Intermolecular distances show all acidic H atoms in (I) to be involved in hydrogen bonding. The molecules form dimers by means of strong hydrogen bonds between their carboxyl groups, O($2^{\rm i}$)···H—O(3) 2.695 Å and O(1)—H···O($4^{\rm i}$) 2.620 Å.* Although carboxyl H atoms were not located in difference maps, O(1) and O(3) are assumed to be protonated on the basis of the C—O bond lengths. The two carboxyl groups are not coplanar, the interplanar angle being 12.3°. Similar hydrogen bonds, 2.69 Å, occur in the crystals of dichloro-(*R*,*S*)-ethionineplatinum(II) (Khan *et al.*, 1991).

In (II), the peptide glycyl-(*S*)-methionine acts as a tridentate ligand *via* the N(amino), N(peptide) and S(thioether) atoms (Fig. 2). The six-membered chelate ring has a boat-like conformation with the S—C(methyl) and C—C(carboxyl) bonds in axial positions on the same side of the ring. The Pt—N(peptide) bond [2.004 (2) Å] is, as expected, shorter than the Pt—N(amino) bond [2.046 (2) Å]. The Pt—S bond length, 2.258 (2) Å, is at the upper end of the range in the amino acid complexes noted above. As in (I), the square-planar geometry of the Pt atom is slightly distorted but the deviations from the plane of best fit are smaller [Pt(1) −0.009, N(1) 0.0001, S(1) 0.0005, N(2) 0.004, Cl(1) 0.004 Å]. There are significant deviations from 90° among the bond angles at the Pt atom.

The N(amino) atom in (II) is hydrogen bonded to an O(peptide) atom O(1) and to an unprotonated O(carboxyl) atom O(3) in adjacent complexes. The protonated O(carboxyl) atom O(2) forms a strong hydrogen bond to the water O atom O(4): O(2)···O($4^{\rm ii}$) 2.562, H(2)···O($4^{\rm ii}$) 1.753 Å. Both H atoms of the water molecule are involved in hydrogen bonds to adjacent complexes: O(4)···O(1) 2.782, H(4*a*)···O(1) 1.92 Å and O(4)···Cl($1^{\rm iii}$) 3.233, H(4*b*)···Cl($1^{\rm iii}$) 2.39 Å.*

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* Symmetry operation: (i) $x, y-1, z$.

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

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Structure of Calcium 2,6-Difluorobenzoate Dihydrate

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Abstract. $Ca^{2+}.2C_7H_3O_2F_2^-.2H_2O$, $M_r = 390.3$, monoclinic, $C2/c$, $a = 17.584$ (4), $b = 10.771$ (3), $c = 7.887$ (2) Å, $\beta = 91.28$ (2)°, $V = 1493$ Å^3, $Z = 4$, $D_m = 1.75$, $D_x = 1.74$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 4.92$ cm^{-1}, $F(000) = 792$, $T = 293$ K, final $R = 0.037$ for 2415 unique observed reflections. The eight-coordinate Ca^{2+} ion is linked to six carboxylate O atoms from four different 2,6-difluorobenzoate ions and two water molecules. Each 2,6-difluorobenzoate ion chelates one Ca^{2+} ion and forms unidentate bridging linkages to two other Ca^{2+} ions leading to a polymeric structure. Unlike

the situation in calcium 2-fluorobenzoate, the two F atoms in this structure are not involved in significant C—F···H—O hydrogen bonding.

Introduction. Although reports of metal ion binding by C-bound F atoms in fluorocarboxylates are still not very common, there have been a number of accounts establishing the existence of direct C—F···*M* interactions where *M* is an alkali-metal ion (Murray-Rust, Stallings, Monti, Preston & Glusker, 1983). In calcium 2-fluorobenzoate dihydrate, an indirect interaction through a rather short water-bridged C—F···H_2O—Ca^{2+} hydrogen bond was found (Karipides & Miller, 1984). As part of a continuing program to study the environments of C-bound F atoms in divalent and trivalent metal-ion salts of fluorocarboxylic acids, we have determined the crystal structure of calcium 2,6-difluorobenzoate dihydrate.

Experimental. Colorless crystals of the title compound were grown by slow evaporation of a solution of the 1:1 salt prepared from the reaction of calcium carbonate and hot aqueous 2,6-difluorobenzoic acid. The density was determined by flotation in a mixture of chloroform and iodoethane. The crystal used for determination of the cell dimensions and data collection was a transparent prism (approximate dimensions 0.32 × 0.50 × 0.60 mm), which gave sharp optical extinction under crossed polarizers. Unit-cell parameters were derived from 25 centered reflections ($2\theta > 30°$) at 293 K. Intensity data out to $\sin\theta/\lambda = 0.7424$ Å^{-1} were collected on an Enraf–Nonius CAD-4 diffractometer using ω–2θ-scan technique. Ranges in indices were: *h*, 0 to 26; *k*, 0 to 15; *l*, −11 to 11. Three standard reflections measured every 4 h showed no variation in intensity. The total number of unique reflections measured was 2556. Of these, 2415, which had $F_o > 1.5\sigma(F_o)$, were taken as observed and used for refinement. Corrections for absorption and secondary extinction were not applied. The structure was solved by a combination of direct and difference Fourier methods and refined by a full-matrix procedure. H atoms were located on difference Fourier maps but H-atom parameters were not refined. Anisotropic refinement (on *F*) of all non-H atoms (114 variable parameters; 21.2 data/parameter) converged to $R = 0.037$, $wR = 0.053$ and goodness-of-fit = 1.42. Calculations were carried out using the *Enraf–Nonius SDP-Plus* program package (Frenz, 1985) as well as other established programs (Karipides, 1979). The weighting scheme used was: $w^{-1} = \{[\sigma(F_o)]^2 + (0.02F)^2\}$, where $\sigma(F_o)$ was obtained from counting statistics. Scattering factors for neutral atoms and anomalous-dispersion terms were taken from Cromer & Waber (1974). The maximum shift/e.s.d. in the final cycle of least-squares refinement was 0.01 while the maximum and minimum in the final difference electron density map were 0.27 and −0.39 e Å^{-3}. Final atomic coordinates are presented in Table 1.* Bond distances and angles are given in Table 2 and *ORTEP*II (Johnson, 1976) plots of the structure are illustrated in Figs. 1 and 2.

Discussion. Calcium 2,6-difluorobenzoate dihydrate and calcium 2-fluorobenzoate dihydrate (Karipides & Miller, 1984) crystallize in the same space group with very similar unit cells and adopt identical modes of ligand–Ca^{2+} binding. [Note that the previously reported unit cell for the 2-fluorobenzoate derivative (Karipides & Miller, 1984) was based on an alternative monoclinic cell; to facilitate comparison, the transformed cell for calcium 2-fluorobenzoate dihydrate consistent with the unit-cell setting used in the present study is: $a = 16.834$ (4), $b = 11.146$ (2), $c = 7.793$ (1) Å, $\beta = 90.39$ (1)°.] Despite these similarities in unit-cell parameters and gross features of the two structures, some structural details, especially those involving F atoms, are notably different in the two compounds. The space group *C*2/*c* imposes crystallographic C_2 symmetry on the structure, and the asymmetric unit consists of one-half Ca^{2+}, one 2,6-difluorobenzoate moiety and one water molecule. Each 2,6-difluorobenzoate anion chelates a Ca^{2+} cation through a carboxylate group forming an essentially planar four-membered ring, while, in addition, each carboxylate O(1) atom binds a different Ca^{2+} ion through a unidentate bridge bond forming planar Ca—O—Ca—O rings leading to a polymeric structure similar to those commonly found in calcium carboxylates (Einspahr & Bugg, 1981; Karipides & Miller, 1984; Karipides, McKinney & Peiffer, 1988). The Ca···Ca distance across these rings is 4.076 (1) Å. The Ca^{2+} ion is eight-coordinate and the irregular coordination polyhedron consists of six O atoms from four different 2,6-difluorobenzoate ions and two water molecules. As is usual in polymeric calcium carboxylates, the Ca—O bridging bond length [2.365 (1) Å] is considerably shorter than the Ca—O chelate distances of 2.694 (1) and 2.458 (1) Å. Although most of the dimensions in the CaO_8 polyhedra occurring in the 2,6-difluoro and 2-fluoro salts are comparable, one very significant difference is the O*W*—Ca—O*W*^{i} angle (Fig. 2) of 116.3 (1)°, which is considerably more open than the angle of 102.8 (1)° found in calcium 2-fluorobenzoate.

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* Lists of structure factors, H-atom coordinates and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54835 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates with e.s.d.'s in parentheses and equivalent isotropic displacement parameters* (Å^2) *for calcium* 2,6-*difluorobenzoate dihydrate*

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ where the anisotropic β_{ij} parameters are defined by: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	B_{eq}
Ca	0.0	0.04784 (3)	$\frac{1}{4}$	1.64
OW	−0.10195 (6)	0.1665 (1)	0.3728 (1)	2.80
F(2)	−0.23949 (5)	−0.2267 (1)	0.2501 (1)	3.39
F(6)	−0.02325 (6)	−0.3527 (1)	0.5662 (2)	4.35
O(1)	−0.05865 (5)	−0.1018 (1)	0.4875 (1)	2.21
O(2)	−0.09080 (6)	−0.1246 (1)	0.2176 (1)	2.72
C(1)	−0.12949 (6)	−0.2822 (1)	0.4077 (1)	1.80
C(2)	−0.20231 (7)	−0.3118 (1)	0.3476 (2)	2.15
C(3)	−0.23917 (8)	−0.4216 (1)	0.3825 (2)	2.76
C(4)	−0.20103 (10)	−0.5090 (1)	0.4802 (2)	3.15
C(5)	−0.12829 (10)	−0.4863 (1)	0.5428 (2)	3.30
C(6)	−0.09455 (8)	−0.3738 (1)	0.5057 (2)	2.53
C(7)	−0.09058 (7)	−0.1610 (1)	0.3682 (1)	1.79

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses for calcium* 2,6-*difluorobenzoate dihydrate*

Ca—O(1)	2.694 (1)	C(2)—C(3)	1.379 (2)
Ca—O(1^{ii})	2.365 (1)	C(2)—F(2)	1.355 (2)
Ca—O(2)	2.458 (1)	C(3)—C(4)	1.381 (2)
Ca—OW	2.421 (1)	C(4)—C(5)	1.383 (2)
C(7)—O(1)	1.258 (1)	C(5)—C(6)	1.383 (2)
C(7)—O(2)	1.251 (1)	C(6)—F(6)	1.351 (2)
C(1)—C(7)	1.509 (2)	OW—H1(OW)	0.97
C(1)—C(2)	1.393 (2)	OW—H2(OW)	0.97
C(1)—C(6)	1.388 (2)	F(2)···OW^{iv}	3.149 (1)
		O(2)···OW^{iii}	2.759 (2)
OW—Ca—OW^{i}	116.29 (6)	C(1)—C(2)—C(3)	124.1 (1)
OW—Ca—O(1)	74.89 (3)	C(2)—C(3)—C(4)	118.1 (1)
OW—Ca—O(2)	87.44 (4)	C(3)—C(4)—C(5)	120.8 (1)
OW—Ca—O(1^{ii})	80.35 (4)	C(4)—C(5)—C(6)	118.5 (1)
OW—Ca—O(1^{i})	153.17 (4)	C(5)—C(6)—C(1)	123.6 (1)
OW—Ca—O(2^{i})	147.35 (5)	C(6)—C(1)—C(2)	114.8 (1)
O(1^{ii})—Ca—OW^{i}	84.73 (4)	F(2)—C(2)—C(1)	117.8 (1)
O(1)—Ca—O(2)	50.40 (3)	F(2)—C(2)—C(3)	118.1 (1)
O(1)—Ca—O(1^{ii})	72.82 (4)	F(6)—C(6)—C(1)	118.2 (1)
O(1^{ii})—Ca—O(1^{iii})	151.53 (5)	F(6)—C(6)—C(5)	118.1 (1)
O(1^{ii})—Ca—O(2)	123.11 (3)	O(1)—C(7)—O(2)	122.9 (1)
O(1^{ii})—Ca—O(2^{i})	79.93 (4)	O(1)—C(7)—C(1)	118.7 (1)
O(1^{ii})—Ca—O(1^{i})	126.13 (4)	O(2)—C(7)—C(1)	118.4 (1)
O(2)—Ca—O(2^{i})	81.90 (6)	Ca—O(1)—Ca^{ii}	107.18 (4)
O(2)—Ca—O(1^{i})	74.55 (4)	F(2)···H1(OW^{iv})—OW^{iv}	123
O(1)—Ca—O(1^{i})	106.49 (4)	O(2)···H2(OW^{iii})—OW^{iii}	167

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

There is a strong hydrogen bond between carboxylate atom O(2) and the coordinated water molecule through H2(OW). A similar hydrogen-bond interaction has also been observed in calcium 2-fluorobenzoate. Of more interest are the environments about each of the F atoms. Murray-Rust, Stallings, Monti, Preston & Glusker (1983) have summarized structural criteria for establishing the existence of C—F···H—O hydrogen bonds. Although there is a somewhat short F(6)···OW^{ii} interaction at 3.009 (1) Å, this contact is not involved in a hydrogen bond, since the water H atoms are not in proper orientation for hydrogen bonding to F(6). As was found in calcium 2-fluorobenzoate dihydrate, an H atom, H1(OW), from a water molecule is still the shortest intermolecular contact to F(2), although in this study there is also an F(2)···aryl ring H-atom, H(C4), contact of the same magnitude. The F(2)···OW^{iv}, F(2)···H1(OW^{iv}), and F(2)···H(C4) distances are 3.149 (1), 2.52 and 2.52 Å, respectively, and the C(2)—F(2)···H1(OW^{iv}) angle is 123°. The corre-

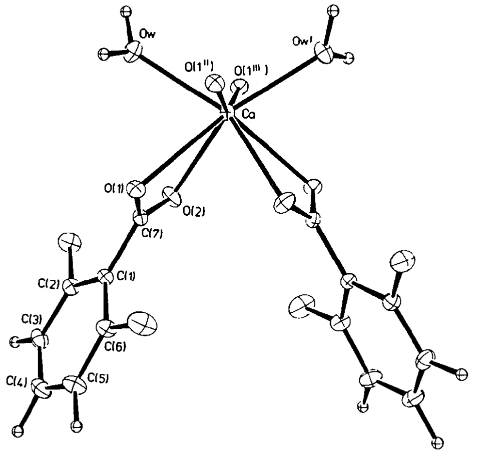

Fig. 1. A view of the structure showing the atom-labeling scheme, mode of 2,6-difluorobenzoate–Ca^{2+} binding and the CaO$_8$ coordination polyhedron.

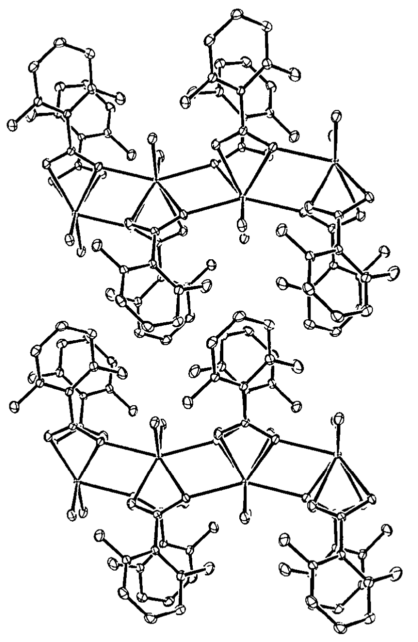

Fig. 2. A view of the crystal packing showing the Ca—O—Ca—O rings in the polymeric units.

sponding quantities in the calcium 2-fluorobenzoate compound are 2.995 (2), 2.04 (2), 2.64 Å and 170°, respectively. Following Murray-Rust, Stallings, Monti, Preston & Glusker (1983) these parameters do not indicate significant C—F···H—O hydrogen bonding in the 2,6-difluorobenzoate salt in contrast to the 2-fluorobenzoate derivative. The degree of twist of the aromatic ring from the carboxylate ring plane also differs in the two salts. In the title compound, this dihedral angle is 48° compared to 41° in calcium 2-fluorobenzoate and 11° in 2-fluorobenzoic acid (Ferguson & Islam, 1975).

These differences in geometry in the two otherwise very similar structures probably result from the substitution of the second F atom for an H atom, which is the only difference in molecular formulation in the two salts. For example, in calcium 2,6-difluorobenzoate dihydrate, the shortest intermolecular nonbonded contact involving F(6) is a phenyl H atom, H(C5) $(-x, -1-y, 1-z)$, at 2.81 Å – whereas, for the corresponding 6 position in the aryl ring in calcium 2-fluorobenzoate dihydrate, the shortest contact to H(C6) is an O atom, OW^{ii}, from a water molecule at 2.67 Å. It is evident that some structural features in these compounds are influenced by the increase in van der Waals radius of F compared to H atoms, as well as differences in the polarities of C—F and C—H bonds.

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Structures of (η-Arene)(η-cyclopentadienyl)iron(II) Salts. (η^6-Benzene)(η^5-cyclopentadienyl ethyl ketone)iron(II) Hexafluorophosphate

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Abstract. $[Fe(C_6H_6)(C_5H_4COCH_2CH_3)][PF_6]$, $M_r = 400.08$, monoclinic, $P2_1/c$, $a = 7.096(3)$, $b = 22.651(9)$, $c = 9.305(4)$ Å, $\beta = 95.09(2)°$, $V = 1490(1)$ Å^3, $Z = 4$, $D_x = 1.78$ g cm^{-3}, λ(Mo $K\alpha$) = 0.710969 Å, $\mu = 12.17$ cm^{-1}, $F(000) = 808$, $T = 208$ K, $R = 0.0439$ ($wR = 0.0424$) for 1938 unique reflections [$R = 0.0346$, $wR = 0.0359$ for 1604 reflections with $I > 2.5\sigma(I)$]. The structure contains planar aromatic rings with the carbonyl substituent group virtually in the plane of the cyclopentadienyl ring (3.4°). The iron–ring distances are 1.668 (2) and 1.547 (2) Å for cyclopentadienyl and benzene, respectively. A comparison with other (η-arene)(η-cyclopentadienyl)iron(II) salt structures is also reported. For all the structures the Fe—C$_{\text{arene}}$ bond lengths are longer than the Fe—C$_{\text{cyclopentadienyl}}$ bond lengths despite the apparent closeness of the arene rings to the Fe atoms.

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