

N	0	0.565 (1)	-0.027 (1)	0.052 (3)
C2	0.117 (2)	0.578 (2)	0.043 (1)	0.12 (1)
C1	0	0.411 (3)	-0.082 (2)	0.11 (1)

† Coordinate fixed to define origin.

Table 2. Selected bond lengths (Å) and angles (°)

Sn—C11	2.515 (4)	N—C1	1.45 (2)
Sn—C12	2.500 (3)	N—C2	1.42 (2)
C11—Sn—C12	90.6 (2)	C1—N—C2	111 (1)
C12—Sn—C12'	89.1 (1)	C2—N—C2'	104 (2)

Symmetry code: (i) $-x, y, z$.

Table 3. Contact distances (Å)

C11 ⁱ ...H6 ⁱⁱ	2.61 (5)	C11 ⁱ ...H4 ⁱⁱⁱ	2.78 (5)
C12 ⁱ ...H6 ⁱⁱ	2.71 (6)	C12 ⁱ ...H1 ⁱⁱⁱ	2.78 (6)

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

Intensity measurements were made with a two-circle diffractometer employing equi-inclination Weissenberg geometry. The angle θ' is the projection of θ onto the equatorial plane. The crystal was set to rotate around the a axis. A separate standard reflection was chosen for each layer. During structure refinement, interlayer scale factors were refined and thereafter fixed. The structure was solved by the use of Patterson and difference syntheses. During refinement H atoms were included at calculated positions with individually refined U_{iso} . Anisotropic displacement parameters were allowed for Sn and Cl only, with isotropic refinement of N and C.

The polarity of the structure was established by competitive refinement. The chosen polarity had a significantly lower conventional R value (0.0314 versus 0.0365), smaller residuals in the final ΔF synthesis and lower uncertainties in the refined parameters.

Data reduction: *DATR* (Small, 1977). Program(s) used to solve structure: *SHELX76* (Sheldrick, 1976), Patterson. Program(s) used to refine structure: *SHELX76*. Molecular graphics: *SNOOPI* (Davies, 1983).

I acknowledge the use of the Cambridge Structural Database (Allen *et al.*, 1991).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1018). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
- Davies, K. (1983). *SNOOPI. Program for Drawing Crystal and Molecular Diagrams*. University of Oxford, England.
- Dillon, K. B., Halfpenny, J. & Marshall, A. (1983). *J. Chem. Soc. Dalton Trans.* pp. 1091–1094.
- Dillon, K. B., Halfpenny, J. & Marshall, A. (1985). *J. Chem. Soc. Dalton Trans.* pp. 1399–1403.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. University of Cambridge England.
- Small, R. W. H. (1977). *DATR. Program for Reducing Raw Stadi-2 Data to Intensities*. University of Lancaster, England.
- Veith, M., Jarczyk, H. M. & Huch, V. (1988). *Chem. Ber.* **121**, 347–355.

Acta Cryst. (1996). **C52**, 342–347

The Role of C—H...O Bonds in Stabilizing 3-Furancarboxylic Acid and its Complexes with Calcium and Strontium

BEATA PALUCHOWSKA,^a JAN K. MAURIN^a AND JANUSZ LECIEJEWICZ^b

^aInstitute of Atomic Energy, 05-400 Otwock-Świerk, Poland, and ^bInstitute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

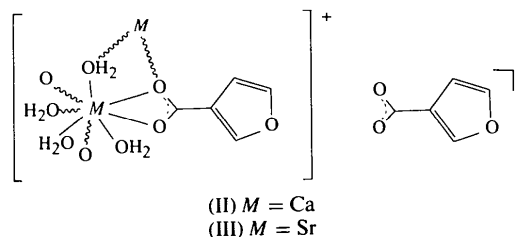
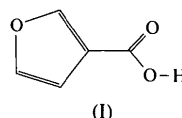
(Received 7 December 1994; accepted 6 March 1995)

Abstract

The crystal structures of 3-furancarboxylic acid, C₅H₄O₃, and both its calcium and strontium complexes, *catena*-poly[*diaquacalcium-μ*-(3-furancarboxylato-*O,O'*)-*μ*-aqua 3-furancarboxylate], [Ca(C₅H₃O₃)(H₂O)₃](C₅H₃O₃), and *catena*-poly[*diaquastrontium-μ*-(3-furancarboxylato-*O,O'*)-*μ*-aqua 3-furancarboxylate], [Sr(C₅H₃O₃)(H₂O)₃](C₅H₃O₃), respectively, are presented. The differences and similarities in the hydrogen-bonding schemes of the title acid and 2-furancarboxylic acid are discussed, and the importance of C—H...O hydrogen bonds in the crystal packing of 3-furancarboxylic acid and its strontium and calcium complexes is highlighted.

Comment

The determination of the crystal structure of 3-furancarboxylic acid, (I), has been performed as an introductory step in the study of coordination compounds in which it acts as a ligand or an anion.



The crystals of 3-furancarboxylic acid are composed of centrosymmetric hydrogen-bonded dimers, forming approximately planar layers of molecules parallel to the (10 $\bar{4}$) plane (Fig. 1). The two O3—H3...O2 hydrogen bonds between the carboxy O atoms, which are responsible for the formation of the dimer, have a

bond length of 2.653 (4) Å and an O3—H3···O2 angle of 173 (4)° (see Table 3). The two planar dimers, symmetry related *via* the 2_1 axis, are inclined at an angle of 134 (4)° to each other (the angle between the central lines of the dimers is defined by atoms C3 and C6 of both parts of the dimer and their symmetric counterparts) and form a dihedral angle of 15 (1)°. The dimers are held together by a system of the two different types of long C—H···O hydrogen bonds. One of them [3.387 (4) Å] links the ring H2 atom with the carboxy O2 atom of the adjacent dimer. The other hydrogen bond [3.410 (4) Å] connects the ring H5 atom with the furan O1 atom (Fig. 1). The layers are separated by a distance of 3.38 (1) Å, adopting the translated β -stacked type of structure. Such an arrangement was reported to be a packing standard for a planar aromatic moiety with a hetero oxygen replacement or an oxygen-containing functional group (Berkovitch-Yellin & Leiserowitz, 1984; Desiraju & Kishan, 1989).

In the crystals of 2-furancarboxylic acid, the hetero O atom does not participate in the intermolecular bonding system. Gilmore, Mallison & Speakman (1983) reported this structure as consisting of sheets of dimers aligned along the [110] direction and separated by a distance of 3.36 (1) Å. The molecules in this dimer interact *via* O—H···O hydrogen bonds [2.673 (4) Å]. An absence of C—H···O contacts (arising most probably from the poor steric condition) caused strong disorder of the carboxy H atom.

In the title structure, the same H atom is well localized due to a C—H···O=C interaction which is specific enough to involve the carbonyl O atom rather than the hydroxy O atom (Leiserowitz, 1976). The distances C6—O3 and C6—O2 are 1.307 (3) and 1.229 (3) Å, respectively. In addition, Fig. 1 reveals that for carbonyl acceptors C—H···O=C and O—H···O=C, there is a marked preference to lie in the plane containing the O-atom sp^2 lone pairs (Taylor & Kennard, 1984) [the

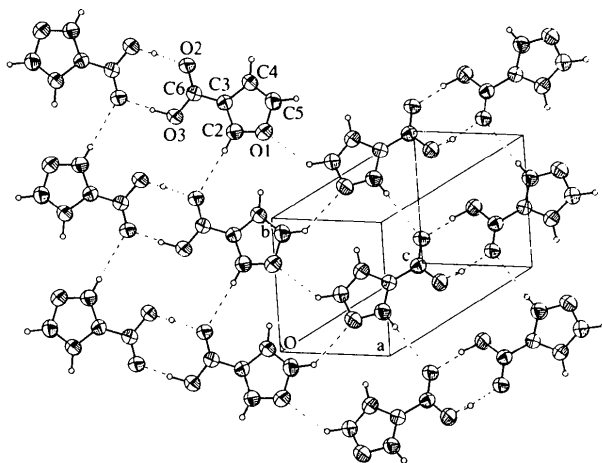


Fig. 1. The packing arrangement in the 3-furancarboxylic acid, (I), crystal. The non-H atoms are shown as 20% probability ellipsoids.

$C6^i=O2^i\cdots H2$ and $C6^{ii}=O2^{ii}\cdots H3$ angles are 136 (1) and 125 (2)°, respectively; symmetry codes: (i) $x, y + 1, z$; (ii) $2 - x, -y, 2 - z$].

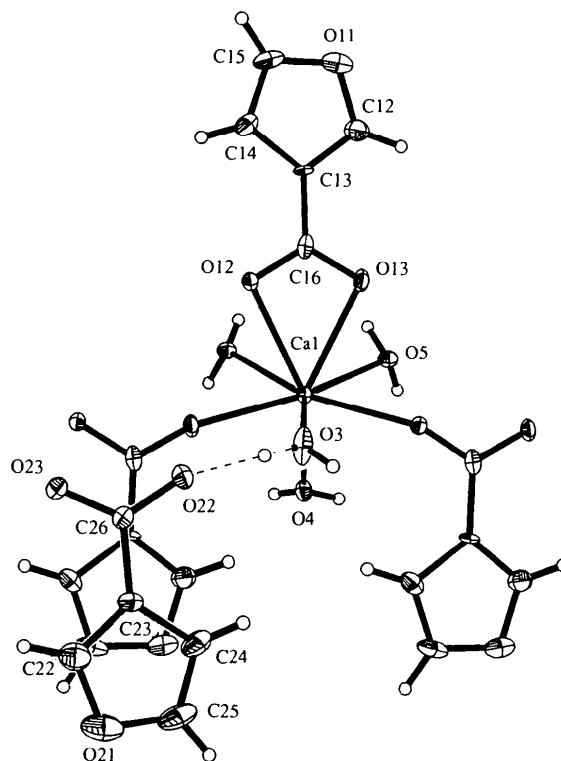


Fig. 2. View of the calcium complex of 3-furancarboxylic acid, (II), showing the labelling of the non-H atoms, which are shown as 20% probability ellipsoids.

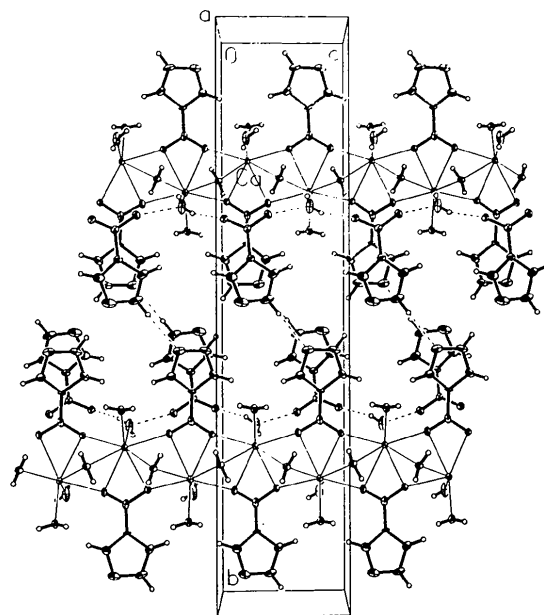


Fig. 3. The packing arrangement in the crystal of the calcium complex of 3-furancarboxylic acid, (II). The non-H atoms are shown as 20% probability ellipsoids.

The structure of *catena*-poly[*diaqua*calcium- μ -(3-furancarboxylato-*O,O'*:*O*)- μ -aqua 3-furancarboxylate], (II), is polymeric, as was most frequently found among the calcium complexes and their derivatives (Einspahr & Bugg, 1981). The chains propagate along the *c* axis and consist of [Ca(3-furoate)(H₂O)₃]⁺ cations and (3-furoate)⁻ anions linked together by intramolecular hydrogen bonds (Fig. 2). The cations are tridentate-*O,O',O* bridged by the carboxylate groups and by O atoms from the coordinated water molecules. The anions are linked to the complex by hydrogen bonds involving the carboxylate O atoms and the H atoms from the water molecules (Fig. 3). The planes of two types of anions (directly bonded and hydrogen bonded) are inclined with respect to each other by 4(1)° and stacked along the *a* axis with an interplanar spacing of 3.6(2) Å. The adjacent chains are held together by C—H...O interactions between the hetero-ring O atom from the ionic bonded anion and the H atom of the symmetry-related molecule.

The structure of *catena*-poly[*diaqua*strontium- μ -(3-furancarboxylato-*O,O'*:*O*)- μ -aqua 3-furancarboxylate], (III), exhibits a similar packing arrangement. The unit cells of the monoclinic crystals show only minor differences, obviously due to the different radii of the Ca²⁺ and Sr²⁺ cations. The [Sr(3-furoate)(H₂O)₃]⁺ cations are inclined to the (3-furoate)⁻ anions by 5(1)°, resulting in an average stacking distance of 3.6(2) Å. The lig-

and atoms occupy the vertices of the distorted dodecahedra around Ca²⁺ and Sr²⁺. The observed deformation is due to the constraints arising from the bidentate nature of carboxylate binding. The coordination sphere of Ca²⁺ consist of four carboxylate O atoms and four water molecules at distances ranging from 2.340(3) to 2.624(4) Å. The bond lengths to Sr²⁺ vary from 2.458(5) to 2.736(6) Å.

Experimental

Crystals of 3-furancarboxylic acid were grown at room temperature from an aqueous solution (Aldrich Chemical Co.). The calcium and strontium complexes were obtained by the reaction of calcium oxide and strontium hydroxide, respectively, with 3-furancarboxylic acid in aqueous solution. The colourless plate-shaped crystals were formed over a week by slow evaporation at room temperature.

Compound (I)

Crystal data

C₅H₄O₃
M_r = 112.08
 Monoclinic
*P*2₁/*c*
a = 5.189(1) Å
b = 5.886(1) Å
c = 16.223(3) Å
 β = 91.06(3)°
V = 495.4(2) Å³
Z = 4
D_x = 1.503 Mg m⁻³

Cu *K*α radiation
 λ = 1.54178 Å
 Cell parameters from 25 reflections
 θ = 20–25°
 μ = 1.101 mm⁻¹
T = 293(2) K
 Parallelepiped
 0.3 × 0.25 × 0.2 mm
 Colourless

Data collection

Kuma KM-4 computer-controlled four-circle κ -axis diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 628 measured reflections
 557 independent reflections
 557 observed reflections
 [*I* > 2σ(*I*)]

*R*_{int} = 0.0290
 θ_{\max} = 69.91°
h = 0 → 6
k = -7 → 0
l = -19 → 19
 3 standard reflections monitored every 100 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R(*F*) = 0.0342
wR(*F*²) = 0.0920
S = 1.118
 557 reflections
 90 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.1516P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} = -0.001

$\Delta\rho_{\max}$ = 0.116 e Å⁻³
 $\Delta\rho_{\min}$ = -0.199 e Å⁻³
 Extinction correction: SHELXL93 (Sheldrick, 1993)
 Extinction coefficient: 0.0501 (47)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

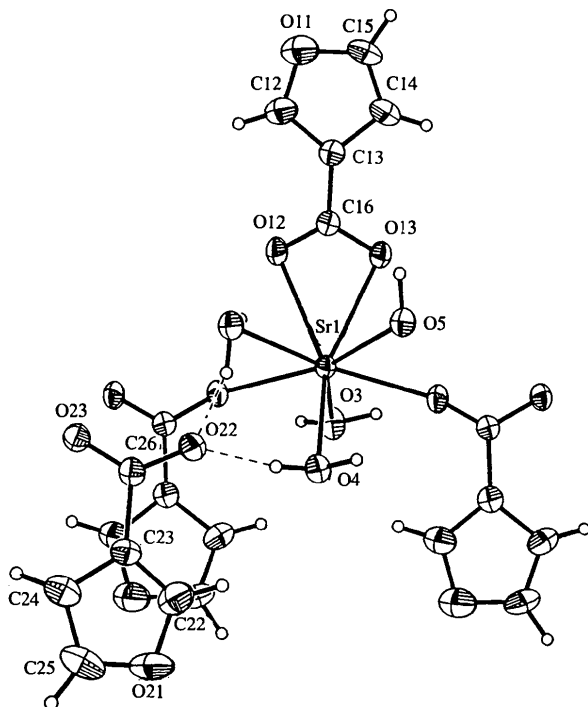


Fig. 4. View of the strontium complex of 3-furancarboxylic acid, (III), showing the labelling of the non-H atoms, which are shown as 20% probability ellipsoids.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (I)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
O3	0.8521 (4)	0.2697 (3)	0.97739 (12)	0.0629 (6)
O2	0.7692 (4)	-0.0833 (3)	0.93373 (11)	0.0590 (6)
C6	0.7247 (5)	0.1218 (4)	0.93255 (14)	0.0465 (6)
C3	0.5194 (5)	0.2179 (4)	0.88183 (14)	0.0458 (6)
C2	0.4500 (6)	0.4374 (5)	0.8779 (2)	0.0564 (7)
O1	0.2511 (4)	0.4676 (3)	0.82405 (12)	0.0648 (6)
C5	0.1933 (6)	0.2567 (5)	0.7925 (2)	0.0623 (8)
C4	0.3504 (5)	0.1016 (5)	0.8255 (2)	0.0579 (7)

Table 2. Selected geometric parameters (\AA , $^\circ$) for (I)

O3—C6	1.307 (3)	C3—C4	1.429 (4)
O2—C6	1.229 (3)	C2—O1	1.351 (4)
C6—C3	1.449 (3)	O1—C5	1.374 (4)
C3—C2	1.342 (4)	C5—C4	1.330 (4)
O2—C6—O3	123.5 (2)	C4—C3—C6	127.7 (2)
O2—C6—C3	121.9 (2)	C3—C2—O1	111.0 (2)
O3—C6—C3	114.5 (2)	C2—O1—C5	106.3 (2)
C2—C3—C4	105.6 (2)	C4—C5—O1	110.0 (3)
C2—C3—C6	126.6 (2)	C5—C4—C3	107.0 (2)

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$) for (I)

D—H...A	H...A	D...A	D—H...A
C5—H5...O1 ⁱ	2.59 (3)	3.410 (4)	137 (2)
C2—H2...O2 ⁱⁱ	2.49 (4)	3.387 (4)	164 (3)
O3—H3...O2 ⁱⁱⁱ	1.63 (5)	2.653 (4)	173 (4)

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x, 1 + y, z$; (iii) $2 - x, -y, 2 - z$.**Compound (II)***Crystal data*[Ca(C₅H₃O₃)(H₂O)₃]-
(C₅H₃O₃) $M_r = 316.28$

Monoclinic

 $P2_1/c$ $a = 7.108 (1) \text{\AA}$ $b = 29.295 (6) \text{\AA}$ $c = 6.565 (1) \text{\AA}$ $\beta = 91.88 (3)^\circ$ $V = 1366.3 (4) \text{\AA}^3$ $Z = 4$ $D_x = 1.538 \text{ Mg m}^{-3}$ *Data collection*Kuma KM-4 computer-
controlled four-circle κ -
axis diffractometer $\omega/2\theta$ scansAbsorption correction:
refined from ΔF (Walker
& Stuart, 1983)

1317 measured reflections

1232 independent reflections

1230 observed reflections

 $[I > 2\sigma(I)]$ *Refinement*Refinement on F^2 $R(F) = 0.0454$ $wR(F^2) = 0.1316$ Cu $K\alpha$ radiation $\lambda = 1.54178 \text{\AA}$ Cell parameters from 25
reflections $\theta = 20\text{--}25^\circ$ $\mu = 4.375 \text{ mm}^{-1}$ $T = 293 (2) \text{ K}$

Plate

 $0.2 \times 0.15 \times 0.1 \text{ mm}$

Colourless

 $R_{\text{int}} = 0.0414$ $\theta_{\text{max}} = 70.10^\circ$ $h = -8 \rightarrow 0$ $k = -24 \rightarrow 0$ $l = -8 \rightarrow 8$ 3 standard reflections
monitored every 100
reflections

intensity decay: none

 $(\Delta/\sigma)_{\text{max}} = -0.052$ $\Delta\rho_{\text{max}} = 0.403 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.500 \text{ e \AA}^{-3}$ $S = 1.063$

1232 reflections

209 parameters

All H-atom parameters

refined

 $w = 1/[\sigma^2(F_o^2) + (0.1068P)^2$
 $+ 1.6780P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none

Atomic scattering factors

from *International Tables*for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 4. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ca1	0.28029 (12)	0.27747 (4)	0.71845 (11)	0.0251 (4)
O13	0.3341 (5)	0.20104 (14)	0.8820 (4)	0.0367 (10)
O12	0.3722 (5)	0.20323 (13)	0.5538 (4)	0.0319 (9)
C16	0.3543 (5)	0.1795 (2)	0.7165 (6)	0.032 (2)
C13	0.3533 (6)	0.1300 (2)	0.7088 (6)	0.0264 (14)
C14	0.3794 (8)	0.1015 (3)	0.5385 (8)	0.048 (2)
C15	0.3627 (9)	0.0588 (3)	0.6014 (12)	0.060 (2)
O11	0.3215 (7)	0.0586 (2)	0.8053 (8)	0.0669 (14)
C12	0.3179 (9)	0.1024 (3)	0.8647 (9)	0.050 (2)
O23	0.8579 (5)	0.33393 (14)	0.0524 (4)	0.0366 (10)
O22	0.8362 (5)	0.32665 (14)	0.3875 (4)	0.0379 (10)
C26	0.8438 (6)	0.3509 (2)	0.2285 (6)	0.030 (2)
C23	0.8384 (7)	0.4005 (2)	0.2516 (7)	0.037 (2)
C24	0.7950 (9)	0.4263 (3)	0.4283 (11)	0.062 (2)
C25	0.8056 (12)	0.4702 (4)	0.3794 (15)	0.080 (3)
O21	0.8582 (9)	0.4748 (2)	0.1831 (11)	0.092 (2)
C22	0.8751 (10)	0.4323 (3)	0.1080 (11)	0.062 (2)
O5	0.0249 (5)	0.2523 (2)	0.9754 (5)	0.0326 (9)
O4	0.0830 (5)	0.34372 (14)	0.7191 (6)	0.0362 (10)
O3	0.5913 (6)	0.3087 (2)	0.7154 (5)	0.067 (2)

Table 5. Selected geometric parameters (\AA , $^\circ$) for (II)

Ca1—O12 ⁱ	2.345 (3)	C13—C14	1.412 (7)
Ca1—O13 ⁱⁱ	2.340 (3)	C14—C15	1.323 (10)
Ca1—O4	2.395 (4)	C15—O11	1.380 (9)
Ca1—O3	2.394 (4)	O11—C12	1.340 (8)
Ca1—O13	2.507 (4)	O23—C26	1.265 (5)
Ca1—O12	2.524 (4)	O22—C26	1.264 (6)
Ca1—O5 ⁱⁱ	2.532 (4)	C26—C23	1.464 (9)
Ca1—O5	2.624 (4)	C23—C22	1.355 (9)
Ca1...Ca1 ⁱⁱ	3.6558 (11)	C23—C24	1.425 (8)
O13—C16	1.269 (5)	C24—C25	1.328 (12)
O12—C16	1.285 (6)	C25—O21	1.361 (10)
C16—C13	1.450 (9)	O21—C22	1.345 (9)
C13—C12	1.335 (8)		
O13 ⁱⁱ —Ca1—O4	84.12 (13)	O12—Ca1—O5	103.16 (14)
O12 ⁱ —Ca1—O4	87.02 (13)	O13—C16—O12	117.3 (6)
O13 ⁱⁱ —Ca1—O3	73.11 (13)	O13—C16—C13	121.8 (4)
O12 ⁱ —Ca1—O3	71.73 (12)	O12—C16—C13	120.9 (4)
O4—Ca1—O3	103.4 (2)	C12—C13—C14	106.3 (6)
O13 ⁱⁱ —Ca1—O13	128.12 (11)	C12—C13—C16	125.4 (5)
O12 ⁱ —Ca1—O13	77.25 (12)	C14—C13—C16	128.2 (5)
O4—Ca1—O13	143.52 (11)	C15—C14—C13	107.3 (6)
O3—Ca1—O13	102.6 (2)	C14—C15—O11	109.3 (6)
O13 ⁱⁱ —Ca1—O12	77.01 (12)	C12—O11—C15	106.6 (5)
O12 ⁱ —Ca1—O12	122.80 (12)	C13—C12—O11	110.6 (5)
O4—Ca1—O12	149.21 (12)	O22—C26—O23	122.8 (6)
O3—Ca1—O12	94.2 (2)	O22—C26—C23	118.1 (4)
O13—Ca1—O12	51.38 (10)	O23—C26—C23	119.1 (5)
O13 ⁱⁱ —Ca1—O5 ⁱⁱ	68.54 (13)	C22—C23—C24	104.8 (7)
O4—Ca1—O5 ⁱⁱ	82.68 (14)	C22—C23—C26	127.2 (6)
O13—Ca1—O5 ⁱⁱ	93.35 (14)	C24—C23—C26	128.1 (6)
O12—Ca1—O5 ⁱⁱ	67.90 (13)	C25—C24—C23	107.4 (7)
O12 ⁱ —Ca1—O5	68.99 (11)	C24—C25—O21	110.1 (7)
O4—Ca1—O5	78.97 (14)	C22—O21—C25	106.6 (7)
O3—Ca1—O5	140.48 (12)	O21—C22—C23	111.0 (7)
O13—Ca1—O5	64.71 (13)		

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

Table 6. Hydrogen-bonding geometry (Å, °) for (II)

D—H...A	H...A	D...A	D—H...A
O3—H32...O22	2.05 (5)	2.861 (5)	176 (5)
O5—H52...O23 ⁱ	1.96 (7)	2.724 (5)	168 (7)
O4—H41...O23 ⁱ	2.04 (6)	2.767 (6)	153 (6)
O4—H42...O22 ⁱⁱ	2.10 (6)	2.796 (5)	151 (6)
O3—H31...O23 ⁱⁱⁱ	2.18 (5)	2.959 (5)	169 (5)
C25—H25...O11 ^{iv}	2.53 (6)	3.456 (5)	174 (6)

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

Compound (III)

Crystal data

[Sr(C₅H₃O₃)(H₂O)₃]-
(C₅H₃O₃)

$M_r = 363.82$

Monoclinic

$P2_1/c$

$a = 7.286$ (1) Å

$b = 28.853$ (6) Å

$c = 6.797$ (1) Å

$\beta = 91.82$ (3)°

$V = 1428.2$ (4) Å³

$Z = 4$

$D_x = 1.692$ Mg m⁻³

Data collection

Kuma KM4 computer-
controlled four-circle κ -
axis diffractometer

$\omega/2\theta$ scans

Absorption correction:

refined from ΔF (Walker
& Stuart, 1983)

$T_{\min} = 0.19$, $T_{\max} = 0.68$

1704 measured reflections

1613 independent reflections

Refinement

Refinement on F^2

$R(F) = 0.0544$

$wR(F^2) = 0.1416$

$S = 0.992$

1315 reflections

186 parameters

Only coordinates of H atoms
refined

$w = 1/[\sigma^2(F_o^2) + (0.1068P)^2 + 1.6780P]$

where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = -0.001

Cu $K\alpha$ radiation

$\lambda = 1.54178$ Å

Cell parameters from 25
reflections

$\theta = 20-25^\circ$

$\mu = 5.642$ mm⁻¹

$T = 293$ (2) K

Plate

$0.3 \times 0.15 \times 0.1$ mm

Colourless

1311 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0511$

$\theta_{\text{max}} = 79.47^\circ$

$h = -9 \rightarrow 6$

$k = 0 \rightarrow 30$

$l = -8 \rightarrow 0$

3 standard reflections

monitored every 100

reflections

intensity decay: none

$\Delta\rho_{\text{max}} = 0.563$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.698$ e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick,
1993)

Extinction coefficient:

0.0109 (26)

Atomic scattering factors

from *International Tables*
for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and
6.1.1.4)

C16	0.1121 (11)	0.1765 (3)	0.7662 (10)	0.051 (2)
C13	0.1191 (13)	0.1256 (4)	0.7762 (12)	0.062 (2)
O11	0.1540 (17)	0.0532 (4)	0.6795 (20)	0.121 (3)
C12	0.1528 (19)	0.0967 (5)	0.6235 (20)	0.091 (3)
C15	0.1194 (21)	0.0534 (4)	0.8751 (25)	0.097 (4)
C14	0.0953 (20)	0.0957 (5)	0.9372 (19)	0.094 (3)
O22	0.6204 (9)	0.3281 (2)	0.1057 (9)	0.068 (2)
O23	0.6000 (10)	0.3335 (2)	0.4314 (9)	0.071 (2)
C23	0.6340 (14)	0.4026 (4)	0.2525 (14)	0.072 (3)
O21	0.6248 (20)	0.4765 (4)	0.3290 (25)	0.134 (4)
C22	0.6036 (22)	0.4330 (6)	0.3910 (23)	0.104 (4)
C26	0.6179 (12)	0.3502 (4)	0.2649 (11)	0.061 (2)
C25	0.678 (3)	0.4729 (7)	0.144 (4)	0.135 (6)
C24	0.6824 (22)	0.4271 (5)	0.0857 (23)	0.102 (4)
O4	0.4382 (8)	0.2517 (2)	0.5160 (8)	0.0647 (15)
O3	0.3998 (10)	0.3499 (2)	0.7691 (8)	0.071 (2)
O5†	-0.134 (7)	0.324 (4)	0.764 (10)	0.088 (13)
O5‡	-0.157 (6)	0.310 (4)	0.782 (15)	0.088 (13)

† Occupancy factor of 0.62 (19). ‡ Occupancy factor of 0.38 (19).

Table 8. Selected geometric parameters (Å, °) for (III)

Sr1—O12 ⁱ	2.458 (5)	C13—C12	1.36 (2)
Sr1—O13 ⁱⁱ	2.461 (5)	C13—C14	1.41 (2)
Sr1—O5 ⁱ	2.58 (2)	O11—C12	1.31 (2)
Sr1—O3	2.582 (7)	O11—C15	1.36 (2)
Sr1—O5	2.59 (2)	C15—C14	1.30 (2)
Sr1—O4 ⁱⁱ	2.670 (6)	O22—C26	1.257 (11)
Sr1—O13	2.671 (7)	O23—C26	1.241 (10)
Sr1—O12	2.677 (7)	C23—C22	1.31 (2)
Sr1—O4	2.736 (6)	C23—C24	1.39 (2)
Sr1...Sr1 ⁱ	3.8263 (9)	C23—C26	1.520 (15)
O13—C16	1.216 (10)	O21—C22	1.33 (2)
O12—C16	1.280 (10)	O21—C25	1.34 (3)
C16—C13	1.469 (14)	C25—C24	1.38 (3)
O12 ⁱ —Sr1—O5 ⁱ	75.1 (23)	O4 ⁱⁱ —Sr1—O4	77.92 (15)
O13 ⁱⁱ —Sr1—O5 ⁱ	71.8 (24)	O13—Sr1—O4	64.9 (2)
O12 ⁱ —Sr1—O3	87.2 (2)	O12—Sr1—O4	99.2 (2)
O13 ⁱⁱ —Sr1—O3	85.3 (2)	C16—O12—Sr1	93.5 (5)
O5 ⁱ —Sr1—O3	109.6 (26)	O13—C16—O12	120.9 (8)
O12 ⁱ —Sr1—O5	71.1 (16)	O13—C16—C13	121.3 (7)
O13 ⁱⁱ —Sr1—O5	72.9 (14)	O12—C16—C13	117.7 (7)
O3—Sr1—O5	100.0 (25)	C12—C13—C14	104.3 (11)
O13 ⁱⁱ —Sr1—O4 ⁱⁱ	68.8 (2)	C12—C13—C16	125.7 (9)
O3—Sr1—O4 ⁱⁱ	80.2 (2)	C14—C13—C16	130.0 (10)
O12 ⁱ —Sr1—O13	79.0 (2)	C12—O11—C15	106.1 (11)
O13 ⁱⁱ —Sr1—O13	126.3 (2)	O11—C12—C13	111.4 (12)
O5 ⁱ —Sr1—O13	100.4 (27)	C14—C15—O11	110.6 (11)
O3—Sr1—O13	142.4 (2)	C15—C14—C13	107.5 (13)
O5—Sr1—O13	108.1 (22)	C22—C23—C24	107.5 (13)
O4 ⁱⁱ —Sr1—O13	92.3 (2)	C22—C23—C26	127.6 (11)
O12 ⁱ —Sr1—O12	122.8 (2)	C24—C23—C26	124.9 (11)
O13 ⁱⁱ —Sr1—O12	78.9 (2)	C22—O21—C25	105.4 (13)
O5 ⁱ —Sr1—O12	92.8 (23)	C23—C22—O21	112.2 (15)
O3—Sr1—O12	146.9 (2)	O23—C26—O22	126.3 (9)
O5—Sr1—O12	102.7 (25)	O23—C26—C23	116.6 (8)
O4 ⁱⁱ —Sr1—O12	67.1 (2)	O22—C26—C23	117.0 (8)
O13—Sr1—O12	47.9 (2)	O21—C25—C24	110.6 (14)
O12 ⁱ —Sr1—O4	69.1 (2)	C25—C24—C23	104.2 (16)
O3—Sr1—O4	77.5 (2)		

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

Table 9. Hydrogen-bonding geometry (Å, °) for (III)

D—H...A	H...A	D...A	D—H...A
O4—H42...O23	1.86 (1)	2.708 (9)	145 (1)
O3—H31...O23	1.84 (1)	2.799 (9)	170 (1)
O5—H51...O22 ⁱ	2.02 (1)	2.98 (7)	151 (3)
O5—H52...O23 ⁱⁱ	1.95 (1)	2.95 (6)	170 (6)
O3—H32...O22 ⁱⁱⁱ	1.83 (1)	2.825 (8)	180 (1)
C25—H25...O11 ^{iv}	2.53 (3)	3.44 (3)	167 (1)

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

Table 7. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (III)

$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
	x	y	z
Sr1	0.17624 (10)	0.28047 (3)	0.76840 (8)
O13	0.1188 (9)	0.1968 (3)	0.6100 (7)
O12	0.0910 (9)	0.1986 (2)	0.9270 (7)
			U_{eq}
			0.0533 (4)
			0.069 (2)
			0.0633 (15)

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 Å). 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 Å 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.

References

- Berkovitch-Yellin, Z. & Leiserowitz, L. (1984). *Acta Cryst.* **B40**, 159–165.
 Desiraju, G. R. & Kishan, K. V. R. (1989). *J. Am. Chem. Soc.* **111**, 4838–4843, and references therein.
 Einspahr, H. & Bugg, C. E. (1981). *Acta Cryst.* **B37**, 1044–1052.
 Gilmore, C. J., Mallison, P. R. & Speakman, J. C. (1983). *Acta Cryst.* **C39**, 1111–1113.
 Kuma (1989). *Kuma KM-4 User's Guide*. Version 3.1. Kuma Diffraction, Wrocław, Poland.
 Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Taylor, R. & Kennard, C. H. L. (1984). *Acc. Chem. Res.* **17**, 320–332.
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1996). **C52**, 347–351

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

BEATA PALUCHOWSKA,^a JAN K. MAURIN^a AND JANUSZ LECIEJEWICZ^b

^a*Institute of Atomic Energy, 05-400 Świerk-Otwock, Poland,* and ^b*Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland*

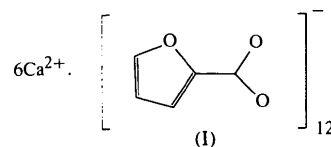
(Received 6 April 1995; accepted 9 August 1995)

Abstract

In the structure of calcium 2-furancarboxylate, Ca²⁺·2C₅H₃O₃[−], 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) Å. 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 Ca²⁺ displays the three possible modes of carboxylate binding – monodentate, bidentate and malonate (Hodgson & Asplund, 1990). Ca²⁺ 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 Ca²⁺ 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 Å 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···O13 3.209 (6) and Ca3···O33 3.242 (5) Å, may suggest the existence of some weaker Ca···O interactions.