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L-Histidinium trichloroacetate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.109
Data-to-parameter ratio = 5.4

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

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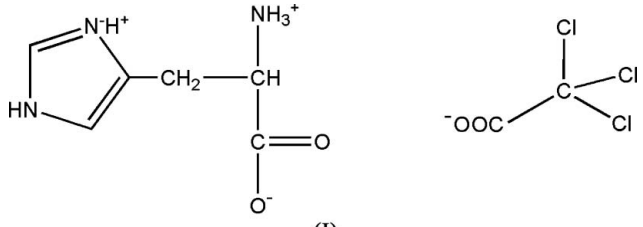
The title compound, $C_6H_{10}N_3O_2^+\cdot C_2Cl_3O_2^-$, crystallizes with two histidinium cations and two trichloroacetate anions in the asymmetric unit. The cations and anions are linked through a number of intermolecular N—H···O hydrogen bonds, forming a three-dimensional network.

Comment

The crystal structures of L-histidine (Madden *et al.*, 1972), L-histidinium trifluoroacetate (Gokul Raj *et al.*, 2006), L-histidinium dinitrate (Benali-Cherif *et al.*, 2002), L-histidine L-tartrate (Marchewka *et al.*, 2003), L-histidinium tertrafluorosuccinate (Akkurt *et al.*, 2004), L-histidine hydrochloride monohydrate (Fuess & Bartunik, 1976) and L-histidinium hemihydrochloride tartrate tartaric acid dihydrate (Rajagopal *et al.*, 2003) have been reported previously. The present work reports the crystal structure of L-histidinium trichloroacetate, (I), an analogue of L-histidinium trifluoroacetate.



(I)

Compound (I) crystallizes with two L-histidinium cations and two trichloroacetate anions in the asymmetric unit. The α-amino group of L-histidine is protonated and each cation exists in the zwitterionic form. The conformation angles of the L-histidinium cation can be described in two ways: χ^1 [C3—C4—C5—N3], [C11—C12—C13—N6] and χ^{21} [N2—C3—C4—C5], [N4—C11—C12—C13] or χ^{22} [C2—C3—C4—C5], [C10—C11—C12—C13] (IUPAC–IUB Commission on Biochemical Nomenclature, 1970). The χ^1, χ^{21} and χ^{22} values for (I) are [157.0 (3), 37.1 (6) and −148.7 (5)°] for the N1-cation and [159.7 (4), −76.8 (6) and 112.5 (6)°] for the N5-cation. The preferred values of χ^{21} are −90 and 90°, but the angle deviates from these ideal values by 37.1 (6) and 23.2 (5)°, due to the interaction of the imidazole ring with the anion.

The imidazole group of the L-histidinium cation is usually in the *gauche*-II conformation with respect to the amino N atom and *trans* with respect to the carboxylate group. However, in the case of the title compound, the conformation angles exhibit quite unusual values [C3—C4—C5—N3 = 157.0 (3)° and C3—C4—C5—C6 = −81.6 (5)°] and [C11—C12—C13—N6 = 159.7 (4)° and C11—C12—C13—C14 = −80.0 (5)°] for the two cations. The corresponding conformation angles for

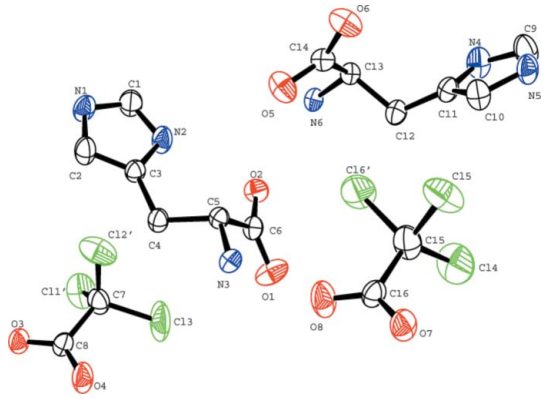


Figure 1
The asymmetric unit of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. For each anion, only one disorder component is shown.

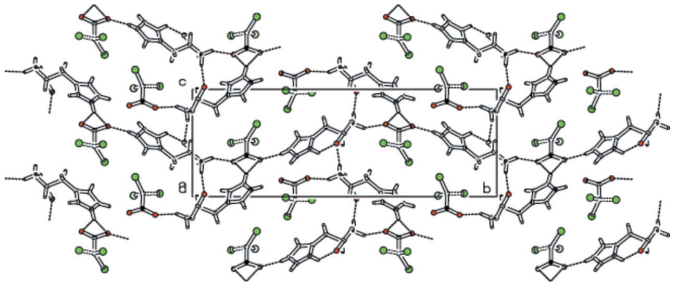


Figure 2
The crystal packing, viewed down the *a* axis. Dashed lines indicate hydrogen bonds. For each anion, only one disorder component is shown.

related compounds are: L-histidinium trifluoroacetate −68.5 (4)/170.3 (3) and −69.9 (4)/168.9 (3)°, bis-L-histidinium sulfate trihydrate −53.8 (7)/-173.8 (5) and −61.9 (7)/175.6 (6)°, L-histidinium hemihydrochloride tartrate tartaric acid dihydrate −61.5 (4) and 174.3 (3)°, DL-histidinium dinitrate −58.5 (4) and −178.8 (3)°.

The structure of the asymmetric unit of (I) is shown in Fig. 1. The bond lengths and angles are unexceptional. A three-dimensional network of N—H···O bonds links the cations and ions, thereby stabilizing the crystal packing (Fig. 2 and Table 1).

Experimental

Crystals of the title compound were grown from a mixture of L-histidine and trichloroacetic acid in a 1:1 molar ratio, by slow evaporation of an aqueous solution at room temperature.

Crystal data

$C_6H_{10}N_3O_2^+\cdot C_2Cl_3O_2^-$
M_r = 318.54
Monoclinic, $P2_1$
a = 5.4505 (18) Å
b = 25.769 (8) Å
c = 9.210 (2) Å
β = 99.98 (2)°
V = 1274.0 (7) Å^3
Z = 4
D_x = 1.661 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.73 mm^{-1}
T = 293 (2) K
Fragment cut from a needle, colourless
0.3 × 0.3 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.879, T_{max} = 0.999 (expected range = 0.760–0.864)
2539 measured reflections
2300 independent reflections
2155 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.0°
2 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.109
S = 1.06
2300 reflections
427 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 0.5935P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.080 (6)
Absolute structure: Flack (1983), 253 Friedel pairs
Flack parameter: 0.21 (11)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O1^{i}	0.89	1.94	2.815 (5)	169
N3—H3B···O8	0.89	1.93	2.681 (5)	141
N3—H3C···O6^{ii}	0.89	2.02	2.787 (5)	144
N6—H6A···O2	0.89	2.02	2.889 (5)	164
N6—H6B···O5^{iii}	0.89	1.96	2.839 (4)	170
N6—H6C···O4^{iv}	0.89	1.88	2.713 (5)	155
N1—H1···O7^{v}	0.85 (5)	1.85 (3)	2.671 (5)	161 (8)
N2—H2···O2	0.85 (4)	1.99 (3)	2.761 (5)	150 (5)
N4—H4···O6^{iii}	0.86 (6)	2.39 (8)	2.923 (6)	122 (8)
N5—H5···O3^{vi}	0.85 (3)	1.88 (1)	2.715 (5)	168 (5)

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

H atoms attached to imidazole-ring C atoms were located in a difference Fourier map. They were refined with a distance restraint of 0.92 (1) Å. The methylene and methine H atoms were positioned geometrically and refined as riding, with C—H = 0.97 and 0.98 Å, respectively, and with U_{iso}(H) = 1.2U_{eq}(C). H atoms attached to ring N atoms were located in a difference Fourier map and refined isotropically, with the N—H distance restrained to 0.85 (1) Å. Other N-bound H atoms were refined in the riding-model approximation (N—H = 0.89 Å); for those attached to N3, U_{iso}(H) = 1.2U_{eq}(N3), and for those attached to N6, the displacement parameters were refined isotropically. Each Cl atom is disordered over two positions; their site occupancies were constrained in such a way that the sum of the occupancies was 3 for each CCl_3 group. The Cl atoms have only moderate anomalous scattering, hence the low precision of the Flack (1983) parameter.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1988); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995) in *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993) in *WinGX*; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-32* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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