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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.022
 wR factor = 0.056
 Data-to-parameter ratio = 6.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

L-Histidinium tetrafluorosuccinate

In the crystal structure of the title compound, $\text{C}_6\text{H}_{11}\text{N}_3\text{O}_2^{2+} \cdot \text{C}_4\text{F}_4\text{O}_4^{2-}$, the anions and cations are linked to each other through hydrogen bonds.

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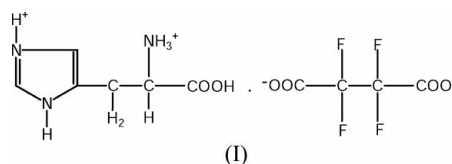
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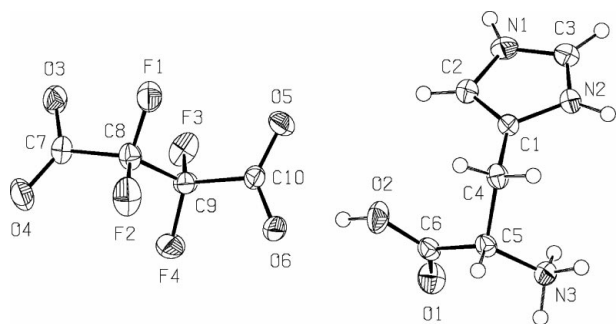
Comment

In the last decade, second-order nonlinear optical (SONLO) crystals have attracted much attention because of their potential applications in many fields. Advanced laser-based imaging, optical communication and data-storage systems require improved nonlinear optical materials. Coherent blue and green light is important for many applications, such as displays, high-resolution printing and signal processing (Marcy *et al.*, 1995; Ding *et al.*, 2000; Wang *et al.*, 2001). Materials with large second-order nonlinearities, short transparency cutoff wavelengths and stable physicochemical properties are needed in order to realise many of these applications. Purely inorganic NLO materials typically have excellent mechanical and thermal properties but possess relatively modest optical nonlinearity, because of the lack of extended π -electron delocalization (Jiang & Fang, 1999; Aggarwal *et al.*, 1999). In recent years, extensive research has been carried out on organic NLO materials, due to their fast and large nonlinear response over a broad frequency range, high optical-damage thresholds and inherent synthetic flexibility. For example, 2-methyl-4-nitroaniline produces large values of $\chi^2[\text{C1}-\text{C4}-\text{C5}-\text{C6}]$, due to the presence of the methyl substituent in the aromatic ring, inducing noncentrosymmetric packing. The non-linearity of an organic NLO material is also due to the presence of delocalized π -electron systems between donor and acceptor groups, which enhance their asymmetric polarizability. However, organic NLO crystals usually have low mechanical and thermal properties (Long, 1995).

Histidine itself exists in orthorhombic and monoclinic forms (Madden, McGandy & Seeman, 1972; Madden, McGandy, Seeman *et al.*, 1972). Neutron and X-ray investigations on histidine hydrochloride have already been reported



(Fuess & Bartunik, 1976; Donohue & Caron, 1964). X-ray studies on the following crystalline complexes have also been reported: DL- and L-histidine with succinic acid (Prasad & Vijayan, 1993), L-histidine with glutaric acid (Saraswathi & Vijayan, 2001), L-histidine with L-aspartic acid (Bhat &

**Figure 1**

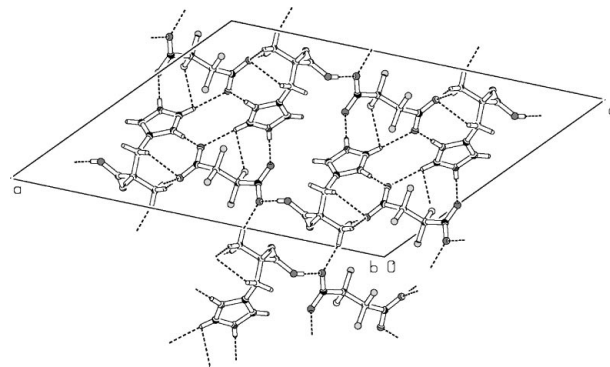
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Vijayan, 1978), two forms of L-histidine with acetic acid (Suresh *et al.*, 1994), L-histidine with formic acid (Suresh & Vijayan, 1995) and DL-histidine with glycolic acid (Suresh & Vijayan, 1996). Against this background, we present here the crystal structure of the title compound, (I).

The two ions of (I) are shown in Fig. 1. The conformation of the histidine side chain can be described by the two torsion angles, χ^1 [C1–C4–C5–N3] and χ^{21} [N2–C1–C4–C5] or χ^{22} [C2–C1–C4–C5] (IUPAC–IUB Commission on Biochemical Nomenclature, 1970). The sum of the absolute values of χ^{21} and χ^{22} is about 180° . χ^1 , which defines the disposition of the side chain with respect to the main chain, can take values in the neighbourhood of -60 , 60 or 180° , corresponding to the open conformation I (g^-), closed conformation (g^+) and open conformation II (t), respectively (Krause *et al.*, 1991). Although the preferred values of χ^{21} are -90 and 90° , the angle often deviates from these ideal values, due to interactions of the imidazole with other groups in the structure. In (I), the cation adopts the sterically most favourable open conformation, I, with $\chi^{21} -102.7(2)$ and $\chi^{22} 79.2(3)^\circ$. The imidazole group is +synclinal to the carboxyl group and –anticlinal to the ammonium group [C1–C4–C5–N3 $67.1(3)$]. The corresponding values observed in other complexes are; L-histidine formate formic acid -60 and -60.9° , DL-histidine formate monohydrate -60 and -67.5° , L-histidine glycolate 58.2 and -96.8° , DL-histidine glycolate 57.2 and -123° , monoclinic L-histidine acetate -61 and 99° , L-histidine semisuccinate trihydrate 59 and 69° , DL-histidine hemisuccinate dihydrate -62 and -86° , L-histidine hydrochloride monohydrate 71 and -120° (Oda & Koyama, 1972), and L-histidine semiglutamate monohydrate -66 and -70° .

The angle between the planes O3/C7/O4/F1/C8/F2 and O5/C10/O6/F3/C9/F4 of the two halves of the tetrafluorosuccinate anion is $5.7(1)^\circ$. The carbon skeleton of the tetrafluorosuccinate is essentially planar [torsion angle C7–C8–C9–C10 $170.4(2)^\circ$]. The bond lengths and angles in (I) agree with the literature values (Allen *et al.*, 1987).

The crystal structure of (I) is stabilized by hydrogen bonds, in addition to van der Waals interactions. The crystal packing, viewed down the b axis, is shown in Fig. 2, and the distances and angles in the hydrogen bonds are given in Table 2.

**Figure 2**

A view of the hydrogen bonds (dashed lines) in the unit cell of (I), along the b axis.

Experimental

The calculated amount of L-histidine and tetrafluorosuccinic acid was dissolved in doubly distilled water using a magnetic stirrer. The mixture was evaporated to dryness by heating at 333 K in a temperature-controlled water bath to avoid any possible decomposition (m.p. $468\text{--}470\text{ K}$). FT-IR (ν , cm^{-1}): 3140 (N–H asym. stretching), 2927 (C–H), 1630 (COO^-), 2954 (C–H sym.) and 2927 (C–H asym.), 1425 (C–O), 1203 , 3140 (N–H asym.), 3054 (N–H), 2985 (C–H), 2927 (C–H), 1720 (C=O), 1615 (N–H asym. bending), 1518 (N–H sym. bending), 1438 (C–O–H in-plane bending), 1267 (C–N stretching), 1119 (C–H in-plane bending), 839 (C–H out of plane bending), 639 (C=O in-plane bending). Elemental analysis, calculated for $\text{C}_{10}\text{H}_{11}\text{O}_6\text{N}_3\text{F}_4$: C 3.2, H 34.78, N 12.17%; found: C 3.44, H 35.24, N 11.98%.

Crystal data

$\text{C}_6\text{H}_{11}\text{N}_3\text{O}_2^{2+}\cdot\text{C}_4\text{F}_4\text{O}_4^{2-}$
 $M_r = 345.22$
 Monoclinic, $C2$
 $a = 21.8863(16)\text{ \AA}$
 $b = 5.1411(4)\text{ \AA}$
 $c = 15.5619(12)\text{ \AA}$
 $\beta = 132.601(5)^\circ$
 $V = 1288.9(2)\text{ \AA}^3$
 $Z = 4$

$D_x = 1.779\text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 21 085 reflections
 $\theta = 1.8\text{--}29.9^\circ$
 $\mu = 0.18\text{ mm}^{-1}$
 $T = 293\text{ K}$
 Block, colourless
 $0.56 \times 0.48 \times 0.36\text{ mm}$

Data collection

Stoe IPDS II two-circle diffractometer
 ω scans
 Absorption correction: by integration ($X\text{-RED32}$; Stoe & Cie, 2002)
 $T_{\min} = 0.906$, $T_{\max} = 0.938$
 12 924 measured reflections

1413 independent reflections
 1374 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\max} = 26.0^\circ$
 $h = -26 \rightarrow 26$
 $k = -6 \rightarrow 6$
 $l = -19 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.056$
 $S = 1.08$
 1413 reflections
 223 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2 + 0.5241P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.19\text{ e \AA}^{-3}$
 Extinction correction: $SHELXL97$ (Sheldrick, 1997)
 Extinction coefficient: $0.0264(18)$

Table 1

Selected geometric parameters (Å, °).

F1—C8	1.358 (2)	O5—C10	1.230 (2)
F2—C8	1.355 (3)	O6—C10	1.244 (2)
F3—C9	1.348 (2)	N1—C3	1.316 (4)
F4—C9	1.353 (2)	N1—C2	1.377 (3)
O1—C6	1.199 (3)	N2—C3	1.316 (3)
O2—C6	1.310 (3)	N2—C1	1.384 (3)
O3—C7	1.236 (2)	N3—C5	1.497 (3)
O4—C7	1.237 (3)		
C2—N1—C3	108.9 (2)	F1—C8—F2	106.61 (17)
C1—N2—C3	109.5 (2)	F1—C8—C7	109.18 (18)
N2—C1—C2	105.74 (19)	F1—C8—C9	107.6 (2)
N2—C1—C4	121.6 (2)	F2—C8—C7	110.9 (2)
N1—C2—C1	107.4 (2)	F2—C8—C9	107.05 (19)
N1—C3—N2	108.5 (2)	F3—C9—F4	106.63 (16)
N3—C5—C4	112.7 (2)	F3—C9—C8	108.04 (18)
N3—C5—C6	108.74 (18)	F3—C9—C10	110.3 (2)
O1—C6—C5	122.9 (2)	F4—C9—C8	107.3 (2)
O2—C6—C5	111.01 (18)	F4—C9—C10	111.41 (18)
O1—C6—O2	126.1 (2)	O5—C10—O6	128.7 (2)
O3—C7—O4	129.3 (3)	O5—C10—C9	116.38 (18)
O3—C7—C8	114.3 (2)	O6—C10—C9	114.90 (17)
O4—C7—C8	116.44 (19)		
N2—C1—C4—C5	−102.7 (2)	C1—C4—C5—C6	−56.6 (3)
C2—C1—C4—C5	79.2 (3)	C7—C8—C9—C10	170.36 (15)
C1—C4—C5—N3	67.1 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1N...O5 ⁱ	0.85	1.96	2.796 (2)	172
N2—H2N...O3 ⁱⁱ	0.93	1.76	2.690 (3)	179
N3—H3A...O4 ⁱⁱⁱ	0.91	2.06	2.958 (3)	168
N3—H3B...O4 ⁱⁱ	0.90	2.22	3.079 (3)	160
N3—H3C...O6 ^{iv}	0.92	1.89	2.775 (2)	161
O2—H22...O6	0.92 (5)	1.63 (5)	2.544 (3)	171 (4)
C3—H3...F3 ^v	0.90	2.54	2.862 (2)	102
C3—H3...O3 ^v	0.90	2.26	3.158 (3)	170
C4—H4A...O4 ⁱⁱ	0.97	2.58	3.359 (4)	138
C5—H5...O1 ^{vi}	0.89	2.29	3.040 (3)	142

Symmetry codes: (i) $1-x, y, 1-z$; (ii) $x-\frac{1}{2}, \frac{3}{2}+y, z$; (iii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (v) $1-x, 1+y, 1-z$; (vi) $x, 1+y, z$.

The H atom on atom O2 was located in a difference map and refined freely. The remaining H atoms were placed at idealized positions (aromatic C—H = 0.90 Å, CH₂ C—H = 0.95–0.97 Å, NH N—H = 0.84–0.93 Å and NH₃ N—H = 0.90–0.92 Å) and constrained using a riding model, with riding isotropic displacement parameters. Owing to the absence of atoms heavier than F, the Friedel opposites

were merged. The absolute configuration was known from the starting L-histidine material.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Farrugia, 1997); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *WinGX* (Farrugia, 1999).

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