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catena-Poly[[aqua(benzoato)(*N*,*N*′-dimethylformamide)calcium(II)]-μ-benzoato]

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Key indicators

Single-crystal X-ray study
T = 143 K
Mean σ(C–C) = 0.004 Å
R factor = 0.045
wR factor = 0.049
Data-to-parameter ratio = 16.5

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

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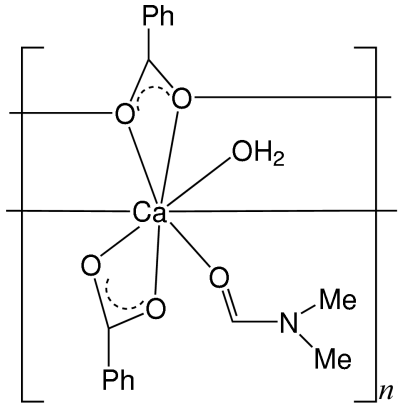
In the title complex, $[Ca(C_7H_5O_2)_2(C_3H_7NO)(H_2O)]_n$, the eightfold coordinated calcium ion is bonded to four carboxylate O atoms from two benzoate ions, an O atom from dimethylformamide and an O atom from a water molecule. One of the carboxylate groups bridges adjacent Ca^{2+} ions to form a polymeric ribbon structure.

Comment

The synthesis and structure determination of inorganic polymers is an interesting subject for basic inorganic chemistry and materials science. In this paper, we report the successful isolation and X-ray crystal structure determination of a unique Ca^{II} polymeric compound, (I), bridged by a benzoate group.



(I)

As shown in Fig. 1, the calcium ion is surrounded by eight O atoms from two bidentate benzoates, an *N*,*N*′-dimethylformamide molecule, a water molecule and two carboxylate groups bridging adjacent Ca^{2+} ions. The octacoordinate CaO_8 polyhedron deviates extensively from idealized octacoordinated geometries. There are two coordinated benzoate groups forming planar four-membered chelate rings. In addition, the O3 and O4 atoms from one of the benzoates link different Ca^{2+} ions by monodentate bridging bonds forming buckled four-membered Ca—O—Ca—O rings which partly form the basis of the extended structure. The polymeric ribbon structure is formed along the 2_1 screw axis parallel to *b*. As is usual in polymeric calcium carboxylates, the Ca—O bridging bond lengths [2.398 (2) and 2.400 (2) Å] are considerably shorter than the Ca—O chelate distances of 2.654 (3) and 2.460 (2) Å. Fairly long Ca—O distances [2.570 (2) and 2.508 (2) Å] are observed in one of the benzoate groups, which has no inter-

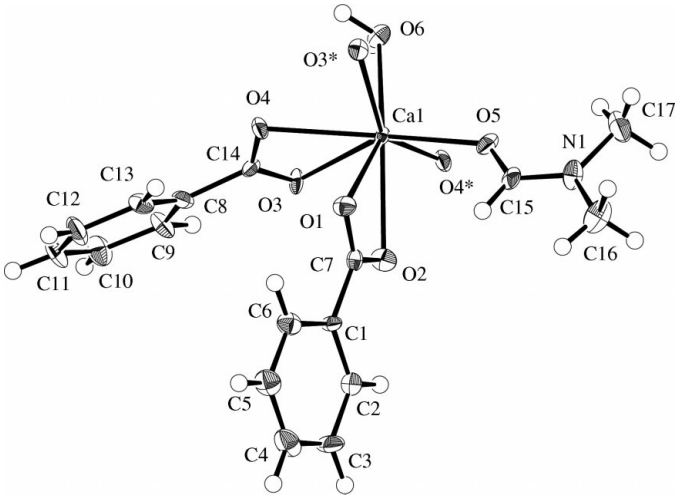


Figure 1
The environment of Ca^{2+} for (I) showing 50% probability displacement ellipsoids.

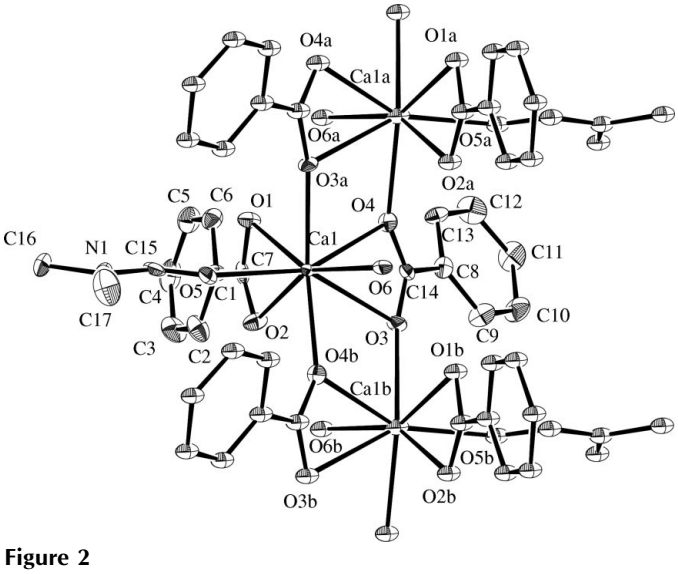


Figure 2
A perspective view of the polymeric structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

action among the neighboring Ca^{2+} ions. These observations indicated the importance of the bridging interactions in the crystal structure of a polymeric network of calcium carboxylates (Karipides *et al.*, 1988; Einspahr & Bugg, 1981).

Experimental

An aqueous solution of benzoic acid (0.74 g, 6.1 mmol) was adjusted to *ca* pH 7.0 with a 0.5 *M* KOH solution. Then $CaCl_2{\cdot}2H_2O$ (0.38 g, 2.6 mmol) was added to the benzoic acid solution with stirring. A 10 ml portion of dimethylformamide was added to the reaction solution. The solution was concentrated to half volume and allowed to stand at room temperature for 24 h. Colorless crystals of (I) were obtained. Yield: 0.32 g (32.9%). Analysis found: C 54.55, H 5.14, N 3.72%; calculated for $C_{17}H_{19}CaNO_6$: C 54.68, H 5.13, N 3.75%.

Crystal data

$[Ca(C_7H_5O_2)_2(C_3H_7NO)(H_2O)]$	D_x = 1.422 Mg m^{-3}
M_r = 373.42	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 9115 reflections
a = 10.8346 (6) Å	θ = 2.8–27.4°
b = 6.7519 (3) Å	μ = 0.39 mm^{-1}
c = 24.363 (1) Å	T = 143.2 K
β = 101.781 (2)°	Prism, colorless
V = 1744.7 (2) Å^3	0.35 × 0.05 × 0.02 mm
Z = 4	

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer	3967 independent reflections
	1789 reflections with $F^2 > 2\sigma(F^2)$
ω scans	R_{int} = 0.048
Absorption correction: multi-scan (Higashi, 1995)	θ_{max} = 27.5°
	$h = -13 \rightarrow 14$
T_{min} = 0.755, T_{max} = 0.992	$k = -8 \rightarrow 8$
8718 measured reflections	$l = -31 \rightarrow 31$

Refinement

Refinement on F^2	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)]$ = 0.045	$w = 1/[\sigma^2(F_o^2) + \{0.002[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3\}^2]$
$wR(F^2)$ = 0.049	$(\Delta/\sigma)_{max} < 0.001$
S = 0.94	$\Delta\rho_{max}$ = 0.82 e Å^{-3}
3739 reflections	$\Delta\rho_{min}$ = −0.80 e Å^{-3}
226 parameters	

Table 1
Selected geometric parameters (Å, °).

Ca1—O1	2.570 (2)	Ca1—O4	2.460 (2)
Ca1—O2	2.508 (2)	Ca1—O4^{ii}	2.400 (2)
Ca1—O3	2.654 (3)	Ca1—O5	2.363 (3)
Ca1—O3^{i}	2.398 (2)	Ca1—O6	2.405 (2)
O1—Ca1—O2	51.54 (7)	O3—Ca1—O4	51.00 (7)
O1—Ca1—O3	98.39 (7)	O3—Ca1—O4^{ii}	72.18 (7)
O1—Ca1—O3^{i}	79.76 (7)	O3—Ca1—O5	149.15 (8)
O1—Ca1—O4	74.96 (7)	O3—Ca1—O6	84.14 (7)
O1—Ca1—O4^{ii}	133.40 (7)	O3^{i}—Ca1—O4	75.78 (8)
O1—Ca1—O5	82.99 (7)	O3^{i}—Ca1—O4^{ii}	143.71 (6)
O1—Ca1—O6	151.76 (8)	O3^{i}—Ca1—O5	86.33 (8)
O2—Ca1—O3	74.37 (8)	O3^{i}—Ca1—O6	75.81 (7)
O2—Ca1—O3^{i}	130.99 (7)	O4—Ca1—O4^{ii}	121.28 (6)
O2—Ca1—O4	94.14 (7)	O4—Ca1—O5	153.62 (8)
O2—Ca1—O4^{ii}	82.48 (7)	O4—Ca1—O6	85.42 (7)
O2—Ca1—O5	82.99 (8)	O4^{ii}—Ca1—O5	84.48 (8)
O2—Ca1—O6	152.28 (8)	O4^{ii}—Ca1—O6	74.28 (7)
O3—Ca1—O3^{i}	124.37 (6)	O5—Ca1—O6	109.09 (7)

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

The H atoms, excluding those of water, were placed in idealized positions and refined as riding atoms with isotropic displacement parameters. Those of water were located from difference Fourier maps and their positional parameters refined using the reflections in the range of $\sin\theta/\lambda < 0.4$; they were fixed at the last stage of the refinement.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976).

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