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Very short F—H···F hydrogen bond in L-argininium fluoride hydrogen fluoride

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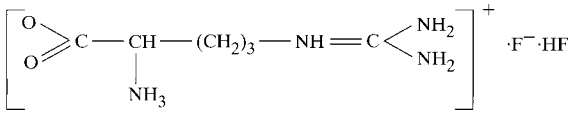
There are two symmetry-independent formula units of the title compound, $C_6H_{15}N_4O_2^+\cdot F^-\cdot HF$, per cell. Both cations have a zwitterionic form, protonated at both the guanidyl and amino groups. The two symmetry-independent cations differ in their conformation. In one of them the C_γ atom is in a *gauche* position to both the amino and carboxyl groups, while in the other this atom is *trans* to the amino group. The two anions have very similar geometry. The F^- ions are strongly hydrogen bonded to an HF molecule [F—H···F 2.233 (2) and 2.248 (3) Å], thereby forming an asymmetric non-linear bifluoride anion. These F···F distances are the shortest reported for an asymmetric HF_2^- anion.

Comment

A number of arginine salts have interesting non-linear optical properties, of which L-arginine phosphate and L-arginine fluoride have the strongest second harmonic generation signal (Monaco *et al.*, 1987), roughly six times that of quartz or four times that of potassium dihydrogen phosphate (KDP). The radiation threshold for these compounds is relatively large, which is important for applications such as harmonic generators for lasers used in fusion experiments. L-Arginine fluoride is optically biaxial and is non-critically phase matched, which is a valuable property for applications that require blue–green light. It crystallizes in the $P2_1$ space group but its crystal structure has not yet been published (Monaco *et al.*, 1987). In an effort to synthesize L-arginine fluoride we have obtained



$$\left[\,{}^{O}_{O}\!\!>\!C-\underset{\displaystyle NH_3}{\underset{|}{CH}}-(CH_2)_3-NH=C\!<\!{}^{NH_2}_{NH_2}\right]^+\cdot F^-\cdot HF$$

(I)

the title compound, (I), which includes an additional HF molecule strongly hydrogen bonded to F^-.

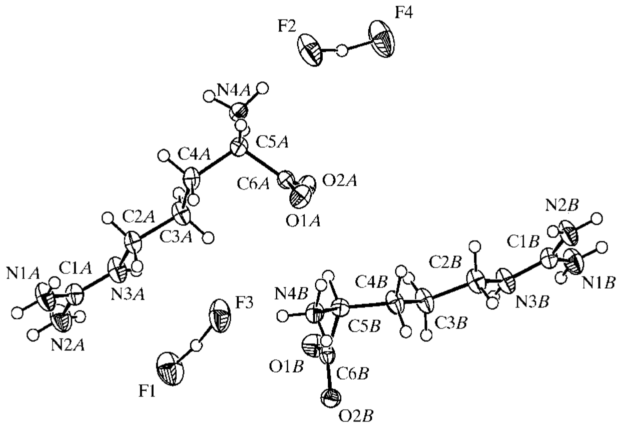


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

The HF_2^- anion is of significant structural and theoretical interest. It is a classic example for semi-ionic three-centre four-electron bonding (Pimentel, 1951) and exhibits the strongest known hydrogen bond (Williams & Schneemeyer, 1973) which, depending on the symmetry of the surrounding crystal field, can be either symmetric or asymmetric (Lautie *et al.*, 1984). Typical dissociation energies reported for the bifluoride anion exceed 24 kcal mol^{-1} (1 cal = 4.184 J).

Both symmetry-independent anions in the crystal of (I) deviate significantly from linearity and have the H atom in an off-centre position, as shown by the F—H···F angles and the F—H and H···F distances (Table 2). This geometry compares well with that established by other studies (Denne & Mackay, 1971; Wittlesey *et al.*, 1997; Williams & Schneemeyer, 1973) but is different from the $D_{\infty h}$ geometry of the isolated ion as given by good quality *ab initio* calculations using extended basis sets (Heidrich *et al.*, 1993). In a few salts in which the bifluoride anion is under the influence of a highly symmetrical crystal field, such as in tetramethylammonium bifluoride (Wilson *et al.*, 1989) and alkali bifluorides (Rush *et al.*, 1972), such a symmetric FHF^- anion has been observed.

The F···F distances for the two bifluoride anions in (I) are 2.248 (3) and 2.233 (2) Å, for ions F1—H1···F3$^-$ and F2—H2···F4$^-$, respectively. These values are considerably less than twice the van der Waals radius of fluorine (1.4 Å), as expected from a very strong hydrogen bond. These F···F distances are the shortest reported for asymmetric bifluoride anions and are only slightly larger than the absolute shortest value reported for the symmetric anion in tetramethyl ammonium bifluoride [2.213 (4) Å; Wilson *et al.*, 1989]. The experimental value for the anionic F···F distance obtained in the gas phase from infrared diode laser spectroscopy is 2.27771 (7) Å (Kawaguchi & Hirota, 1986). There has also been much theoretical effort in *ab initio* calculations of the ground state geometry and vibrational properties of the bifluoride anion. For the isolated symmetric anion a range of values (2.256–2.298 Å) for the F···F distance has been reported. In a recent calculation (Heidrich *et al.*, 1993) for the

Table 1
Selected geometric parameters (Å, °).

O1*A*—C6*A*	1.255 (3)	O2*B*—C6*B*	1.252 (3)
O2*A*—C6*A*	1.242 (3)	O1*B*—C6*B*	1.246 (3)
O2*A*—C6*A*—O1*A*	126.1 (2)	O1*B*—C6*B*—O2*B*	125.9 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
F1—H1···F3	1.01 (6)	1.26 (6)	2.248 (3)	163 (5)
F2—H2···F4	1.04 (6)	1.22 (5)	2.233 (2)	161 (5)
N1*A*—H1*A*1···F4$^{\rm i}$	0.86	1.98	2.825 (3)	168
N1*A*—H1*A*2···O1*A*$^{\rm ii}$	0.86	2.15	3.002 (3)	173
N2*A*—H2*A*1···O2*A*$^{\rm ii}$	0.86	2.20	2.987 (3)	153
N2*A*—H2*A*2···F1$^{\rm iii}$	0.86	2.10	2.939 (3)	167
N3*A*—H3*A*···F3$^{\rm iii}$	0.86	1.98	2.829 (3)	168
N4*A*—H4*A*1···O2*B*$^{\rm iv}$	0.89	1.96	2.835 (3)	168
N4*A*—H4*A*3···F2	0.89	1.78	2.632 (3)	160
N4*A*—H4*A*2···O1*A*$^{\rm iii}$	0.89	2.05	2.876 (3)	155
N2*B*—H2*B*1···F1$^{\rm v}$	0.86	2.05	2.897 (3)	169
N2*B*—H2*B*2···O1*B*$^{\rm v}$	0.86	2.34	3.078 (3)	144
N2*B*—H2*B*2···O2*B*$^{\rm vi}$	0.86	2.62	3.290 (3)	135
N1*B*—H1*B*1···O2*B*$^{\rm vi}$	0.86	2.02	2.828 (3)	156
N1*B*—H1*B*2···F4$^{\rm vii}$	0.86	1.99	2.831 (3)	165
N3*B*—H3*B*···F2$^{\rm vii}$	0.86	2.04	2.883 (3)	168
N4*B*—H4*B*1···O2*A*$^{\rm viii}$	0.89	2.14	2.979 (3)	157
N4*B*—H4*B*1···O1*A*	0.89	2.54	3.080 (3)	120
N4*B*—H4*B*3···F3	0.89	1.78	2.652 (3)	168
N4*B*—H4*B*2···O1*B*$^{\rm viii}$	0.89	2.00	2.882 (3)	174

Symmetry codes: (i) $x, y, 1+z$; (ii) $x-1, y, 1+z$; (iii) $x-1, y, z$; (iv) $x-1, 1+y, z$; (v) $1+x, y, z-1$; (vi) $x, y, z-1$; (vii) $x, y-1, z$; (viii) $1+x, y, z$.

$(HF)_3$ molecule, which may be partitioned into the two conceivable subunits FH_2^+ and F_2H^-, the bifluoride anion deviates 27.7° from the linear geometry and the F···F distance is 2.255 Å.

The two protonated arginine molecules in (I) exist as positively charged zwitterions, with both the guanidyl and amino groups protonated. Inspection of the C═O distances in the carboxyl groups (1.242–1.255 Å) shows that these are deprotonated. The conformations of the amino acid cations in the two molecules *A* and *B* are best described by the torsion angles according to the rules of IUPAC–IUB (1970): φ^1 = 155.50 (18) and 134.1 (2), φ^2 = −23.9 (3) and −47.2 (2), χ^1 = 60.1 (3) and 175.9 (2), χ^2 = −179.4 (2) and 164.4 (2), χ^3 = 170.8 (2) and 178.2 (2), χ^4 = −174.6 (2) and −168.6 (3), χ^{51} = −4.0 (4) and −1.0 (4), and χ^{52} = 177.9 (2) and 177.9 (2)°, for molecules *A* and *B*, respectively. The two arginine molecules have different conformations, as can be seen from the internal rotation angles about the C4—C5 bond, resulting in different staggered positions of the C3 atom. In the molecule labelled *A*, atom C3*A* is found in a *gauche* position to both the amino and carboxyl groups, while in molecule *B*, atom C3*B* is in a *trans* position to the amino group.

The structure of (I) is held together by a complex three-dimensional hydrogen-bond network. Full capability for hydrogen bonding of the guanidyl and amino groups of the two argininium ions is achieved. Both F atoms of each bifluoride anion accept two protons each, besides the shared inner proton. The anions bridge the cations *via* hydrogen bonds involving the amino and guanidyl groups. Details of the hydrogen bonding are given in Table 2.

It should be mentioned that because there is no significant anomalous dispersion by any atom in compound (I) at the Mo *Kα* wavelength, the enantiomorph was not determined from the X-ray data and the chirality assigned to the molecule is the well known chirality of L-arginine (the configuration of the chiral C_α atom is *S*). Measurements of the optical properties of this compound are under way.

Experimental

Crystals of (I) were prepared by reacting fluoric acid (40%, Merck) with a dilute aqueous solution of L-arginine (98% purity, Aldrich). Good quality transparent single crystals grew from the solution by slow evaporation at room temperature over several weeks.

Crystal data

$C_6H_{15}N_4O_2^+\cdot F^-\cdot HF$
$M_r = 214.23$
Triclinic, $P1$
$a = 5.1813$ (11) Å
$b = 9.2173$ (18) Å
$c = 10.6278$ (17) Å
$\alpha = 87.878$ (14)°
$\beta = 74.948$ (16)°
$\gamma = 86.653$ (17)°
$V = 489.18$ (16) Å^3

$Z = 2$
$D_x = 1.454$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 8.33$–16.52°
$\mu = 0.133$ mm^{-1}
$T = 293$ (2) K
Irregular, colourless
0.39 × 0.24 × 0.24 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: none
3023 measured reflections
3004 independent reflections
2635 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.057$

$\theta_{\rm max} = 27.47$°
$h = -6 \rightarrow 6$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 13$
3 standard reflections
frequency: 180 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.094$
$S = 1.093$
3004 reflections
261 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.1464P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

All H atoms could be located in a difference Fourier map at an intermediate stage of the refinement. The coordinates of the H atoms of the anion were refined freely with an isotropic displacement parameter $U({\rm H})_{\rm eq} = 1.5U_{\rm eq}$ of the parent F atom. The other H atoms were placed at calculated positions and refined as riding using the *SHELXL*97 (Sheldrick, 1997*a*) defaults. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1997);

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program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1087). Services for accessing these data are described at the back of the journal.

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