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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
Disorder in main residue
 R factor = 0.044
 wR factor = 0.134
Data-to-parameter ratio = 9.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

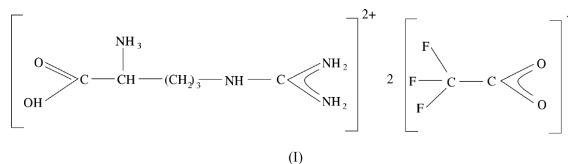
L-Argininium bis(trifluoroacetate)

In the title compound, $\text{C}_6\text{H}_{16}\text{N}_4\text{O}_2^{2+} \cdot 2\text{C}_2\text{F}_3\text{O}_2^-$, the cations have their amino, guanidyl and carboxylate groups protonated, thus featuring a double positive charge. One of the anions shows rotational disorder of its CF_3 group. A network of hydrogen bonds links the ions together, utilizing all possible arginine donor atoms.

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Comment

Crystalline trifluoroacetic acid tetrahydrate exhibits phase transitions at low temperature, for both undeuterated and deuterated forms (Mootz & Schilling, 1992). Motivated by the interesting physical properties of this acid, we have engaged in the study of trifluoroacetate salts, searching for compounds displaying phase transitions and superstructures (Rodrigues *et al.*, 2000, 2001*a,b*), and synthesized the title compound, L-argininium bis(trifluoroacetate), (I). The cations have their amino, guanidyl and carboxylate groups protonated, thus featuring a double positive charge. The C—O distances [O5—C10 = 1.194 (4) Å and O6—C10 = 1.298 (4) Å] show clearly the presence of an H atom bonded to O6 in the carboxylate group. Electrical neutrality is achieved by the presence of two symmetry-independent anions. In the protonated arginine molecule, C7 is in a staggered position *trans* to the amino group and *gauche* to the carboxylic acid group. The torsion angles that define the arginine conformation are $\varphi^1 = 136.9$ (4)°, $\varphi^2 = -44.7$ (3)°, $\chi^1 = -162.3$ (2)°, $\chi^2 = -172.9$ (2)°, $\chi^3 = -62.3$ (4)°, $\chi^4 = 129.1$ (3)°, $\chi^{51} = -15.9$ (5)° and $\chi^{52} = 165.2$ (3)°. In the anions, the bond lengths in the carboxylate groups show values compatible with a full proton transfer to the arginine molecule [1.225 (4)–1.251 (3) Å]. The displacement parameters of the F atoms are large and in one of the ions, two disordered orientations (70:30%) can be found related by a rotation of the CF_3 group around the central C—C bond. In addition to the electrostatic interaction, a network of hydrogen bonds further links the ions together, utilizing all possible arginine donor atoms. Each arginine cation shares H atoms with six anions and another cation in a three-dimensional network.



Experimental

An excess of trifluoroacetic acid was added to an aqueous solution of L-arginine. The solution was slightly warmed and left to evaporate at

room temperature. After some weeks, small single crystals were grown and their quality was appraised using Laue photographs.

Crystal data

$C_6H_{16}N_4O_2^{2+} \cdot 2C_2F_3O_2^-$
 $M_r = 402.27$
 Monoclinic, $P2_1$
 $a = 9.8457$ (9) Å
 $b = 5.7677$ (13) Å
 $c = 14.5035$ (12) Å
 $\beta = 95.178$ (7)°
 $V = 820.2$ (2) Å³
 $Z = 2$

$D_x = 1.629$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 6.7$ – 16.3 °
 $\mu = 0.17$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 $0.51 \times 0.41 \times 0.25$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Profile data from ω - 2θ scans
 Absorption correction: none
 2752 measured reflections
 2610 independent reflections
 1917 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$

$\theta_{max} = 30.1$ °
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 8$
 $l = -20 \rightarrow 20$
 3 standard reflections
 frequency: 180 min
 intensity decay: 2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.134$
 $S = 1.02$
 2610 reflections
 267 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2 + 0.2789P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.28$ e Å⁻³
 $\Delta\rho_{min} = -0.27$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.028 (6)

Table 1

Selected geometric parameters (Å, °).

O1–C1	1.225 (4)	N2–C5	1.326 (4)
O2–C1	1.232 (4)	N3–C5	1.322 (4)
O3–C3	1.251 (3)	N3–C6	1.466 (4)
O4–C3	1.229 (4)	N4–C9	1.488 (4)
N1–C5	1.317 (4)		
O1–C1–O2	127.8 (4)	N1–C5–N2	118.7 (3)
O1–C1–C2	116.4 (3)	N3–C5–N2	118.9 (2)
O2–C1–C2	115.8 (3)	N3–C6–C7	113.0 (3)
O4–C3–O3	127.6 (3)	O5–C10–O6	125.2 (3)
N1–C5–N3	122.5 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O6–H6 ⁱ ···O3 ⁱ	0.82	1.78	2.581 (3)	164
O6–H6 ⁱ ···F5B ⁱ	0.82	2.51	2.94 (2)	114
N1–H1A ⁱ ···O4 ⁱⁱ	0.86	2.07	2.874 (3)	155
N1–H1B ⁱ ···O4 ⁱⁱⁱ	0.86	2.03	2.889 (4)	174
N2–H2A ⁱ ···O3 ⁱⁱⁱ	0.86	2.09	2.943 (4)	174
N2–H2B ⁱ ···O1	0.86	2.21	2.990 (4)	150
N3–H3 ⁱ ···O1	0.86	2.35	3.058 (3)	139
N3–H3 ⁱ ···F1	0.86	2.54	3.185 (4)	133
N4–H4A ⁱ ···O5 ⁱⁱⁱ	0.89	2.09	2.803 (4)	137
N4–H4B ⁱ ···O1 ⁱ	0.89	2.07	2.899 (4)	154
N4–H4B ⁱ ···O2 ⁱ	0.89	2.41	3.102 (4)	135
N4–H4C ⁱ ···O2 ^{iv}	0.89	1.89	2.772 (4)	171

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

H atoms of the carboxylate and NH₃ groups were constrained to an ideal geometry (with O–H = 0.82 Å and N–H = 0.89 Å) but were allowed torsional freedom. All other H atoms were placed in ideal

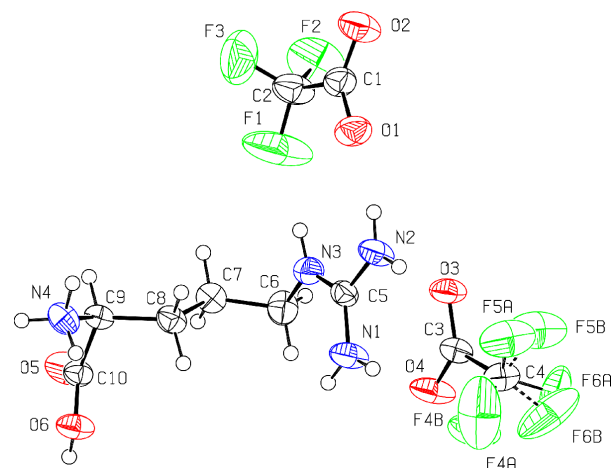


Figure 1

ORTEPII (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% level.

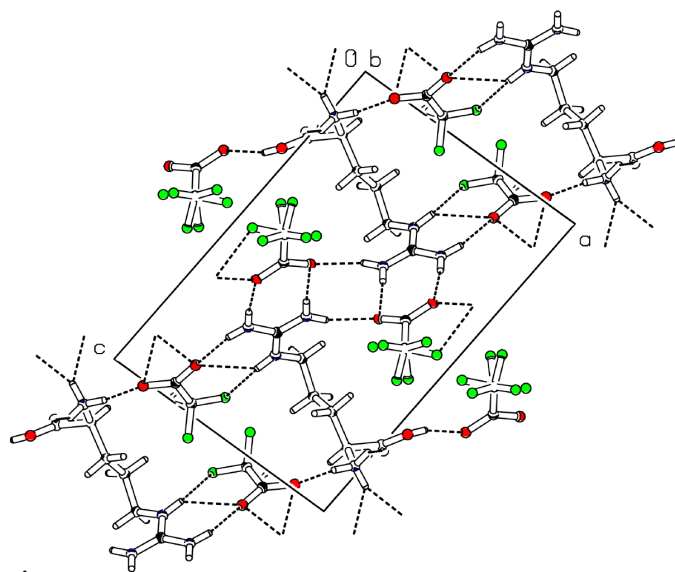


Figure 2

View of the unit-cell contents projected along b . Hydrogen bonds are shown as dashed lines.

ized positions and constrained to ride on their parent atoms, with N–H = 0.86 Å, and C–H = 0.97 or 0.98 Å [$U_{iso}(H) = 1.2$ times $U_{eq}(\text{parent atom})$]. In the disordered anion the C–F distances were restrained to be equal. Because of the lack of significant anomalous dispersion, at the Mo $K\alpha$ wavelength, the absolute configuration of the L-argininium cations was chosen to define the enantiomer and Friedel pairs were merged prior to refinement.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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