Monoclinic, $P2_1/n$
a = 5.3477 (4) Å
b = 26.6084 (18) Å
c = 7.7367 (5) Å
β = 106.715 (2)°
V = 1054.37 (13) Å^3
Z = 2
$F(000)$ = 492
D_x = 1.482 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9843 reflections
θ = 2.9–27.4°
μ = 0.36 mm^{-1}
T = 100 K
Block, clear light white
0.35 × 0.25 × 0.15 mm

Data collection

Bruker D8 Venture diffractometer
Mirrors monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.661, T_{max} = 0.746
32373 measured reflections
2384 independent reflections
2242 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
θ_{max} = 27.4°, θ_{min} = 2.9°
h = −6→6
k = −34→34
l = −10→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.133
S = 1.39
2384 reflections
158 parameters
6 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + 3.3804P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ca1	0.5	0.5	1.0	0.0115 (2)
O1	0.6722 (4)	0.55435 (8)	0.8323 (3)	0.0144 (4)
O2	0.8347 (4)	0.54948 (9)	0.5982 (3)	0.0164 (5)
O3	0.5527 (5)	0.66992 (9)	0.6702 (3)	0.0199 (5)
O4	0.4402 (4)	0.60021 (8)	0.3776 (3)	0.0144 (4)
O5	0.2000 (4)	0.56223 (9)	1.0277 (3)	0.0167 (5)
H5A	0.041 (3)	0.5599 (16)	0.972 (4)	0.030 (12)*
H5B	0.210 (7)	0.5750 (15)	1.129 (3)	0.033 (12)*
O6	0.1782 (4)	0.47510 (9)	0.7438 (3)	0.0158 (5)
H6A	0.208 (8)	0.4613 (13)	0.655 (3)	0.028 (12)*
H6B	0.070 (7)	0.4981 (12)	0.703 (5)	0.043 (14)*
C1	0.6624 (6)	0.56196 (11)	0.6687 (4)	0.0116 (6)
C2	0.4144 (6)	0.58769 (12)	0.5516 (4)	0.0121 (6)
H2	0.2671	0.5632	0.5335	0.015*
C3	0.3443 (6)	0.63398 (12)	0.6413 (5)	0.0171 (6)
H3A	0.1807	0.6488	0.5636	0.021*
H3B	0.316	0.6247	0.7582	0.021*
C4	0.6346 (6)	0.67786 (12)	0.5198 (4)	0.0160 (6)
C5	0.7822 (7)	0.72053 (13)	0.5151 (5)	0.0226 (7)
H5	0.8188	0.7437	0.6124	0.027*
C6	0.8762 (7)	0.72926 (13)	0.3682 (5)	0.0261 (8)
H6	0.9784	0.7583	0.3656	0.031*
C7	0.8210 (7)	0.69567 (14)	0.2255 (5)	0.0251 (8)
H7	0.8838	0.702	0.1246	0.03*
C8	0.6745 (6)	0.65272 (13)	0.2289 (4)	0.0191 (7)
H8	0.6373	0.6297	0.1311	0.023*
C9	0.5828 (6)	0.64388 (11)	0.3781 (4)	0.0129 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0075 (4)	0.0198 (4)	0.0070 (4)	0.0002 (3)	0.0018 (3)	0.0016 (3)
O1	0.0118 (10)	0.0243 (12)	0.0078 (10)	0.0001 (8)	0.0037 (8)	0.0026 (8)
O2	0.0128 (10)	0.0270 (12)	0.0100 (10)	0.0058 (9)	0.0041 (8)	0.0011 (9)
O3	0.0215 (12)	0.0206 (12)	0.0194 (12)	−0.0010 (9)	0.0089 (9)	−0.0046 (9)
O4	0.0146 (10)	0.0181 (11)	0.0091 (10)	−0.0028 (8)	0.0013 (8)	0.0012 (8)
O5	0.0087 (10)	0.0279 (12)	0.0125 (11)	0.0006 (9)	0.0015 (8)	−0.0042 (9)
O6	0.0144 (11)	0.0227 (12)	0.0095 (10)	0.0042 (9)	0.0022 (8)	−0.0015 (9)
C1	0.0105 (13)	0.0133 (13)	0.0107 (13)	−0.0024 (10)	0.0025 (11)	−0.0008 (10)
C2	0.0080 (13)	0.0196 (15)	0.0090 (13)	−0.0004 (11)	0.0027 (10)	0.0020 (11)
C3	0.0113 (14)	0.0227 (16)	0.0209 (16)	0.0027 (12)	0.0103 (12)	0.0029 (13)
C4	0.0125 (14)	0.0164 (15)	0.0179 (15)	0.0035 (11)	0.0023 (12)	0.0026 (12)
C5	0.0173 (16)	0.0154 (15)	0.0330 (19)	0.0005 (12)	0.0039 (14)	0.0005 (14)
C6	0.0172 (17)	0.0210 (17)	0.038 (2)	−0.0025 (13)	0.0051 (15)	0.0121 (15)
C7	0.0187 (16)	0.0316 (19)	0.0244 (18)	0.0005 (14)	0.0053 (14)	0.0144 (15)

C8	0.0182 (16)	0.0249 (17)	0.0124 (15)	0.0016 (13)	0.0016 (12)	0.0059 (12)
C9	0.0077 (13)	0.0177 (15)	0.0141 (14)	0.0025 (11)	0.0041 (11)	0.0042 (11)

Geometric parameters (Å, º)

Ca1—O1^{i}	2.304 (2)	O6—H6B	0.839 (10)
Ca1—O1	2.304 (2)	C1—C2	1.535 (4)
Ca1—O6^{i}	2.317 (2)	C2—C3	1.513 (4)
Ca1—O6	2.317 (2)	C2—H2	1.0
Ca1—O5^{i}	2.358 (2)	C3—H3A	0.99
Ca1—O5	2.358 (2)	C3—H3B	0.99
Ca1—H6B	2.74 (4)	C4—C9	1.386 (4)
O1—C1	1.268 (4)	C4—C5	1.389 (5)
O2—C1	1.243 (4)	C5—C6	1.388 (5)
O3—C4	1.372 (4)	C5—H5	0.95
O3—C3	1.437 (4)	C6—C7	1.385 (6)
O4—C9	1.389 (4)	C6—H6	0.95
O4—C2	1.432 (3)	C7—C8	1.390 (5)
O5—H5A	0.838 (10)	C7—H7	0.95
O5—H5B	0.838 (10)	C8—C9	1.397 (4)
O6—H6A	0.837 (10)	C8—H8	0.95
O1^{i}—Ca1—O1	180.0	O1—C1—C2	116.1 (3)
O1^{i}—Ca1—O6^{i}	90.95 (8)	O4—C2—C3	110.2 (2)
O1—Ca1—O6^{i}	89.05 (8)	O4—C2—C1	111.0 (2)
O1^{i}—Ca1—O6	89.05 (8)	C3—C2—C1	112.3 (2)
O1—Ca1—O6	90.95 (8)	O4—C2—H2	107.7
O6^{i}—Ca1—O6	180.00 (10)	C3—C2—H2	107.7
O1^{i}—Ca1—O5^{i}	90.17 (8)	C1—C2—H2	107.7
O1—Ca1—O5^{i}	89.83 (8)	O3—C3—C2	109.3 (2)
O6^{i}—Ca1—O5^{i}	85.49 (8)	O3—C3—H3A	109.8
O6—Ca1—O5^{i}	94.51 (8)	C2—C3—H3A	109.8
O1^{i}—Ca1—O5	89.83 (8)	O3—C3—H3B	109.8
O1—Ca1—O5	90.17 (8)	C2—C3—H3B	109.8
O6^{i}—Ca1—O5	94.51 (8)	H3A—C3—H3B	108.3
O6—Ca1—O5	85.49 (8)	O3—C4—C9	122.0 (3)
O5^{i}—Ca1—O5	180.0	O3—C4—C5	118.1 (3)
O1^{i}—Ca1—H6B	94.9 (10)	C9—C4—C5	119.9 (3)
O1—Ca1—H6B	85.1 (9)	C6—C5—C4	120.0 (3)
O6^{i}—Ca1—H6B	163.5 (6)	C6—C5—H5	120.0
O6—Ca1—H6B	16.5 (6)	C4—C5—H5	120.0
O5^{i}—Ca1—H6B	109.8 (6)	C7—C6—C5	120.0 (3)
O5—Ca1—H6B	70.2 (6)	C7—C6—H6	120.0
C1—O1—Ca1	138.9 (2)	C5—C6—H6	120.0
C4—O3—C3	113.1 (2)	C6—C7—C8	120.5 (3)
C9—O4—C2	113.2 (2)	C6—C7—H7	119.7
Ca1—O5—H5A	121 (3)	C8—C7—H7	119.7
Ca1—O5—H5B	120 (3)	C7—C8—C9	119.2 (3)

H5A—O5—H5B	107 (2)	C7—C8—H8	120.4
Ca1—O6—H6A	124 (3)	C9—C8—H8	120.4
Ca1—O6—H6B	112 (3)	C4—C9—O4	122.1 (3)
H6A—O6—H6B	106 (2)	C4—C9—C8	120.4 (3)
O2—C1—O1	124.9 (3)	O4—C9—C8	117.5 (3)
O2—C1—C2	118.9 (3)		
Ca1—O1—C1—O2	−102.2 (4)	O3—C4—C5—C6	178.0 (3)
Ca1—O1—C1—C2	76.5 (4)	C9—C4—C5—C6	0.4 (5)
C9—O4—C2—C3	45.0 (3)	C4—C5—C6—C7	0.6 (5)
C9—O4—C2—C1	−79.9 (3)	C5—C6—C7—C8	−0.8 (5)
O2—C1—C2—O4	−8.8 (4)	C6—C7—C8—C9	0.2 (5)
O1—C1—C2—O4	172.4 (2)	O3—C4—C9—O4	1.4 (5)
O2—C1—C2—C3	−132.6 (3)	C5—C4—C9—O4	178.9 (3)
O1—C1—C2—C3	48.5 (4)	O3—C4—C9—C8	−178.6 (3)
C4—O3—C3—C2	48.5 (3)	C5—C4—C9—C8	−1.1 (5)
O4—C2—C3—O3	−63.0 (3)	C2—O4—C9—C4	−15.5 (4)
C1—C2—C3—O3	61.3 (3)	C2—O4—C9—C8	164.4 (3)
C3—O3—C4—C9	−19.4 (4)	C7—C8—C9—C4	0.8 (5)
C3—O3—C4—C5	163.1 (3)	C7—C8—C9—O4	−179.1 (3)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*A*···O1^{ii}	0.84 (2)	1.96 (2)	2.800 (3)	178 (4)
O5—H5*B*···O4^{iii}	0.84 (3)	2.07 (3)	2.828 (3)	149 (4)
O6—H6*A*···O2^{iv}	0.83 (3)	1.93 (2)	2.707 (3)	155 (3)
O6—H6*B*···O2^{ii}	0.84 (3)	1.88 (4)	2.715 (3)	176 (3)
C2—H2···O2^{ii}	1.00	2.53	3.379 (4)	143
C6—H6···O3^{v}	0.95	2.54	3.357 (4)	145

Symmetry codes: (ii) *x*−1, *y*, *z*; (iii) *x*, *y*, *z*+1; (iv) −*x*+1, −*y*+1, −*z*+1; (v) *x*+1/2, −*y*+3/2, *z*−1/2.