

The Formic Acid 1D Array with H Bonds All Reversed: Structure of a Cocrystal with Hydrogen Fluoride^{1,2}

Dirk Wiechert, Dietrich Mootz,* and Thomas Dahlems

Institut für Anorganische Chemie und Strukturchemie
Heinrich-Heine-Universität Düsseldorf
D-40225 Düsseldorf, Federal Republic of Germany

Received July 14, 1997

In solid formic acid, the molecules are linked by hydrogen bonds O—H···O in a one-dimensional array (A) in which the conformation of the carboxyl groups is synplanar.³ The peculiar

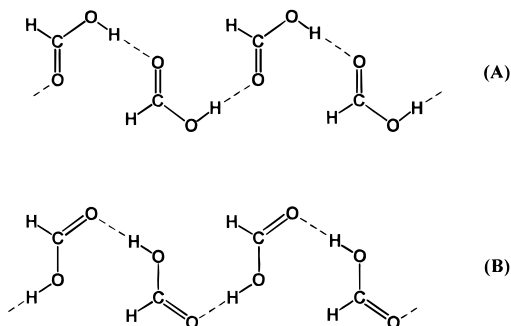


Figure 1. Structure of the adduct HCOOH·HF. Two adjacent main chains of molecules HCOOH corresponding to motif (B) are shown, plus the laterally bonded HF. The ellipsoids for the non-hydrogen atoms correspond to 50% probability. The very weak hydrogen bonds C—H···O and C—H···F are indicated only once.

Table 1. Interatomic Distances and Angles, with H Atom Positions Not Corrected for Systematic Errors

| Bond Lengths, Å | | | |
|-------------------------|----------|----------|-------------|
| C—O1 | 1.232(2) | O2—H2 | 0.91(2) |
| C—O2 | 1.298(2) | F—H3 | 0.81(4) |
| C—H1 | 0.92(2) | | |
| Bond Angles, deg | | | |
| O1—C—O2 | 120.0(1) | O2—C—H1 | 121(2) |
| O1—C—H1 | 119(2) | C—O2—H2 | 114(2) |
| Hydrogen Bonds | | | |
| D—H···A | D···A, Å | H···A, Å | ∠ at H, deg |
| C—H1···O2 ^a | 3.240(2) | 2.57(2) | 130(2) |
| C—H1···F ^b | 3.238(2) | 2.37(3) | 157(2) |
| O2—H2···O1 ^a | 2.649(2) | 1.74(3) | 179(3) |
| F—H3···O1 | 2.556(2) | 1.75(4) | 178(3) |

^a0.5 + x, y, 0.5 - z. ^b0.5 + x, y, 1.5 - z.

case (B) of an isomer of the whole array with merely the hydrogen bonds all reversed, and the carboxyl groups thus altered to antiplanar,⁴ has now been found in an adduct of the acid with hydrogen fluoride.⁵

Cocrystallization of the “smallest” organic and inorganic acids has been studied by difference thermal analysis and temperature-dependent X-ray powder diffraction. Two compounds, of composition HCOOH·HF and HCOOH·3HF, have been identified, melting at 242 and incongruently at 156 K, respectively. The crystal structure of the 1:1 compound has been determined at 123 K.⁶

The two acids are present as neutral molecules (Figure 1 and Table 1). Those of formic acid are O—H···O hydrogen-bonded

(1) Dedicated to Professor Bryan M. Craven on the occasion of his retirement from the University of Pittsburgh Department of Crystallography, and in remembrance of a great place for academic education and research.

(2) This is paper 42 of the series Fluorides and Fluoro Acids. For paper 41, see: Klapdor, M. F.; Beckers, H.; Poll, W.; Mootz, D. *Z. Naturforsch.* **1997**, *52b*, 1051–1054.

(3) Single-crystal X-ray analysis with film methods at 223 K: Holtzberg, F.; Post, B.; Fankuchen, I. *Acta Crystallogr.* **1953**, *6*, 127–130. Refinement with diffractometer data at 98 K: Nahringsbauer, I. *Acta Crystallogr.* **1978**, *B34*, 315–318. Neutron powder diffraction of a perdeuterated sample at 4.5 K: Albinati, A.; Rouse, K. D.; Thomas, M. W. *Acta Crystallogr.* **1978**, *B34*, 2188–2190.

(4) For the isolated formic acid molecule, the antiplanar conformer has been calculated to be less stable than the synplanar one by up to 30 kJ mol⁻¹. See ref 5b and: Marcoccia, J. F.; Csizmadia, I. G.; Peterson, M. R.; Poirier, R. A. *Gazz. Chim. Ital.* **1990**, *120*, 77–87.

(5) Relevance of motif B also for formic acid by itself has been suggested in connection with a phase transition around 207–218 K derived from IR spectroscopy and DTA: (a) Zelsmann, H. R.; Bellon, F.; Marechal, Y.; Bullemer, B. *Chem. Phys. Lett.* **1970**, *6*, 513–515. (b) Karpfen, A. *Chem. Phys.* **1984**, *88*, 415–423 and references therein.

(6) A crystal was grown by miniature zone melting¹¹ with the sample sealed in a PE tubing of 0.8 mm inner diameter, which in turn was enclosed in a thin-walled glass capillary for mechanical fixation: orthorhombic, space group *Pnma*, *a* = 6.551(3) Å, *b* = 5.651(3) Å, *c* = 7.347(4) Å, *V* = 272.0(2) Å³ at 123 K, *Z* = 4, *d* (calcd) = 1.61 mg mm⁻³; Siemens-Stoe AED 2 diffractometer adapted for measurements at low temperatures, graphite-monochromated Mo Kα radiation (*λ* = 0.71073 Å), *μ* = 0.19 mm⁻¹, 2θ (max) = 70°, 638 independent reflections with *F*_o² > 3σ_{*F*}², of which 566 with |*F*_o| > 4σ_{*F*} observed; direct methods, 34 variables refined on *F*², *R*(*F*) (obsd) = 0.039, *wR*(*F*²) (all) = 0.128, residual electron density between -0.44 and +0.23 e Å⁻³; computer programs SHELXS-86, SHELXL-93, and SHELXTL PLUS.¹²

in a homomolecular main chain just as in motif B. By further strong hydrogen bonds, of the rare type F—H···O to the carbonyl O atoms, the molecules of hydrogen fluoride are attached to the chain on both sides.

Adjacent units of this kind, with all atoms on the mirror plane of the space group, interlock with each other and are cross-linked into a layer by much weaker hydrogen bonds C—H···F. These belong to bifurcated interactions, completed by also very weak hydrogen bonds C—H···O. The latter are effective *within* the chains and involve the O atoms of the hydroxyl groups.⁷ In the third dimension, the layer recurs in an ABAB... sequence, with the polar chains “pointing” alternately in opposite directions.

The structure is surprising also when compared to that of the homologous adduct where the formic is replaced by acetic acid. There the components are again present as neutral molecules, but alternating in a *heteromolecular* chain.⁸ Truly molecular hydrogen fluoride adducts have seldom been char-

(7) A very weak hydrogen bond C—H···O, in addition to the reported O—H···O, suggests itself also in the crystal structure of formic acid alone, loc. cit. For a recent discussion of this unconventional kind of hydrogen bonding see: Steiner, T. *Chem. Commun.* **1997**, 727–734 and references therein.

(8) Bartmann, K.; Mootz, D. *Z. Anorg. Allg. Chem.* **1991**, *601*, 31–40.

acterized otherwise,⁹ an apparent prerequisite being that this acid is not present in a larger excess. Thus, the adduct HCOOH·3HF (see above) and its acetic acid homologue⁸ most probably are composed of ions, [RC(OH)₂]⁺ (R = H, Me) and [H₂F₃]⁻,¹⁰ linked by strong hydrogen bonds O—H···F. How-

(9) Some more examples are the 1:1 adducts (a–c) with triphenylphosphane oxide, pyridine, acetonitrile, and the particular case (d) of the adduct 2D₂O·3DF observed only deuterated. (a) Thierbach, D.; Huber, F. *Z. Anorg. Allg. Chem.* **1979**, *451*, 137–142. (b) Boenigk, D.; Mootz, D. *J. Am. Chem. Soc.* **1988**, *110*, 2135–2139. (c) Dunkelberg, O.; Haas, A.; Klapdor, M. F.; Mootz, D.; Poll, W.; Appelman, E. H. *Chem. Ber.* **1994**, *127*, 1871–1875. (d) Poll, W.; Lohmeyer, M.; Mootz, D. *Z. Naturforsch.* **1989**, *44b*, 1359–1364.

(10) Other 1:3 adducts with this anion, confirmed by structure analysis, are those of pyridine^{9b} and two trialkylamines: Wiechert, D.; Mootz, D.; Franz, R.; Siegemund, G. *Z. Kristallogr.* **1997**, Suppl. Issue No. 12, 40.

ever, none of these has so far been obtained as a single crystal suitable for structure analysis.

Acknowledgment. This work was supported by Fonds der Chemischen Industrie.

Supporting Information Available: Tables of atomic coordinates and displacement parameters for the title compound (1 page). See any current masthead page for ordering and Internet access instructions.

JA972337F

(11) Brodalla, D.; Mootz, D.; Boese, R.; Osswald, W. *J. Appl. Crystallogr.* **1985**, *18*, 316–319.

(12) (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473. (b) Sheldrick, G. M. Program for the Refinement of Crystal Structures, Universität Göttingen, 1993. (c) SHELXTL PLUS, Structure Determination System Revision 4.21/V, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.