

- GRITSENKO, O. V., VYSOTSKAYA, R. V., BAGATURYANTS, A. A. & KAZANSKII, V. B. (1984). *Koord. Khim.* **10**, 1397–1400.
- IMMIRZI, A. & MUSCO, A. (1977). *Inorg. Chim. Acta*, **22**, L35–L36.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KIN-CHEE, H., McLAUGHLIN, G. M., MCPARTLIN, M. & ROBERTSON, G. B. (1982). *Acta Cryst.* **B38**, 421–425.
- POWELL, J., GREGG, M. R. & SAWYER, J. F. (1984). *J. Chem. Soc. Chem. Commun.* pp. 1149–1150.
- POWELL, J., SAWYER, J. F. & SMITH, S. J. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1312–1313.
- POWELL, J., SAWYER, J. F. & STAINER, M. V. R. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1314–1316.
- RUSSELL, D. R. & TUCKER, P. A. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2222–2225.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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## Structure of Calcium Bis(4-fluorobenzoate) Trihydrate

BY ANASTAS KARIPIDES, CAROLYN MCKINNEY AND KAREN PEIFFER

*Department of Chemistry, Miami University, Oxford, Ohio 45056, USA*

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**Abstract.** Ca<sup>2+</sup>·2C<sub>7</sub>H<sub>4</sub>FO<sub>2</sub>·3H<sub>2</sub>O, *M<sub>r</sub>* = 372.3, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 7.239 (2), *b* = 33.173 (6), *c* = 6.534 (1) Å, β = 92.27 (2)°, *V* = 1568 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.56, *D<sub>x</sub>* = 1.58 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 4.5 cm<sup>-1</sup>, *F*(000) = 768, *T* ≈ 293 K, final *R* = 0.048 for 3070 observed unique reflections. Only one of the two independent 4-fluorobenzoate ions in the asymmetric unit is coordinated to Ca<sup>2+</sup> ions. The eight-fold-coordinated Ca<sup>2+</sup> is linked to four carboxylate O atoms from three different 4-fluorobenzoate ions and four O atoms from three different water molecules. Both the carboxylate group and one of the coordinated water molecules bridge adjacent Ca<sup>2+</sup> ions to form a polymeric network.

**Introduction.** Recently, we reported the crystal structure of calcium bis(2-fluorobenzoate) dihydrate where the aromatic F atom was found to participate in a rather short hydrogen bond with a coordinated water molecule (Karipides & Miller, 1984). Continuing our studies to investigate the structural characteristics of fluorine interactions in crystalline metal salts of fluorine-containing carboxylic acids, we have determined the crystal structure of calcium bis(4-fluorobenzoate) trihydrate.

**Experimental.** Colorless prismatic crystals of the title compound were grown from an aqueous solution of the 1:1 salt by slow evaporation. Crystal size: 0.18 × 0.32 × 0.60 mm. The density was determined by flotation in a bromobenzene/iodoethane mixture. Cell parameters obtained from 15 centered reflections (2θ > 25°) at 293 ± 1 K. Intensity data out to sinθ/λ = 0.6168 Å<sup>-1</sup> collected on a Nicolet diffractometer equipped with a graphite monochromator using an

ω-scan technique. Each of six check reflections recorded every 300 reflections showed no change in intensity. Index range: *h* 0 to 8; *k* 0 to 40; *l* -8 to 8. Total number of unique reflections measured was 3070. E.s.d.'s calculated from σ(*F*) = {[σ(*F<sub>o</sub>)]<sup>2</sup> + (0.02*F<sub>o</sub>*)<sup>2</sup>}<sup>1/2</sup> with σ(*F<sub>o</sub>*) obtained from counting statistics. All reflections had *F<sub>o</sub>* > σ(*F<sub>o</sub>*) and no reflections were taken as unobserved. Absorption and secondary-extinction corrections were not applied. Structure was solved by Patterson and difference Fourier methods and refined by a full-matrix least-squares procedure. H atoms were located from difference maps but hydrogen parameters were not refined. Scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974). All calculations were performed on an IBM 4341 using established programs (Karipides, 1979). Anisotropic refinement (on *F*) of all non-H atoms (217 variable parameters) converged to *R* = 0.048, *wR* = 0.048 and goodness-of-fit of 1.47. Maximum shift/e.s.d. in final least-squares cycle was 0.03. Maxima and minima in the final difference Fourier maps: 0.36, -0.38 e Å<sup>-3</sup>. Final atom coordinates are given in Table 1.\**

**Discussion.** Bond distances and angles are given in Table 2. A view of a portion of the polymeric structural unit with atom-numbering scheme is presented in Fig. 1. There are no symmetry conditions imposed on the structure.

\* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters and hydrogen-bonding parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44345 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates with e.s.d.'s and equivalent isotropic temperature factors for calcium bis(4-fluorobenzoate) trihydrate

$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i a_j$ , where the anisotropic thermal parameters ( $\beta_{ij}$ ) are defined by  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . Isotropic thermal parameters for H atoms were fixed at 5.0 Å<sup>2</sup>.

	x	y	z	$B_{eq}$ (Å <sup>2</sup> )
Ca	0.24971 (5)	0.27322 (1)	0.71711 (5)	1.72
O(w)	0.5653 (2)	0.29627 (6)	0.7160 (2)	4.32
O(w2)	-0.0036 (2)	0.25150 (4)	0.9736 (2)	2.22
O(w3)	0.0506 (2)	0.33076 (4)	0.7234 (2)	2.44
O(1A)	0.3370 (2)	0.20761 (4)	0.5514 (2)	2.31
O(2A)	0.3014 (2)	0.20530 (4)	0.8814 (2)	2.43
O(1B)	0.8282 (2)	0.17725 (4)	0.5543 (2)	2.63
O(2B)	0.8064 (2)	0.18154 (4)	0.8912 (2)	2.57
F(4A)	0.3564 (3)	0.01937 (4)	0.6927 (3)	5.89
F(4B)	0.8450 (3)	-0.00717 (4)	0.7899 (3)	6.04
C(1A)	0.3350 (3)	0.14264 (6)	0.7088 (3)	1.98
C(2A)	0.3011 (3)	0.12035 (6)	0.8825 (3)	2.74
C(3A)	0.3073 (4)	0.07839 (7)	0.8775 (4)	3.58
C(4A)	0.3485 (4)	0.06019 (6)	0.6983 (4)	3.55
C(5A)	0.3826 (4)	0.08100 (7)	0.5220 (4)	3.46
C(6A)	0.3747 (3)	0.12278 (6)	0.5274 (3)	2.65
C(7A)	0.3243 (3)	0.18764 (6)	0.7141 (3)	1.74
C(1B)	0.8223 (3)	0.11616 (6)	0.7436 (3)	2.24
C(2B)	0.7838 (3)	0.09730 (7)	0.9274 (4)	2.96
C(3B)	0.7906 (4)	0.05564 (7)	0.9441 (4)	3.80
C(4B)	0.8364 (4)	0.03382 (7)	0.7755 (4)	3.78
C(5B)	0.8755 (4)	0.05095 (7)	0.5910 (4)	3.67
C(6B)	0.8672 (3)	0.09285 (6)	0.5770 (3)	2.88
C(7B)	0.8172 (3)	0.16154 (6)	0.7284 (3)	1.99

There are two independent 4-fluorobenzoate ions, designated (A) and (B), in the asymmetric unit, but only those of type (A) are coordinated to Ca<sup>2+</sup> ions. Each 4-fluorobenzoate (A) symmetrically chelates a Ca<sup>2+</sup> ion through its carboxylate group forming an essentially planar four-membered chelate ring. In addition, O atoms O(1A) and O(2A) each link different Ca<sup>2+</sup> ions by unidentate bridging bonds forming buckled four-membered Ca—O—Ca—O rings which partly form the basis of the extended structure. As is usual in polymeric calcium carboxylates the Ca—O bridging bond lengths [2.338 (1), 2.350 (1) Å] are considerably shorter than the Ca—O chelate distances of 2.517 (2) and 2.522 (1) Å, which emphasizes the importance of the bridging interactions in the crystalline structure (Einspahr & Bugg, 1981).

All three of the unique water molecules are bound to the Ca<sup>2+</sup> ion. In a somewhat unusual bonding motif each O(w2) water molecule acts as a bridging ligand between adjacent Ca<sup>2+</sup> ions. The Ca—O(w2)—Ca<sup>1</sup> bridging angle is 89.04°. The Ca—O(w2)—Ca—O(1) rings formed as a result of this bridging are severely buckled. Thus, pairs of Ca<sup>2+</sup> ions are linked by triple bridging and the Ca...Ca distance across the resultant four-membered chelate rings is rather short with Ca...Ca<sup>1</sup> 3.612 (1) Å.

The eight-coordinate CaO<sub>8</sub> polyhedron deviates extensively from idealized eight-coordinate geometries. An analysis of shape parameters defined by Muttterties

& Guggenberger (1974) reveals the polyhedron most closely resembles a bicapped trigonal prism although there is significant distortion towards square antiprismatic geometry.

The dimensions of the two independent 4-fluorobenzoate ions are similar to corresponding values reported in other structures containing the 4-fluorobenzoate moiety (Colapietro, Domenicano & Caccarini, 1979; Longo & Richardson, 1982). The dihedral angles between the aryl ring plane and the corre-

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.'s for calcium bis(4-fluorobenzoate) trihydrate.

Superscripts are defined in Fig. 1.			
Ca—O(1A)	2.522 (1)	C(3A)—C(4A)	1.361 (4)
Ca—O(2A)	2.517 (2)	C(4A)—C(5A)	1.374 (4)
Ca—O(1A')	2.338 (1)	C(5A)—C(6A)	1.388 (3)
Ca—O(2A <sup>ii</sup> )	2.350 (1)	C(4A)—F(4A)	1.356 (2)
Ca—O(w1)	2.409 (2)	C(7B)—O(1B)	1.256 (2)
Ca—O(w2)	2.633 (2)	C(7B)—O(2B)	1.259 (2)
Ca—O(w2 <sup>ii</sup> )	2.517 (2)	C(7B)—C(1B)	1.509 (3)
Ca—O(w3)	2.393 (2)	C(9B)—C(2B)	1.392 (3)
C(7A)—O(1A)	1.259 (2)	C(1B)—C(6B)	1.384 (3)
C(7A)—O(2A)	1.257 (2)	C(2B)—C(3B)	1.387 (3)
C(7A)—C(1A)	1.495 (3)	C(3B)—C(4B)	1.370 (4)
C(1A)—C(2A)	1.385 (3)	C(4B)—C(5B)	1.372 (4)
C(1A)—C(6A)	1.396 (3)	C(5B)—C(6B)	1.394 (3)
C(2A)—C(3A)	1.393 (3)	C(4B)—F(4B)	1.364 (3)

O(1A)—Ca—O(2A)	51.34 (4)	C(2B)—C(1B)—C(6B)	119.2 (2)
O(w2 <sup>ii</sup> )—Ca—O(w2)	78.76 (4)	C(1B)—C(2B)—C(3B)	120.5 (2)
O(1A')—Ca—O(2A <sup>ii</sup> )	137.92 (5)	C(2B)—C(3B)—C(4B)	118.2 (2)
C(2A)—C(1A)—C(6A)	119.5 (2)	C(3B)—C(4B)—C(5B)	123.5 (2)
C(1A)—C(2A)—C(3A)	120.5 (2)	C(4B)—C(5B)—C(6B)	117.4 (2)
C(2A)—C(3A)—C(4A)	118.2 (2)	C(5B)—C(6B)—C(1B)	121.1 (2)
C(3A)—C(4A)—C(5A)	123.5 (2)	F(4B)—C(4B)—C(3B)	118.9 (2)
C(4A)—C(5A)—C(6A)	118.1 (2)	F(4B)—C(4B)—C(5B)	117.6 (2)
C(5A)—C(6A)—C(1A)	120.2 (2)	O(1B)—C(7B)—O(2B)	123.7 (2)
F(4A)—C(4A)—C(3A)	118.5 (2)	O(1B)—C(7B)—C(1B)	118.1 (2)
F(4A)—C(4A)—C(5A)	118.0 (2)	O(2B)—C(7B)—C(1B)	118.2 (2)
O(1A)—C(7A)—O(2A)	120.4 (2)		
O(1A)—C(7A)—C(1A)	120.0 (2)		
O(2A)—C(7A)—C(1A)	119.6 (2)		

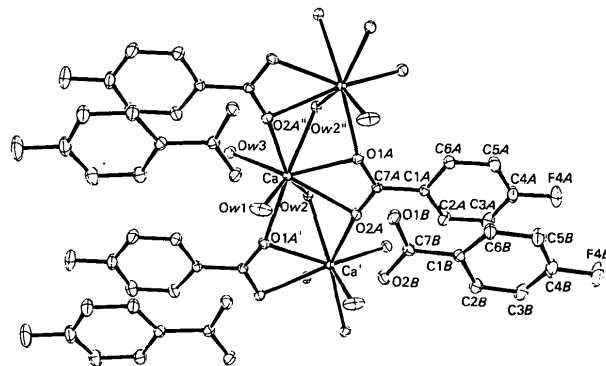


Fig. 1. A *bc* projection of a portion of the polymeric unit showing the spatial relationship between the two independent 4-fluorobenzoate ions, the CaO<sub>8</sub> coordination polyhedron and the mode of 4-fluorobenzoate—Ca<sup>2+</sup> binding. H atoms have been omitted for clarity. The superscripts specify the symmetry-related positions of the atoms given in Table 1: (i)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (ii)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ .

sponding carboxylate group are 6.3 and 10.8° for fluorobenzoate (*A*) and (*B*), respectively.

Although not involved in Ca<sup>2+</sup> binding, the 4-fluorobenzoate ion (*B*) is extensively involved in the hydrogen-bonding scheme. All six H atoms from the three water molecules are hydrogen-bonded to the O(3*B*) and O(4*B*) carboxylate O atoms. In addition, there is a C(2*A*)—H(2*A*)...O(*w*3<sup>1</sup>) hydrogen bond with H(2*A*)...O(*w*3<sup>1</sup>) 2.37, C(2*A*)...O(*w*3<sup>1</sup>) 3.346 (3), C(2*A*)—H(2*B*) 1.08 Å and the C(2*A*)—H(2*A*)...O(*w*3<sup>1</sup>) angle 149°. These parameters are well within the range reported for C—H...O hydrogen bonds (Taylor & Kennard, 1982).

The two F atoms in this structure are not involved in short interactions with water molecules, which is in contrast to the situation in calcium bis(2-fluorobenzoate) dihydrate. The closest immediate neighbors about each F atom are aromatic H atoms with the

shortest distance being F(4*B*)...H(3*A*)(1−*x*, *y*, 2−*z*) at 2.40 Å with the C(4*B*)—F(4*B*)...H(3*A*) angle 139°.

#### References

- COLAPIETRO, M., DOMENICANO, A. & CECCARINI, C. P. (1979). *Acta Cryst.* B35, 890–894.  
 EINSBAHR, H. & BUGG, C. E. (1981). *Acta Cryst.* B37, 1044–1052.  
*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 KARIPIDES, A. (1979). *Inorg. Chem.* 18, 3034–3037.  
 KARIPIDES, A. & MILLER, C. (1984). *J. Am. Chem. Soc.* 106, 1494–1495.  
 LONGO, J. & RICHARDSON, M. F. (1982). *Acta Cryst.* B38, 2482–2483.  
 MUTTERTIES, E. L. & GUGGENBERGER, L. J. (1974). *J. Am. Chem. Soc.* 96, 1748–1756.  
 TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* 104, 5063–5070.

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## μ-{4-Methyl-1,2,6-triphosphatricyclo[2.2.1.0<sup>2,6</sup>]heptane-*P*<sup>1</sup>,*P*<sup>2</sup>,*P*<sup>3</sup>}-tris[pentacarbonylchromium(0)]

BY HELMUTH ZIMMERMANN\* AND MARTIN GOMM

*Institut für Angewandte Physik, Lehrstuhl für Kristallographie der Universität Erlangen-Nürnberg, Bismarckstrasse 10, D-8520 Erlangen, Federal Republic of Germany*

AND EBERHARD KÖCK AND JOCHEN ELLERMANN

*Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-8520 Erlangen, Federal Republic of Germany*

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**Abstract.** [ $\{\text{Cr}(\text{CO})_5\}_3(\text{C}_5\text{H}_9\text{P}_3)$ ],  $M_r = 738.19$ , monoclinic,  $P2_1/c$ ,  $a = 9.632(1)$ ,  $b = 10.995(1)$ ,  $c = 27.807(8)$  Å,  $\beta = 92.84(2)^\circ$ ,  $V = 2941(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.67$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.70926$  Å,  $\mu = 12.88$  cm<sup>-1</sup>,  $F(000) = 1464$ ,  $T = 295(2)$  K; final  $R = 0.054$  for 3858 reflections (including 54 unobserveds). The complex consists of the  $P_3$ -nortricyclane  $\text{CH}_3\text{C}(\text{CH}_2\text{P})_3$  (4-methyl-1,2,6-triphosphatricyclo[2.2.1.0<sup>2,6</sup>]heptane), which coordinates *via* the P atoms as a tridentate ligand to three  $\text{Cr}(\text{CO})_5$  groups. The structure of the  $P_3$ -nortricyclane ligand has already been determined by X-ray analysis [Zimmermann, Gomm, Köck & Ellermann (1986). *Acta Cryst.* C42, 1757–1759]. In the complex  $\text{CH}_3\text{C}(\text{CH}_2\text{P})_3[\text{Cr}(\text{CO})_5]_3$  the P—P distances are slightly longer [P(1)—P(2) 2.218(1), P(2)—P(3) 2.217(1) and P(3)—P(1)

2.213(1) Å] than in the free ligand. The P—Cr distances range from 2.331(1) to 2.345(1) Å. Bond lengths and bond angles within the  $\text{Cr}(\text{CO})_5$  groups are normal.

**Introduction.** Organocyclotriphosphanes and heteronortriacyclanes with a  $P_3$  unit, *e.g.* (*t*-BuP)<sub>3</sub>, P[Si(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>P<sub>3</sub>, P[PSi(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>P<sub>3</sub>, and CH<sub>3</sub>C(CH<sub>2</sub>P)<sub>3</sub> are of interest due to their unusual coordination properties. P[PSi(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>P<sub>3</sub> (Fritz, 1982; Fritz, Härer & Schneider, 1982) shows no coordination tendency, whereas the donor properties of (*t*-BuP)<sub>3</sub> (Baudler, Salzer & Hahn, 1982) and P[Si(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>P<sub>3</sub> (Fritz, Uhlmann, Hoppe, Hönle & von Schnering, 1982) to one or two metal centres are well established by X-ray analysis (Tebbe & Feher, 1984; Hönle & von Schnering, 1980). The compound CH<sub>3</sub>C(CH<sub>2</sub>P)<sub>3</sub> (Ellermann & Demuth, 1984) coordinates to one, two and three

\* Author for correspondence.