

Since 3-furancarboxylic acid showed a tendency to sublime during the measurements, the crystal was mounted in a Lindemann capillary. The Kuma diffractometer system (Kuma, 1989) was used for data collection, cell refinement and data reduction. The intensities of three standard reflections showed no significant attenuation during the data collection so that the correction for decomposition turned out to be unnecessary. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990). The initial *E* map clearly revealed the position of all non-H atoms. All H atoms attached to the ring and the carboxylic H atom were subsequently found on the difference Fourier map and refined isotropically without any restraints. The crystals of the calcium and strontium complexes proved to be stable since the three standard reflections measured indicated no significant change in their intensities. The Kuma diffractometer system (Kuma, 1989) was used for data collection, cell refinement and data reduction. The structures were solved by the Patterson method using *SHELXS86*. H atoms bonded to C atoms were included in geometrically calculated positions ($C-H = 0.93 \text{ \AA}$). In the case of the calcium complex, H atoms bonded to O atoms were found from a $\Delta\rho$ map and refined without any restraints. For the strontium complex, an examination of the subsequent $\Delta\rho$ maps revealed one of the coordinated water atoms (O5) being disordered between two positions, with occupancy factors of 0.62 and 0.38. The water H atoms were restrained to be bound to their O atoms at a distance of 0.98 \AA and refined isotropically with displacement coefficients 1.5 times the respective parameters of the O atoms. *SHELXL93* (Sheldrick, 1993) was used for the refinement of all compounds.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with a view of the packing arrangement in the crystal of the strontium complex, have been deposited with the IUCr (Reference: JZ1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Carboxylate and Furan-Ring Oxygen Bonded to Calcium in Polymeric Calcium Furoate

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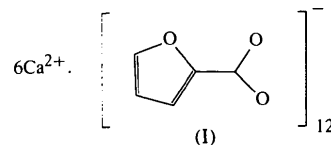
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Abstract

In the structure of calcium 2-furancarboxylate, $Ca^{2+} \cdot 2C_5H_3O_3^-$, three different coordination polyhedra were found around calcium. The polyhedra are linked to form a three-dimensional polymeric molecular framework. Both carboxylate O atoms and furan ring O atoms coordinate to the calcium cations, with Ca—O distances in the range $2.291(4)$ – $3.114(5) \text{ \AA}$. There are six formula units in the asymmetric unit.

Comment

Calcium–carboxylate interactions attract considerable interest because of the vital role calcium plays in living organisms (Einspahr & Bugg, 1977; Williams, 1977). It has been shown that Ca^{2+} displays the three possible modes of carboxylate binding – monodentate, bidentate and malonate (Hodgson & Asplund, 1990). Ca^{2+} can also adopt a variety of coordination geometries showing great flexibility when bonding with mixed ligands (Helems, Cole & Holt, 1988). The results of the present study of (I) reveal that the geometries of the coordination polyhedra around eight independent Ca^{2+} are not the same. The coordination numbers for Ca1, Ca2, Ca3 and Ca4, located in general positions in the unit cell, are 7, 10, 8 and 7, respectively. Two cations (Ca5 and Ca6) situated on the twofold axes are eight-coordinate, whereas those occupying the inversion centres (Ca7 and Ca8) exhibit coordination numbers of 6 and 8, respectively.†



†The value of 3.14 \AA as the sum of van der Waals radii has been arbitrarily chosen as a criterion for Ca—O bond distances in constructing the coordination polyhedra for the various Ca cations. However, slightly longer contacts with acceptable geometry, e.g. $Ca1 \cdots O13$ $3.209(6)$ and $Ca3 \cdots O33$ $3.242(5) \text{ \AA}$, may suggest the existence of some weaker $Ca \cdots O$ interactions.

The analysis of Ca—O distances shows that, as well as the carboxylate O atoms, the furan ring O atoms also take part in bonding interactions (see Table 2). The O atoms are disposed around the Ca cations in such a way as to give rise to distorted polyhedral surroundings for each coordination number. All Ca^{2+} ions are bridged in a tri-

dentate ($O:O,O'$ -) or tetradentate ($O,O':O,O'$ - in the case of Ca1 and Ca3) fashion by O atoms from the carboxylate group of the anions Fu_x , where $x = 1-12$ (see Table 1). The Ca1—Fu11 and Ca4—Fu2 linkages show the symmetrical and unsymmetrical bidentate modes of binding. Whereas the Ca1—Fu11 contacts are equal [2.583 (4) Å], the Ca4—Fu2 distances differ significantly [2.463 (4) and 2.932 (4) Å]. Direct bonding of the furan ring O atom (Fu1, Fu4, Fu6, Fu7, Fu8, Fu10) to the Ca^{2+} cation gives rise to the formation of five-membered rings (Ca^{2+} , O_{furan} , two C_{furan} and $\text{O}_{\text{carboxylate}}$). Such a process does not affect the geometry of the 2-furancarboxylate ions. The geometries of the anions do not differ from those found in 2-furancarboxylic acid (Gilmore, Mallison & Speakman, 1983).

The structure of calcium 2-furancarboxylate is polymeric. It consists of cross-linked zigzag chains of Ca^{2+} , which propagate along [010] and [001]. A projection of the Ca^{2+} network along the c axis is shown in Fig. 1. A similar arrangement appears in a projection along the b axis. The distances between neighbouring Ca^{2+} ions belonging to the chains, lying almost in the (001) and (010) planes, range from 3.835 (3) to 4.278 (2) Å. Approximately hexagonal cavities in the b and c directions are filled by 2-furancarboxylate ions.

The Ca— $\text{O}_{\text{carboxylate}}$ bond distances listed in Table 2 are in good agreement with the data reported for the other calcium carboxylate structures (Einspahr & Bugg, 1981). The Ca— O_{furan} contacts observed for Ca2, Ca5, Ca6 and Ca8 (Fig. 2) of the title compound are visibly longer, which could be explained as the result of the σ -electron

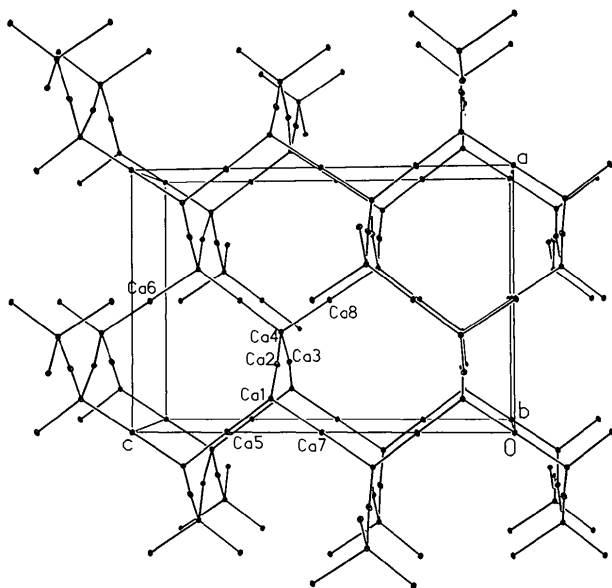


Fig. 1 View of the polymer motif in the unit cell of calcium 2-furancarboxylate showing the arrangement of all independent Ca^{2+} ions.

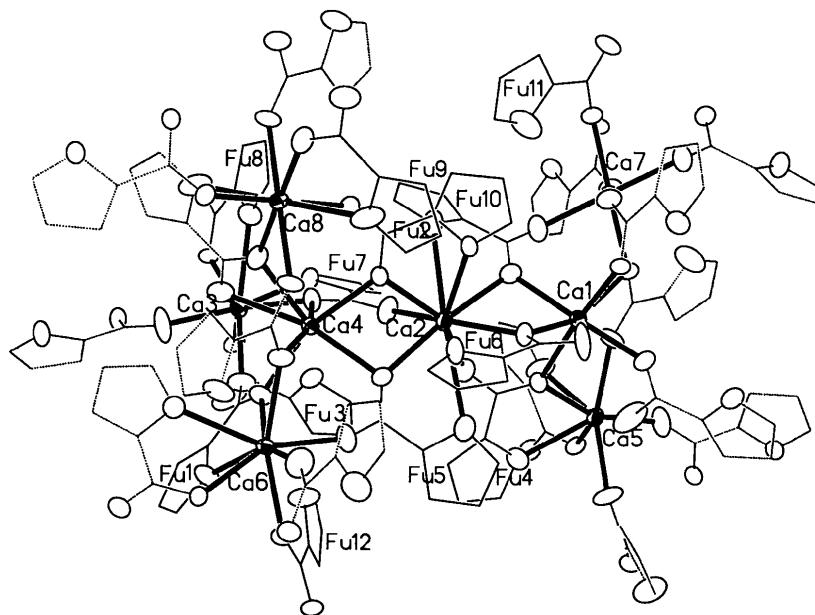


Fig. 2. Perspective view of calcium 2-furancarboxylate. The furancarboxylate moieties are represented schematically except for the O atoms which are plotted as displacement ellipsoids. The furancarboxylate moieties are labelled Fu1 to Fu12 and correspond to O and C atoms with labels appended by 1 to 12 respectively (see Table 1).

donor properties of hetero ring O atoms. Such bonds are sometimes described as 'dative bonds' (Haaland, 1989). In the structure of calcium 3-furancarboxylate (Paluchowska, Maurin & Leciejewicz, 1996) contacts between cations and O_{furan} atoms were not observed. This could be explained as a result of less favourable steric conditions in forming six-membered rings involving the hetero ring O atom in the three position to the carboxylate group. In this compound the electron-donor properties of the furan ring O atom manifest themselves by C—H...O hydrogen-bond formation.

Experimental

Calcium 2-furancarboxylate was obtained by reaction of calcium oxide with a hot aqueous solution of furoic acid in 1:2 molar ratio. Crystals were formed over a week by slow evaporation at room temperature and were stable in air.

Crystal data

Ca²⁺·2C₅H₃O₃[−]
M_r = 262.23
 Monoclinic
*P*2/*c*
a = 18.262 (4) Å
b = 12.956 (7) Å
c = 26.518 (20) Å
 β = 90.40 (3)°
V = 6274 (4) Å³
Z = 24
D_x = 1.666 Mg m^{−3}

Data collection

Kuma KM-4 computer-controlled four-circle κ -axis diffractometer
 $\omega/2\theta$ scans
 Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
T_{min} = 0.09, *T_{max}* = 0.20
 12980 measured reflections
 12713 independent reflections

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.0548
wR (*F*²) = 0.1156
S = 1.175
 12710 reflections
 921 parameters
 H-atom parameters not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0730P)^2 + 0.4561P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = 0.031

Cu *K*α radiation
 λ = 1.5418 Å
 Cell parameters from 25 reflections
 θ = 20–25°
 μ = 5.366 mm^{−1}
T = 293 (2) K
 Irregular shape
 0.4 × 0.35 × 0.3 mm
 Colourless

5539 observed reflections
 [*I* > 2σ(*I*)]
R_{int} = 0.0916
 θ_{max} = 80.43°
h = −20 → 21
k = 0 → 16
l = −30 → 0
 3 standard reflections monitored every 100 reflections
 intensity decay: none

$\Delta\rho_{max}$ = 0.665 e Å^{−3}
 $\Delta\rho_{min}$ = −0.642 e Å^{−3}
 Extinction correction: SHELXL93 (Sheldrick, 1993)
 Extinction coefficient: 0.00042 (3)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ca1	0.12664 (5)	0.01757 (7)	0.63353 (3)	0.0257 (2)
Ca2	0.25135 (6)	0.26901 (7)	0.63153 (4)	0.0309 (2)
Ca3	0.24870 (5)	0.77175 (7)	0.62670 (3)	0.0269 (2)
Ca4	0.37295 (5)	0.51360 (7)	0.63474 (3)	0.0257 (2)
Ca5	0	0.03205 (10)	3/4	0.0307 (3)
Ca6	1/2	0.53564 (10)	3/4	0.0280 (3)
Ca7	0	0	1/2	0.0282 (3)
Ca8	1/2	1/2	1/2	0.0302 (3)
Fu1				
O11	0.4480 (2)	0.7126 (3)	0.79042 (13)	0.0462 (10)
O21	0.3952 (2)	0.6181 (2)	0.70789 (12)	0.0351 (8)
O31	0.3022 (2)	0.7293 (3)	0.70319 (12)	0.0431 (9)
C21	0.3887 (3)	0.7538 (4)	0.7656 (2)	0.0371 (12)
C31	0.3682 (4)	0.8417 (4)	0.7889 (2)	0.052 (2)
C41	0.4174 (4)	0.8543 (5)	0.8303 (2)	0.057 (2)
C51	0.4643 (4)	0.7759 (5)	0.8300 (2)	0.054 (2)
C61	0.3595 (3)	0.6971 (3)	0.7220 (2)	0.0298 (11)
Fu2				
O12	0.5369 (3)	0.2784 (4)	0.51407 (14)	0.0598 (12)
O22	0.5741 (2)	0.3975 (3)	0.43853 (13)	0.0445 (9)
O32	0.6285 (2)	0.2701 (3)	0.39784 (13)	0.0483 (10)
C22	0.5686 (3)	0.2338 (4)	0.4735 (2)	0.0382 (12)
C32	0.5751 (4)	0.1314 (5)	0.4802 (3)	0.081 (2)
C42	0.5451 (6)	0.1146 (7)	0.5299 (4)	0.121 (4)
C52	0.5232 (5)	0.2033 (9)	0.5478 (3)	0.100 (3)
C62	0.5921 (3)	0.3038 (4)	0.4339 (2)	0.0308 (11)
Fu3				
O13	0.1464 (2)	0.6574 (3)	0.70908 (13)	0.0447 (10)
O23	0.1515 (2)	0.8533 (3)	0.67355 (12)	0.0368 (8)
O33	0.0912 (3)	0.9102 (4)	0.7397 (2)	0.090 (2)
C23	0.1159 (3)	0.7349 (4)	0.7359 (2)	0.0408 (13)
C33	0.0841 (4)	0.6979 (5)	0.7774 (2)	0.064 (2)
C43	0.0935 (4)	0.5889 (5)	0.7759 (2)	0.060 (2)
C53	0.1309 (4)	0.5690 (4)	0.7351 (2)	0.0489 (15)
C63	0.1194 (3)	0.8398 (4)	0.7148 (2)	0.0429 (14)
Fu4				
O14	0.0573 (2)	0.1936 (3)	0.79627 (13)	0.0527 (11)
O24	0.0984 (2)	0.1239 (2)	0.70602 (12)	0.0347 (8)
O34	0.1606 (2)	0.2690 (3)	0.69148 (13)	0.0453 (9)
C24	0.1064 (3)	0.2492 (4)	0.7693 (2)	0.0332 (11)
C34	0.1321 (3)	0.3256 (4)	0.7986 (2)	0.0458 (14)
C44	0.0964 (4)	0.3188 (5)	0.8450 (2)	0.056 (2)
C54	0.0518 (4)	0.2394 (5)	0.8424 (2)	0.065 (2)
C64	0.1226 (3)	0.2126 (4)	0.7184 (2)	0.0313 (11)
Fu5				
O15	0.2904 (2)	0.2003 (3)	0.7410 (2)	0.0553 (11)
O25	0.3307 (2)	0.3706 (3)	0.68799 (12)	0.0407 (9)
O35	0.4162 (2)	0.4028 (3)	0.7454 (2)	0.0526 (11)
C25	0.3357 (3)	0.2724 (4)	0.7625 (2)	0.0372 (12)
C35	0.3459 (4)	0.2517 (5)	0.8120 (2)	0.063 (2)
C45	0.3037 (4)	0.1588 (5)	0.8210 (3)	0.065 (2)
C55	0.2729 (4)	0.1310 (5)	0.7779 (3)	0.069 (2)
C65	0.3632 (3)	0.3555 (4)	0.7300 (2)	0.0351 (12)
Fu6				
O16	0.3845 (2)	0.1718 (2)	0.65324 (14)	0.0401 (9)
O26	0.2505 (2)	0.0830 (2)	0.64332 (12)	0.0320 (8)
O36	0.3017 (2)	−0.0723 (3)	0.6449 (2)	0.0618 (13)
C26	0.3772 (3)	0.0679 (4)	0.6589 (2)	0.0343 (11)
C36	0.4376 (3)	0.0279 (5)	0.6773 (3)	0.061 (2)
C46	0.4884 (3)	0.1101 (5)	0.6831 (3)	0.063 (2)
C56	0.4534 (3)	0.1948 (5)	0.6689 (2)	0.0474 (14)
C66	0.3046 (3)	0.0233 (4)	0.6483 (2)	0.0353 (11)

Fu7					Ca2—O16	2.795 (4)	Ca6—O212	2.463 (3)
O17	0.1256 (2)	0.6740 (2)	0.59829 (13)	0.0359 (8)	Ca2—O19	3.068 (5)	Ca6—O11	2.706 (4)
O27	0.2551 (2)	0.5858 (2)	0.61458 (13)	0.0352 (8)	Ca2—O15	3.114 (5)	Ca7—O38'	2.294 (4)
O37	0.2028 (2)	0.4320 (3)	0.6258 (2)	0.0547 (11)	Ca3—O36 ^{III}	2.291 (4)	Ca7—O211	2.366 (4)
C27	0.1274 (3)	0.5701 (3)	0.6098 (2)	0.0305 (10)	Ca3—O31	2.312 (4)	Ca7—O39	2.368 (4)
C37	0.0593 (3)	0.5352 (4)	0.6160 (2)	0.0481 (14)	Ca3—O32 ^{II}	2.401 (4)	Ca8—O310	2.296 (3)
C47	0.0113 (4)	0.6200 (5)	0.6080 (2)	0.056 (2)	Ca3—O23	2.417 (4)	Ca8—O312 ^Δ	2.325 (4)
C57	0.0537 (3)	0.7008 (5)	0.5976 (2)	0.0480 (14)	Ca3—O27	2.434 (3)	Ca8—O22	2.506 (4)
C67	0.1998 (3)	0.5264 (4)	0.6168 (2)	0.0334 (11)	Ca3—O28	2.503 (3)	Ca8—O12	2.971 (5)
					Ca3—O17	2.684 (4)		
Fu8					O29—Ca1—O23 ^I	162.30 (13)	O32 ^{IV} —Ca3—O23	158.22 (13)
O18	0.2447 (2)	0.7446 (3)	0.52281 (13)	0.0390 (9)	O29—Ca1—O24	88.37 (13)	O36 ^{III} —Ca3—O27	151.73 (14)
O28	0.1796 (2)	0.8975 (2)	0.57282 (11)	0.0324 (8)	O23 ^I —Ca1—O24	101.10 (12)	O31—Ca3—O27	81.96 (13)
O38	0.1204 (2)	0.9499 (3)	0.50323 (12)	0.0404 (9)	O29—Ca1—O26	70.59 (12)	O32 ^{IV} —Ca3—O27	72.22 (13)
C28	0.2007 (3)	0.8125 (4)	0.4969 (2)	0.0331 (11)	O23 ^I —Ca1—O26	95.08 (12)	O23—Ca3—O27	122.47 (13)
C38	0.2012 (4)	0.7903 (5)	0.4477 (2)	0.063 (2)	O24—Ca1—O26	85.39 (12)	O36 ^{III} —Ca3—O28	75.93 (13)
C48	0.2484 (4)	0.7019 (5)	0.4420 (2)	0.069 (2)	O29—Ca1—O28 ^I	97.96 (13)	O31—Ca3—O28	149.79 (12)
C58	0.2722 (3)	0.6783 (4)	0.4873 (2)	0.0491 (15)	O23 ^I —Ca1—O28 ^I	69.82 (11)	O32 ^{IV} —Ca3—O28	117.42 (13)
C68	0.1638 (3)	0.8917 (3)	0.5262 (2)	0.0295 (10)	O24—Ca1—O28 ^I	166.43 (12)	O23—Ca3—O28	68.88 (11)
					O26—Ca1—O28 ^I	85.43 (12)	O27—Ca3—O28	126.40 (12)
Fu9					O29—Ca1—O311 ^{II}	110.08 (14)	O36 ^{III} —Ca3—O17	145.82 (13)
O19	0.1818 (2)	0.3345 (3)	0.5309 (2)	0.0543 (11)	O23 ^I —Ca1—O311 ^{II}	87.45 (14)	O31—Ca3—O17	118.83 (13)
O29	0.1397 (2)	0.1707 (3)	0.58567 (13)	0.0431 (9)	O24—Ca1—O311 ^{II}	67.44 (12)	O32 ^{IV} —Ca3—O17	126.82 (12)
O39	0.0366 (2)	0.1563 (3)	0.5389 (2)	0.0514 (10)	O26—Ca1—O311 ^{II}	152.65 (12)	O23—Ca3—O17	74.56 (12)
C29	0.1111 (3)	0.3006 (4)	0.5277 (2)	0.0376 (12)	O28 ^I —Ca1—O311 ^{II}	120.66 (12)	O27—Ca3—O17	62.40 (11)
C39	0.0693 (4)	0.3689 (5)	0.5026 (2)	0.058 (2)	O29—Ca1—O211 ^{II}	95.76 (13)	O28—Ca3—O17	74.25 (11)
C49	0.1190 (5)	0.4516 (5)	0.4888 (3)	0.069 (2)	O23 ^I —Ca1—O211 ^{II}	93.98 (12)	O36 ^{III} —Ca3—O18	109.22 (15)
C59	0.1837 (5)	0.4265 (5)	0.5061 (3)	0.068 (2)	O24—Ca1—O211 ^{II}	113.98 (12)	O31—Ca3—O18	148.03 (12)
C69	0.0947 (3)	0.2012 (4)	0.5526 (2)	0.0349 (12)	O26—Ca1—O211 ^{II}	156.52 (11)	O32 ^{IV} —Ca3—O18	73.79 (12)
					O28 ^I —Ca1—O211 ^{II}	77.47 (12)	O23—Ca3—O18	123.42 (12)
Fu10					O311 ^{II} —Ca1—O211 ^{II}	49.39 (11)	O27—Ca3—O18	75.20 (11)
O110	0.3064 (2)	0.1810 (2)	0.54956 (12)	0.0402 (9)	O37—Ca2—O34	76.44 (14)	O28—Ca3—O18	60.42 (10)
O210	0.3446 (2)	0.3671 (2)	0.58184 (11)	0.0353 (8)	O37—Ca2—O26	156.66 (14)	O17—Ca3—O18	69.24 (11)
O310	0.3939 (2)	0.4065 (3)	0.50758 (12)	0.0394 (9)	O34—Ca2—O26	84.63 (12)	O21—Ca4—O27	96.13 (12)
C210	0.3436 (3)	0.2444 (4)	0.5171 (2)	0.0306 (11)	O37—Ca2—O25	76.90 (14)	O21—Ca4—O210	161.51 (12)
C310	0.3554 (4)	0.1957 (5)	0.4734 (2)	0.052 (2)	O34—Ca2—O25	90.19 (14)	O27—Ca4—O210	89.34 (13)
C410	0.3247 (4)	0.0955 (5)	0.4784 (2)	0.064 (2)	O26—Ca2—O25	117.18 (12)	O21—Ca4—O212 ^Δ	71.00 (11)
C510	0.2957 (4)	0.0908 (4)	0.5244 (2)	0.056 (2)	O37—Ca2—O210	76.27 (14)	O27—Ca4—O212 ^Δ	161.73 (12)
C610	0.3631 (3)	0.3469 (4)	0.5370 (2)	0.0304 (10)	O34—Ca2—O210	148.98 (12)	O210—Ca4—O212 ^Δ	106.97 (12)
					O26—Ca2—O210	125.12 (12)	O21—Ca4—O25	90.73 (13)
Fu11					O25—Ca2—O210	69.45 (12)	O27—Ca4—O25	97.85 (13)
O111	0.1134 (3)	0.1475 (4)	0.4241 (2)	0.0771 (15)	O37—Ca2—O110	119.29 (13)	O210—Ca4—O25	71.00 (12)
O211	-0.0126 (2)	0.0493 (3)	0.41447 (12)	0.0388 (9)	O34—Ca2—O110	147.37 (13)	O212 ^Δ —Ca4—O25	95.29 (12)
O311	0.0074 (3)	0.0028 (3)	0.33763 (13)	0.0572 (12)	O26—Ca2—O110	71.49 (11)	O21—Ca4—O22 ^{IV}	108.01 (13)
C211	0.1013 (3)	0.0894 (4)	0.3810 (2)	0.0459 (14)	O25—Ca2—O110	120.20 (13)	O27—Ca4—O22 ^{IV}	89.92 (13)
C311	0.1577 (5)	0.0954 (7)	0.3504 (3)	0.086 (2)	O210—Ca2—O110	61.67 (11)	O210—Ca4—O22 ^{IV}	89.60 (12)
C411	0.2110 (4)	0.1606 (7)	0.3754 (3)	0.086 (3)	O37—Ca2—O29	96.57 (14)	O212 ^Δ —Ca4—O22 ^{IV}	82.20 (13)
C511	0.1818 (5)	0.1873 (8)	0.4187 (4)	0.102 (3)	O34—Ca2—O29	76.42 (13)	O25—Ca4—O22 ^{IV}	158.89 (12)
C611	0.0276 (3)	0.0439 (4)	0.3770 (2)	0.0326 (11)	O26—Ca2—O29	65.36 (11)	O21—Ca4—O32 ^{IV}	72.55 (11)
					O25—Ca2—O29	166.24 (12)	O27—Ca4—O32 ^{IV}	63.66 (11)
Fu12					O210—Ca2—O29	121.24 (12)	O210—Ca4—O32 ^{IV}	125.34 (11)
O112	0.3568 (2)	0.5420 (4)	0.81767 (13)	0.0543 (11)	O110—Ca2—O29	73.56 (12)	O212 ^Δ —Ca4—O32 ^{IV}	99.37 (12)
O212	0.4992 (2)	0.4983 (3)	0.84106 (11)	0.0372 (8)	O37—Ca2—O16	139.80 (14)	O25—Ca4—O32 ^{IV}	152.56 (12)
O312	0.4670 (2)	0.4535 (3)	0.91826 (12)	0.0406 (9)	O34—Ca2—O16	119.13 (13)	O22 ^{IV} —Ca4—O32 ^{IV}	47.42 (11)
C212	0.3765 (3)	0.5191 (4)	0.8660 (2)	0.0343 (11)	O26—Ca2—O16	62.12 (11)	O33 ^I —Ca5—O33 ^{III}	93.9 (3)
C312	0.3185 (3)	0.5311 (3)	0.8960 (2)	0.0492 (14)	O25—Ca2—O16	66.91 (12)	O33 ^I —Ca5—O311 ^{II}	77.9 (2)
C412	0.2590 (3)	0.5624 (3)	0.8652 (2)	0.063 (2)	O210—Ca2—O16	75.15 (12)	O33 ^I —Ca5—O24 ^{IV}	87.1 (2)
C512	0.2849 (4)	0.5666 (6)	0.8184 (3)	0.064 (2)	O110—Ca2—O16	68.99 (12)	O33 ^I —Ca5—O24 ^{IV}	156.45 (13)
C612	0.4528 (3)	0.4890 (4)	0.8759 (2)	0.0316 (10)	O29—Ca2—O16	122.39 (11)	O311 ^{VI} —Ca5—O24 ^{IV}	70.37 (12)
					O37—Ca2—O19	62.01 (13)	O33 ^I —Ca5—O24	75.2 (2)
					O34—Ca2—O19	107.73 (14)	O311 ^{VI} —Ca5—O24	121.38 (14)
					O26—Ca2—O19	112.54 (11)	O33 ^I —Ca5—O14	108.2 (2)
					O25—Ca2—O19	128.36 (11)	O311 ^{VI} —Ca5—O14	71.07 (14)
					O210—Ca2—O19	71.41 (12)	O24—Ca5—O14	63.09 (11)
					O110—Ca2—O19	64.15 (12)	O35 ^V —Ca6—O35	83.4 (2)
					O29—Ca2—O19	55.19 (11)	O35—Ca6—O21	77.61 (14)
					O16—Ca2—O19	131.18 (12)	O35—Ca6—O212	84.10 (13)
					O37—Ca2—O15	114.21 (14)	O21—Ca6—O212	121.45 (12)
					O34—Ca2—O15	61.19 (14)	O35—Ca6—O11	114.77 (14)
					O26—Ca2—O15	66.31 (11)	O21—Ca6—O11	62.40 (11)
					O25—Ca2—O15	56.99 (11)	O212—Ca6—O11	76.91 (12)
					O210—Ca2—O15	118.88 (12)	O38 ^I —Ca7—O211	101.47 (13)
					O110—Ca2—O15	123.66 (13)	O38 ^I —Ca7—O39	87.61 (14)
					O29—Ca2—O15	117.02 (11)	O211—Ca7—O39	102.26 (13)
					O16—Ca2—O15	59.07 (12)	O310—Ca8—O312 ^Δ	89.72 (13)
					O19—Ca2—O15	168.74 (12)	O310—Ca8—O22	103.72 (13)
					O36 ^{III} —Ca3—O31	81.3 (2)	O312 ^Δ —Ca8—O22	109.36 (12)

Table 2. Selected geometric parameters (Å, °)

Ca1—O29	2.368 (4)	Ca3—O18	2.778 (4)
Ca1—O23 ^I	2.420 (3)	Ca4—O21	2.398 (3)
Ca1—O24	2.424 (3)	Ca4—O27	2.403 (4)
Ca1—O26	2.429 (3)	Ca4—O210	2.414 (3)
Ca1—O28 ^I	2.443 (3)	Ca4—O212 ^Δ	2.425 (4)
Ca1—O311 ^{II}	2.583 (4)	Ca4—O25	2.457 (4)
Ca1—O211 ^{II}	2.583 (4)	Ca4—O22 ^{IV}	2.463 (4)
Ca2—O37	2.295 (4)	Ca4—O32 ^{IV}	2.932 (4)
Ca2—O34	2.305 (4)	Ca5—O33 ^I	2.313 (4)
Ca2—O26	2.430 (3)	Ca5—O311 ^{VI}	2.370 (4)
Ca2—O25	2.458 (4)	Ca5—O24	2.457 (3)
Ca2—O210	2.507 (3)	Ca5—O14	2.638 (4)
Ca2—O110	2.659 (4)	Ca6—O35	2.305 (4)
Ca2—O29	2.688 (4)	Ca6—O21	2.454 (3)

O36 ^{III} —Ca3—O32 ^{IV}	82.1 (2)	O310—Ca8—O12	70.72 (13)
O31—Ca3—O32 ^{IV}	78.14 (13)	O312 ^{IV} —Ca8—O12	64.89 (11)
O36 ^{III} —Ca3—O23	79.42 (15)	O22—Ca8—O12	56.42 (11)
O31—Ca3—O23	87.72 (13)		

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

The Kuma diffractometer system (Kuma, 1989) was used for data collection, cell refinement and data reduction. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1990) and refined on F^2 with *SHELXL93* (Sheldrick, 1993). Most of the non-H atoms were located from an E map. The remaining non-H atoms were revealed from a subsequent $\Delta\rho$ synthesis. In the final least-squares cycle non-H atoms were refined anisotropically. H atoms were included in geometrically calculated positions with C—H = 0.93 Å and each with an isotropic displacement coefficient 1.5 times that of its parent C atom. The atomic coordinates and the β angle of 90.40 (3) $^\circ$ suggested the possibility of orthorhombic symmetry (*Pbcn*). However, the higher symmetry is ruled out by (a) too many systematic absence violations and (b) the R_{int} values (0.09 and 0.43 for monoclinic and orthorhombic, respectively). Nonetheless, the structure can be interpreted as a pseudo-orthorhombic *Pbcn* structure, where atoms Ca1 and Ca3, Ca2 and Ca4, Ca5 and Ca6, Ca7 and Ca8 are symmetrically equivalent counterparts. The same is true for the respective furancarboxylate pairs.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1058). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis(*o*-benzoylbenzoato-*O,O'*)lead(IV) Dichloromethane Solvate

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Abstract

In the title complex, [Pb(C₁₄H₉O₃)₄].CH₂Cl₂, the Pb atom is located at a point of symmetry (4) and is coordinated by eight carboxylate O atoms of four benzoylbenzoate anions at the corners of a somewhat distorted trigonal dodecahedron [Pb—O 2.317 (9) and 2.235 (9) Å]. The dichloromethane solvent molecule is disordered in holes in the crystal structure, on the fourfold inversion axis between the Pb atoms.

Comment

Lead(IV) reagents find considerable application in organic synthesis and have been found to mediate both oxidative processes (Rubottom, 1982) and C—C bond-forming reactions (Pinhey, 1991; Abramovitch, Barton & Finet, 1988; Barton, 1990). We have been interested in extending the synthetic applications of lead(IV) reagents and to this end are investigating the synthesis, characterization and reactivity of a wide range of lead(IV) tetracarboxylates. These compounds can be readily prepared by metathesis of tetrakis(acetato)-lead(IV) and another suitable carboxylic acid (Buston, Coop, Keady, Moloney & Thompson, 1994). Although most lead(IV) tetracarboxylates have been isolated as amorphous powders, tetrakis(*o*-benzoylbenzoato)-lead(IV), (I), prepared from tetrakis(acetato)lead(IV) and *o*-benzoylbenzoic acid using the literature procedure (Buston *et al.*, 1994), could be readily crystallized from a dichloromethane/light petroleum mixture, to give yellow crystals from which a limited diffraction pattern could be obtained.

