

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,<sup>13</sup> and Cram's cavitands<sup>11</sup> meet criterion 2. Spherands<sup>1c</sup> enjoy the benefits of both criteria (with a resulting astounding binding power) while Stetter's<sup>14</sup> and related<sup>15</sup> complexes meet neither. The latter have, in fact, been shown recently by X-ray *not* to form intracavity complexes.<sup>15,16</sup>

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**Supplementary Material Available:** Proton ASIS effects in pyridine-*d*<sub>5</sub> 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.

(13) Odashima, K.; Itai, A.; Yitaka, Y.; Koga, K. *J. Am. Chem. Soc.* **1980**, *102*, 2504-2505.

(14) Stetter, H.; Roos, E. E. *Chem. Ber.* **1955**, *88*, 1390-1395.

(15) Vögtle, F.; Puff, H.; Friedrichs, E.; Müller, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 431.

(16) Hilgenfeld, R.; Saenger, W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21* (10), 787.

### 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<sup>1</sup> as well as in other systems.<sup>2</sup> Perhaps the most significant account of such binding occurs in the elegant structural model proposed for the inhibition and inactivation of aconitase, an Fe<sup>2+</sup>-containing enzyme occurring in the Krebs cycle, by the substrate fluorocitrate.<sup>1a,3</sup>

(1) C-F...Na<sup>+</sup>: (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<sup>+</sup>: (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<sup>+</sup>: (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<sup>+</sup>: (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<sup>+</sup> (j) Videnova, V.; Baran, J.; Glowiak, T.; Ratajczak, H. *Acta Crystallogr., Sect. B* **1980**, *B36*, 459.

(2) (a) Dwivedi, G. L.; Srivastava, R. C. *Acta Crystallogr., Sect. B* **1971**, *B27*, 2315. (b) Cook, P. M.; Dahl, L. F.; Dickerhoof, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5511. (c) Wulfsberg, G.; West, R.; Rao, V. N. M. *J. Organomet. Chem.* **1975**, *86*, 303. (d) Prokofev, A. K. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 519. (e) Charbonnier, F.; Faure, R.; Liseleur, H. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3598. (f) Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 7748.

(3) (a) Glusker, J. P. *J. Mol. Biol.* **1968**, *38*, 149. (b) Carrell, H. L.; Glusker, J. P.; Villafranca, J. J.; Mildvan, A. S.; Dummel, R. J.; Kun, E. *Science (Washington D.C.)* **1970**, *170*, 1412. (c) Murray-Rust, P.; Stallings, W. C.; Monti, C. T.; Preston, R. K.; Glusker, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 3206.

In this model the covalently bound fluorine atom is coordinated to the Fe<sup>2+</sup> ion. This C-F...Fe<sup>2+</sup> interaction, which is impossible for a carbon-bound hydrogen atom to emulate, has been proposed as the cause of the extreme toxicity of fluorocitrate.<sup>3</sup>

Glusker and co-workers<sup>3c</sup> 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<sup>2+</sup> 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<sup>2+</sup> 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 solution prepared from the reaction of calcium carbonate with 2-fluorobenzoic acid. The crystal structure was determined from a three-dimensional structural analysis<sup>4,5</sup> and a view of a portion of the structure is illustrated in Figure 1. The space group imposes crystallographic C<sub>2</sub> 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<sub>w</sub>, which is indicated by the following parameters: F...O<sub>w</sub> 2.994 (2) Å, F...H<sup>1</sup> 2.04 Å, O<sub>w</sub>-H1 0.96 Å, F...H1-O<sub>w</sub> angle 170°. To the best of our knowledge, this example is the strongest C-F...H-O hydrogen bond heretofore reported.<sup>3</sup>

The structure is dominated by planar Ca-O-Ca-O rings formed as a result of the strong carboxylate bridging interactions<sup>6</sup> 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<sup>2+</sup> ion so that, although direct C-F...Ca<sup>2+</sup> binding is absent, there is indirect outer-sphere coordination of fluorine to the Ca<sup>2+</sup> through this hydrogen bond. This is the first reported instance of water-mediated coordination<sup>10</sup> involving a carbon-bound fluorine atom. The biological importance of water-bridged coordination of metal ions with oxygen- or nitro-

(4) Crystal data for [Ca(C<sub>7</sub>H<sub>4</sub>FO<sub>2</sub>)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>]: 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<sup>3</sup>, Z = 4, d<sub>c</sub> = 1.62 g cm<sup>-3</sup>, d<sub>m</sub> = 1.60 g cm<sup>-3</sup>. 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 Crystalitics 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<sub>F</sub> = 0.034 and R<sub>wF</sub> = 0.031 for 1627 unique reflections. All computations were carried out on an IBM 4341 computer by using programs described previously.<sup>6</sup>

(5) Each 2-fluorobenzoate anion chelates a Ca<sup>2+</sup> through its carboxylate group forming a four-membered ring while, in addition, each carboxylate oxygen, O(1), binds a separate Ca<sup>2+</sup> ion through a unidentate bridging bond. The CaO<sub>3</sub> coordination polyhedron resembles most closely a dodecahedron although it is somewhat distorted towards a C<sub>2v</sub>-bicapped trigonal prism.<sup>7</sup>

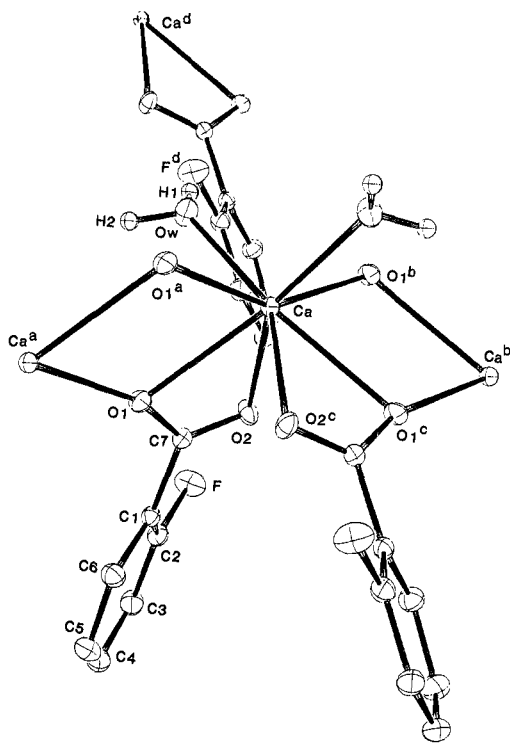
(6) Karipides, A. *Inorg. Chem.* **1979**, *18*, 3034.

(7) Mutterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

(8) The Ca-O(1<sup>a</sup>) bridging bond length of 2.360 (1) Å is considerably shorter than the Ca-O(1) and Ca-O(2) nonbridging carboxylate lengths of 2.629 (1) and 2.463 (1) Å, respectively, and attests to the tight packing.

(9) Ferguson, G.; Islam, K. M. S. *Cryst. Struct. Commun.* **1975**, *4*, 389.

(10) (a) Glassman, T. A.; Cooper, C.; Harrison, L. W.; Swift, T. J. *Biochemistry* **1971**, *10*, 843. (b) Granot, J.; Fiat, D. *J. Am. Chem. Soc.* **1977**, *99*, 70.



**Figure 1.** A portion of the structure showing the  $\text{CaO}_8$  coordination polyhedron, mode of ligand- $\text{Ca}^{2+}$  binding, and the spatial relationship of the  $\text{O}_w\text{-H1}\cdots\text{F}^d$  hydrogen bond. The aryl hydrogen atoms have been omitted for clarity. The superscripts refer to the following symmetry-related positions: (a)  $-x, -y, 1-z$ ; (b)  $x, -y, z-1/2$ ; (c)  $-x, y, 1/2-z$ ; (d)  $-x-1/2, 1/2+y, -z-1/2$ .

gen-containing donors has been demonstrated. For example, this type of binding occurs in the metal complexes of adenosine triphosphate<sup>10</sup> as well as in the  $\text{Fe}^{3+}\text{-OH}_2\text{-histidine}$  portion of ferrimyoglobin.<sup>11</sup>

Calcium(II) ion has a high preferential affinity for oxygen donor groups, and we anticipate that in aqueous solution  $\text{Ca}^{2+}\cdots\text{water}$  and  $\text{Ca}^{2+}\cdots\text{carboxylate}$  interactions predominate. Since coordinated water molecules are the most acidic water molecules in solution and in view of the expected polarity of the C-F bond, the formation of weak water-bridged  $\text{C-F}\cdots\text{H}_2\text{O}\cdots\text{Ca}^{2+}$  interactions, however tenuous, is not unreasonable, especially since this water-mediated coordination survives in the crystal. We are not certain of all the factors whereby a carbon-bound fluorine atom could actually displace a coordinated water molecule or other donor group. There is ample crystallographic evidence that such displacement does occur in many alkali metal salts of fluorocarboxylates. It may very well also prove to occur for large alkaline-earth ions.

For divalent or trivalent transition-metal cations, however, we would expect coordinated water molecules to be more acidic and considerably less labile than for alkali metal ions. In these systems direct C-F $\cdots$ M binding may be relatively less favorable compared to the water-bridged structure, C-F $\cdots$ H<sub>2</sub>O $\cdots$ M. We suggest that such outer-sphere coordination of carbon-bound fluorine through a hydrogen bond may play an important role in explaining fluorocitrate inhibition of aconitase.

**Registry No.**  $[\text{Ca}(\text{C}_7\text{H}_4\text{FO}_2)_2(\text{H}_2\text{O})_2]$ , 88686-23-1.

**Supplementary Material Available:** Tables of fractional coordinates, thermal parameters, interatomic distances and angles, and shape parameters and a list of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

(11) Nobbs, C. L.; Watson, H. C.; Kendrew, J. C. *Nature (London)* **1966**, *209*, 339.

## Synthesis and X-ray Crystal Structure of a Transition-Metal Cluster Involving Framework Phosphorus-Phosphorus Double Bonds

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The synthesis and X-ray crystal structure of the first diphosphene by Yoshifuji and co-workers in 1981 has generated considerable interest in multiple bonding among the heavier main-group 5 elements.<sup>1</sup> So far, structural reports have dealt with compounds having unsupported P-P,<sup>2</sup> P-As,<sup>3</sup> or As-As<sup>4</sup> double bonds and their simple transition-metal complexes.<sup>5</sup> In this paper we report the synthesis and structure of a rare transition-metal cluster involving P-P double bonds. This is the compound  $[\text{Ni}_5(\text{CO})_6(\text{Me}_3\text{Si})_2\text{CHP}=\text{PCH}(\text{SiMe}_3)_2\text{Cl}]$  (**1**), which represents a significant development in both transition-metal cluster and diphosphene chemistry.

The synthesis of **1** involved the addition of a solution of P- $[\text{CH}(\text{SiMe}_3)_2]\text{Cl}_2$  (1 equiv) in ether to a freshly prepared solution of  $\text{Na}_2[\text{Ni}_6(\text{CO})_{12}]$  (1 equiv).<sup>6</sup> The ether was removed after stirring for 12 h, and the residue was redissolved in *n*-hexane to give a red-brown solution. Filtration and subsequent cooling gave **1** as red-brown crystals in ca. 15% yield (based on phosphorus), IR (Nujol) 2018, 1723  $\text{cm}^{-1}$ . <sup>31</sup>P NMR indicated that the *n*-hexane solution contained other species in addition to **1**, and work is in progress to characterize these. The singlet seen at 353 ppm (in  $\text{C}_6\text{D}_6$  relative to 85%  $\text{H}_3\text{PO}_4$ ) has been assigned to **1**.

The structure of **1** was determined by X-ray diffraction<sup>7</sup> and is illustrated in Figure 1. The molecular geometry involves four of the five nickel atoms in a butterfly arrangement. These four nickels are bound to terminal carbonyls, and two additional carbonyls triply bridge the underside of each butterfly wing. The two diphosphene ligands bridge two wing tips and hinge metal centers to the fifth nickel atom, Ni(1), which is also bonded to chlorine. The Ni-Ni distances within the butterfly average ca. 2.55 Å while Ni(1)-Ni(3) and Ni(1)-Ni(5) distances are somewhat longer, averaging 2.69 Å (cf. ref 6). The diphosphene ligands interact most closely with Ni(3) and Ni(5) as exemplified by the short Ni-P distances, average ca. 2.18 Å.<sup>8</sup> The P-Ni(1),

(1) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587-4589.

(2) Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Pakulski, M.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4045-4046.

(3) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R. *J. Chem. Soc., Chem. Commun.* **1983**, 881-882.

(4) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M. *J. Am. Chem. Soc.* **1983**, *105*, 5506-5507.

(5) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085-2086. Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Ibid.* **1983**, *105*, 7460-1. Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Ibid.* **1983**, *105*, 7750-1. Cowley, A.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *Ibid.* **1983**, *105*, 7751-2.

(6) Longoni, G.; Chini, P.; Cavalieri, A. *Inorg. Chem.* **1975**, *15*, 3025-3029. Calabrese, J. C.; Dahl, L. F.; Cavalieri, A.; Chini, P.; Longoni, G.; Martinego, S. *J. Am. Chem. Soc.* **1974**, *96*, 2616-2618.

(7) A red-brown crystal of **1** of dimensions 0.10 × 0.12 × 0.14 mm was mounted on a Syntex P<sub>21</sub> diffractometer equipped with a graphite monochromator. With Mo K $\alpha$  ( $\lambda = 0.71069$  Å) and crystal cooled to 140 K, crystal data were as follows: monoclinic  $P2_1/c$ ;  $a = 19.853$  (4) Å,  $b = 13.686$  (3) Å,  $c = 23.298$  (4) Å;  $\beta = 113.13$  (1)°;  $Z = 4$ ;  $\mu = 19.5$   $\text{cm}^{-1}$  (range of absorption correction factors 1.2-1.36). Data were collected to  $2\theta_{\text{max}}$  of 45° with a  $\omega$  scan technique. A total of 7592 unique data were collected of which 5484 had  $I > 2\sigma(I)$ . Scattering factors and corrections for anomalous scattering were from Vol. IV of the International Tables. The structures were solved by direct methods. Computer programs were those of SHELXTL, version 3, July 1981 package. The refinement was marred by a disorder of all four Si's on one of the diphosphene groups that exhibited 50-50 disorder with another set of four Si's. Two of the three methyl groups were shared by these disordered Si's. Occupancy factors were initially refined to 0.51-0.49 and subsequently fixed at 0.50. With an absorption correction and anisotropic thermal parameters for atoms other than methyl carbons and hydrogens  $R = 0.07$  and  $R_w = 0.074$ .