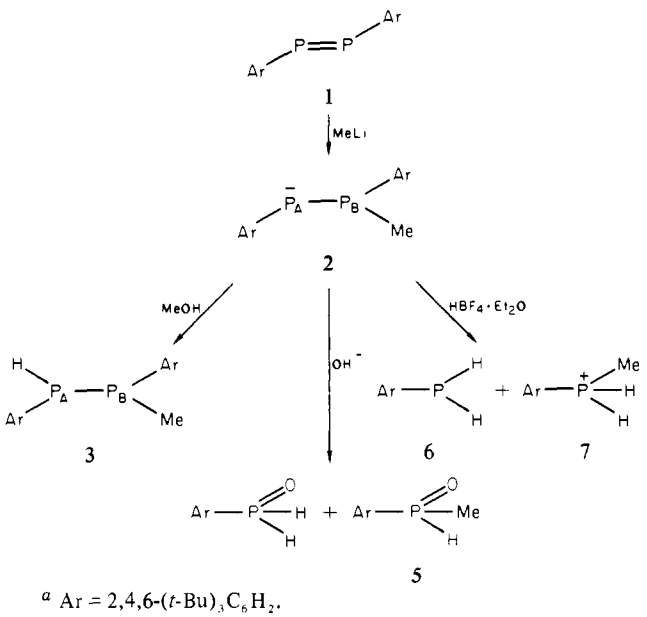
Scheme I[a]



[a] Ar = 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$.

carbonyl fragments.[7] We present the first evidence that diphosphenes are reactive toward nucleophiles, thus greatly extending the synthetic utility of these compounds.

Typically, ArP=PAr (**1**)[5] (Ar = 2,4,6-(*t*-Bu)$_3$C$_6$H$_2$) was treated with an equimolar quantity of MeLi in THF at −78 °C affording a deep red solution. The presence of the novel anion **2** (Scheme I) was established unequivocally by the $^{31}P\{^1H\}$ NMR[8] spectrum, which comprised an AB pattern with δ_A −94.0, δ_B −43.0, and $^1J_{P_AP_B}$ = 408 Hz. Treatment of a solution of **2** with MeOH resulted in the new diphosphine **3**.[9] $^{31}P\{^1H\}$ NMR for **3**: AB pattern with δ_A −60.5, δ_B −45.0, $^1J_{P_AP_B}$ = 201 Hz. The corresponding proton-coupled spectrum was of the ABR_3X type with $^1J_{P_AH}$ = 207.0, $^2J_{P_BH}$ = 12.0, $^2J_{P_BMe}$ = 5.7, and $^3J_{P_AMe}$ = 1.0 Hz. Quenching of **2** with aqueous LiOH resulted in equimolar quantities of the known phosphine oxide **4**[10] and the new phosphine oxide **5**. ^{31}P NMR for **5**: δ +24.0 (d, $^1J_{PH}$ = 575 Hz). Compounds **4** and **5** presumably arise via Arbuzov rearrangements of initially formed Ar(R)POH (R = H, Me). Treatment of **2** with HBF_4·OEt_2 also resulted in P-P bond cleavage. With a 100% excess of HBF_4·OEt_2, the isolated products were $ArPH_2$ (**6**)[11] and the new phosphonium salt $[ArP(Me)H_2][BF_4]$ (**7**). ^{31}P NMR for **7**: δ −28.5 (t of q, $^1J_{PH}$ = 521, $^2J_{PH}$ = 17 Hz).

Initially, the $^{31}P\{^1H\}$ spectra of mixtures of **1** and *t*-BuLi in THF were complex. However, after ~12 h at 25 °C, the spectra anticipated for the anion $[ArP-P(Ar)(t\text{-}Bu)]^-$ (**8**) were detected.[12] $^{31}P\{^1H\}$ NMR for **8**: AB pattern, δ_A −57.0, δ_B +72.5, $^1J_{P_AP_B}$ = 325 Hz. The diphosphine, Ar(H)P-P(Ar)(*t*-Bu) (**9**), plus traces of **6** and Ar(*t*-Bu)PH (**10**) were detected upon treatment of the reaction mixture with MeOH. $^{31}P\{^1H\}$ NMR for **9**: AB pattern with δ_A −78.9, δ_B +42.4, $^1J_{P_A,P_B}$ = 325 Hz. ^{31}P NMR for **10**: δ −72.0 (d, $^1J_{PH}$ = 218 Hz).

The reaction of **1** with K[*s*-Bu_3BH] in THF is slow (~4 days at 25 °C), and the only species detectable by ^{31}P NMR is the diphosphine Ar(H)P-P(H)(Ar) (**11**).[11] In turn, **11** disproportionates to **1** and **6** upon standing ~2 weeks at 25 °C.[13] It was not possible to detect the anion, $[ArP-P(H)(Ar)]^-$ (**12**) in these reaction mixtures; moreover, treatment of **11** with *n*-BuLi resulted in ArPHLi (**13**)[11] rather than **12**.

Further studies of nucleophilic reactivity are in progress.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation for generous financial support.

(6) Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1982**, 609.

(7) (a) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7751. (b) Cowley, A. H.; Lasch, J. C.; Norman, N. C.; Pakulski, M. *Angew. Chem.* **1983**, *95*, 1019; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 978.

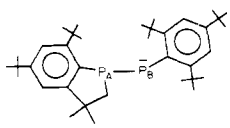
(8) All ^{31}P NMR spectra measured at a spectrometer frequency of 32.384 MHZ.

(9) Al new compounds except the anions **2** and **8** were characterized by high-resolution mass spectroscopy and/or elemental analysis. These and other details will be furnished in a subsequent full paper.

(10) Yoshifuji, M.; Shibayama, K.; Toyota, K.; Inamoto, N. *Tetrahedron Lett.* **1983**, *24*, 4227.

(11) (a) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *J. Am. Chem. Soc.* **1982**, *104*, 5820. (b) Issleib, K.; Schmidt, H.; Wirkner, C. *Z. Anorg. Allg. Chem.* **1982**, *488*, 75.

(12) A second anion is also detectable at this stage. We assign the following structure on the basis of NMR data (e.g., $^{31}P\{^1H\}$ NMR δ_A +7.0, δ_B −116.0, $^1J_{P_AP_B}$ = 458 Hz).



(13) A somewhat similar reaction, viz., $5(PhPH)_2 \rightleftarrows 5PhPH_2 + (PhP)_5$, has been observed by Albrand and Gagnaire (Albrand, J. P.; Gagnaire, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 8630).

Novel Cyclophane-Based Hosts with Functionally Neutral Cavities

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Boxlike molecules,[1] those containing cavities capable of accommodating molecular guests, are of current interest as a structural basis for constructing enzymelike catalysts. In this context we wish to report the novel naphthalenophanes **2**-C_2 and **2**-σ, molecular boxes having cavities of 5.2 × 5.6 × 3.7 Å. We describe here their synthesis and structure and evidence for their well-defined cavity and interaction with guest molecules via insertion into the hole.

Cyclization precursors **1a-d**[2] were synthesized from 5-methylnaphthalene-1,4-diol as in Scheme I. Cyclization of **1b** ($Cu(OAc)_2$, pyridine, 40 °C, 60–90 min) gave in 25–40% yield a separable mixture of two cyclophanes **2b**-σ and **2b**-C_2 (both mp >300 °C) in a ratio of 1.5–9:1. Conversion of the two proton methylene singlets of **1b** to AB quartets in their proton NMR spectra[3] was consistent with formation of a rigid cagelike structure.

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(2) All new compounds are characterized by elemental analysis and appropriate spectra.

(3) **2b**-σ: ^1H NMR ($CDCl_3$, 270 MHz) 8.04 (2 H, d, *J* = 8.6 Hz, H8), 7.89 (2 H, br s, H5), 7.60 (2 H, d of d, *J* = 8.6, 1.3 Hz, H7), 7.46 (4 H, d, *J* = 8.3 Hz, tosyl), 7.29 (4 H, d, *J* = 8.3 Hz, tosyl), 6.94 (4 H, s, phenylene), 6.58 (4 H, s, H2/H3), 5.22 (2 H, d, *J* = 15.5 Hz, $ArCH_2N$), 4.94 (2 H, d, *J* = 16.8 Hz, $ArOCH_2$), 4.92 (2H, d, *J* = 16.4 Hz, $ArOCH_2'$), 4.87 (2 H, d, *J* = 16.8 Hz, $ArOCH_2$), 4.82 (2 H, d, *J* = 16.4 Hz, $ArOCH_2'$), 4.63 (2 H, d, *J* = 15.5 Hz, $ArCH_2N$), 2.49 (6 H, s, tosyl CH_3). **2b**-C_2: ^1H NMR ($CDCl_3$, 270 MHz) 8.12 (2 H, d, *J* = 8.8 Hz, H8); 7.81 (2 H, d of d, *J* = 8.8, 1.1 Hz, H7), 7.73 (2 H, br s, H5), 7.42 (4 H, d, *J* = 8.3 Hz, tosyl), 7.33 (4 H, d, *J* = 8.3 Hz, tosyl), 6.93 (4 H, s, phenylene), 6.67 (2 H, d, *J* = 8.4 Hz, H2), 6.55 (2 H, d, *J* = 8.4 Hz, H3), 5.43 (2 H, d, *J* = 15.1 Hz, $ArCH_2N$), 4.98 (2 H, d, *J* = 17.4 Hz, $ArOCH_2$), 4.90 (2 H, d, *J* = 17.4 Hz, $ArOCH_2$), 4.88 (2 H, d, *J* = 17.2 Hz, $ArOCH_2'$), 4.75 (2 H, d, *J* = 17.2 Hz, $ArOCH_2'$), 4.32 (2 H, d, *J* = 15.1 Hz, $ArCH_2N$), 2.48 (6 H, s, tosyl CH_3). (All compounds **2a-d**-σ and **2a-d**-C_2 melt >300 °C.)

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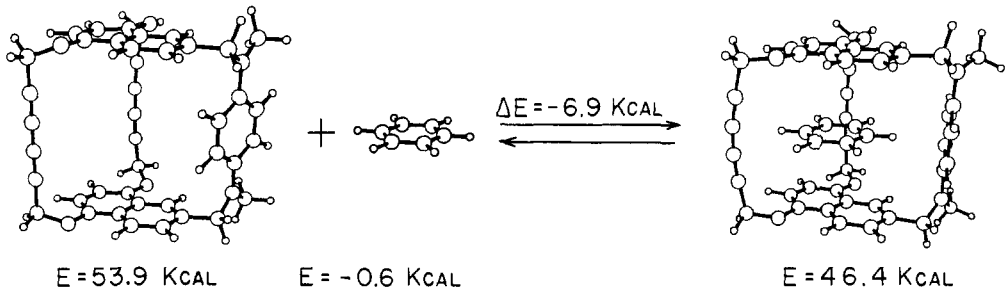


Figure 1.

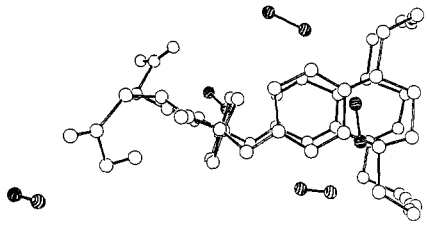
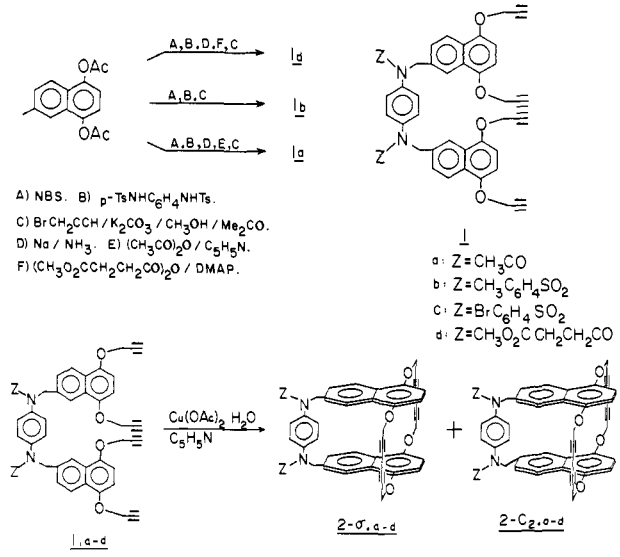


Figure 2.

Scheme I



Molecular weight measurements (isothermal distillation and mass spectra) of their hexadecahydro derivatives excluded baglike dimeric structures.

Two modes of cyclization of tetrayne **1** are possible, producing *meso*-**2** with a bisecting plane of symmetry (**2**-σ) or racemic **2** with a 2-fold axis (**2**-C_2). Meso isomer **2**-σ is the more interesting of the two as its interior has a larger opening to the outside. That the major isomer produced is in fact **2**-σ follows from these observations:

(1) The spanning phenylene meta protons of **2a**-σ are equivalent by free rotation about the NAc–NAc axis, and the ortho protons are enantiotopic.[4] Addition of a chiral shift reagent converted these to an AB quartet.[5] In racemic **2a**-C_2 (either enantiomer) all four phenylene protons are equivalent (by rotation and symmetry).

(2) Molecular mechanics calculations[6] show **2**-σ to be ca. 5 kcal more stable (strain energy) than **2**-C_2. Some fraction of this should appear in the first product-determining step of the cyclization.

(3) Single-crystal X-ray structure determination of the major isomer of **2d**-σ shows it to be the meso isomer and to have a structure in very close agreement with that derived from molecular mechanics calculations.[7]

These cyclophanes, in particular **2**-σ, possess cavities in the sense of being able to engulf guests[8] by the following experimental criteria:

(1) In aromatic solvents proton NMR ASIS effects[1a] are consistent with the occupancy of the hole (**2b**-σ) by solvent.

(2) Molecular mechanics calculations[6] show a *decrease* in steric energy of 6.9 kcal on inserting a benzene molecule into the hole of **2**-σ. This stabilization reflects slight van der Waals stabilization and, more importantly, no compensating nonbonded host–guest repulsions. This picture (see Figure 1) is strongly supported by complexation studies (see below).

(3) The X-ray structure of **2d**-σ clearly shows the presence of a molecule of methanol centrally located in the interior of the molecular cavity, with two additional methanols flanking the cavity,[9] (Figure 2).

(4) NMR complexation studies of the water-soluble dipotassium salt **2e**-σ with pyridine in D_2O ([**2e**-σ] $<10^{-3}$ M, [C_5H_5N] = 0–12 M) indicate an enthalpy-driven intercalation of pyridine into the cavity (Figure 1). Except for the phenylene protons, which move downfield, maximum shifts are large (ca. 0.8 ppm) and in an upfield direction and increase with increasing pyridine concentration (to ca. 0.3 M) and decreasing temperature. This behavior and the **2e**-σ–pyridine association constant determined ($K \simeq 10$ M^{-1} at 23 °C) are consistent with the complexation model (Figure 1) and the general picture of DNA intercalation and base stacking.[10]

A remarkably diverse set of molecules have now been examined as potential cavity-based hosts. Our above results,[8] the seminal work of Cram on cavitands[11] and spherands,[1c,12] and other literature examples lead us to suggest two generally useful principles in designing this type of molecule.

(1) A conformationally flexible (i.e., collapsible) host will collapse with loss of complexation ability *unless* suitable intracavity

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(5) Tris(3-((heptafluoropropyl)hydroxymethylene)-2-camphorato)europium; Shift reagent, **2a**-σ = 20.6; $\Delta\delta$ = 20 Hz (200 MHz); $J_{aa'}$ = 6 Hz. Kainsho, M.; Ajisaka, K.; Prickle, W. H.; Beare, S. D. *J. Am. Chem. Soc.* **1972**, *94*, 5924–5926. Fraser, R. R.; Petit, M. A.; Miskow, M. *Ibid.* **1972**, *94*, 3253–3254.

(6) Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, DC, 1982. The Allinger program MM2 (QCPE 395) modified locally was used.

(7) A satisfactory solution set could only be obtained using MULTAN78 with MM2-derived geometry input as a rigid group.

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(9) Three other methanols were located in the asymmetric unit. A listing of the atomic coordinates and other pertinent data from this crystal structure is available as supplementary material.

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(11) Moran, J. P.; Karbach, S.; Cram, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 5827–5831.

(12) For a review of guest-sticky hosts, see: Cram, D. J.; Trueblood, K. N. *Topics Curr. Chem.* **1981**, *98*, 43–106.

attractive interactions are present. Collapsible hosts must be "guest sticky".

(2) Hosts with functionally neutral cavities will accept guests *if* the cavity is maintained rigidly. Rigid hosts need not be guest sticky.

Thus, the flexible cryptands and crown ethers meet criterion 1, while the cyclodextrins, **2**, Koga's diphenylmethane-based hosts,[13] and Cram's cavitands[11] meet criterion 2. Spherands[1c] enjoy the benefits of both criteria (with a resulting astounding binding power) while Stetter's[14] and related[15] complexes meet neither. The latter have, in fact, been shown recently by X-ray *not* to form intracavity complexes.[15,16]

Acknowledgment. Partial support of this work by the National Science Foundation is acknowledged. We thank Dr. Kenneth J. Haller for invaluable assistance with the X-ray crystal structures.

Supplementary Material Available: Proton ASIS effects in pyridine-d_5 and chloroform-*d*, X-ray derived coordinates of **2d**-σ, and pyridine concentration dependent chemical shifts of **2e**-σ in aqueous pyridine (6 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Calcium 2-Fluorobenzoate Dihydrate: Indirect Calcium···Fluorine Binding through a Water-Bridged Outer-Sphere Intermolecular Hydrogen Bond

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Metal ion binding by halogen atoms that are covalently bonded to carbon has not received much attention by coordination chemists. Although such halogen atoms do contain lone pairs of electrons, they are generally considered to be poor donors toward metal ions. Yet, in recent years, there have been increasing (albeit fragmented) reports of C–X···M coordination occurring in alkali metal salts of halogen-substituted carboxylic acids[1] as well as in other systems.[2] Perhaps the most significant account of such binding occurs in the elegant structural model proposed for the inhibition and inativation of aconitase, an Fe^{2+}-containing enzyme occurring in the Krebs cycle, by the substrate fluorocitrate.[1g,3] In this model the covalently bound fluorine atom is coordinated to the Fe^{2+} ion. This C–F···Fe^{2+} interaction, which is impossible for a carbon-bound hydrogen atom to emulate, has been proposed as the cause of the extreme toxicity of fluorocitrate.[3]

Glusker and co-workers[3c] have very recently summarized the status of intermolecular C–F···M interactions occurring in some crystalline alkali metal salts of fluorine-substituted carboxylic acids. As yet, no crystallographic examples of direct C–F···M binding with multiple-valent cations in halogen-substituted carboxylates have been reported. In view of the importance of direct C–F···Fe^{2+} coordination proposed in fluorocitrate/aconitase binding, we have been investigating the structural coordination chemistry of a variety of divalent and trivalent cation salts of halogen-substituted carboxylic acids. We report here an X-ray investigation of calcium 2-fluorobenzoate dihydrate that reveals a novel mode of C–F···Ca^{2+} binding, which is mediated through a uniquely short C–F···H–O hydrogen bond.

Clear, colorless, prismatic crystals suitable for X-ray diffraction were obtained by slow evaporation at ambient temperature of an aqueous soltuion prepared from the reaction of calcium carbonate with 2-fluorobenzoic acid. The crystal structure was determined from a three-dimensional structural analysis[4,5] and a view of a portion of the structure is illustrated in Figure 1. The space group imposes crystallographic C_2 symmetry on the structure.

The most significant feature of this structure is the presence of a short intermolecular hydrogen bond, C(2)–F···H1–O_w, which is indicated by the following parameters: F···O_w 2.994 (2) Å, F···H^1 2.04 Å, O_w–H1 0.96 Å, F···H1–O_w angle 170°. To the best of our knowledge, this example is the strongest C–F···H–O hydrogen bond heretofore reported.[3]

The structure is dominated by planar Ca–O–Ca–O rings formed as a result of the strong carboxylate bridging interactions[8] and these form the basis of the polymeric framework of the crystalline structure. In this environment, although the C–F···H–O hydrogen bonding scheme is relatively much less significant in stabilizing the crystal, it nevertheless plays an important role in dictating the conformational features of the molecular stereochemistry. Hence, the carboxylate group, O(1)–C(7)–O(2), is twisted by 41° from the plane of the aryl ring. In 2-fluorobenzoic acid this dihedral angle is 10.6°.

The water molecule involved in the C–F···H–O hydrogen bond is bound to the Ca^{2+} ion so that, although direct C–F···Ca^{2+} binding is absent, there is indirect outer-sphere coordination of fluorine to the Ca^{2+} through this hydrogen bond. This is the first reported instance of water-mediated coordination[10] involving a carbon-bound fluorine atom. The biological importance of water-bridged coordination of metal ions with oxygen- or nitro-

(1) C–F···Na^+: (a) Vedavathi, B. M.; Vijayan, K. *Acta Crystallogr., Sect. B* **1977**, *B33*, 946. (b) Hurley, T. J.; Carrell, H. L.; Gupta, R. K.; Schwartz, J.; Glusker, J. *Arch. Biochem. Biophys.* **1979**, *193*, 478. C–F···K^+: (c) Griffin, R. G.; Yeuny, H. N.; Laprade, M. D.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 777. (d) Mattes, R.; Gohler, D. *J. Mol. Struct.* **1980**, *68*, 59. (e) Spek, A. L.; Lenstra, A. T. H.J. *Cryst. Struct. Commun.* **1981**, *10*, 1527. C–F···Rb^+: (f) Macintyre, W. M.; Zirakzadeh, M. *Acta Crystallogr.* **1964**, *17*, 2305. (g) Carrell, H. L.; Glusker, J. P. *Acta Crystallogr., Sect. B* **1973**, *B29*, 674. C–Cl···K^+: (h) Ellison, R. D.; Levy, H. A. *Acta Crystallogr.* **1965**, *19*, 260. (i) Golic, L.; Lazarini, F. *Cryst. Struct. Commun.* **1974**, *3*, 645. C–Br···Rb^+ (j) Videnova, V.; Baran, J.; Glowiak, T.; Ratajczak, H. *Acta Crystallogr., Sect. B* **1980**, *B36*, 459.

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(4) Crystal data for $[Ca(C_7H_4FO_2)_2(H_2O)_2]$: monoclinic, space group $C2/c$, a = 23.023 (4) Å, b = 11.146 (2) Å, c = 7.793 (1) Å, β = 133.00 (1)°, V = 1462.6 Å^3, Z = 4, d_c = 1.62 g cm^{-3}, d_m = 1.60 g cm^{-3}. X-ray diffraction intensity data were collected at 20 °C by using a crystal with approximate dimensions of 0.35 × 0.35 × 0.85 mm on a Nicolet automated four-circle diffractometer located at Crystalytics Co., Lincoln, Nebraska. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares. A total of 105 parameters were varied, which included anisotropic temperature factors for all nonhydrogen atoms. Hydrogen atom positional and isotropic temperature factors were not refined. The largest ratio of maximum least-square shift in any parameter to error was 0.01. Final agreement factors are R_F = 0.034 and R_{wF} = 0.031 for 1627 unique reflections. All computations were carried out on an IBM 4341 computer by using programs described previously.[6]

(5) Each 2-fluorobenzoate anion chelates a Ca^{2+} through its carboxylate group forming a four-membered ring while, in addition, each carboxylate oxygen, O(1), binds a separate Ca^{2+} ion through a unidentate bridging bond. The CaO_8 coordination polyhedron resembles most closely a dodecahedron although it is somewhat distorted towards a C_{2v}-bicapped trigonal prism.[7]

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