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Bis(L-histidinium sulfate) trihydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
Disorder in solvent or counterion
R factor = 0.052
wR factor = 0.147
Data-to-parameter ratio = 6.7

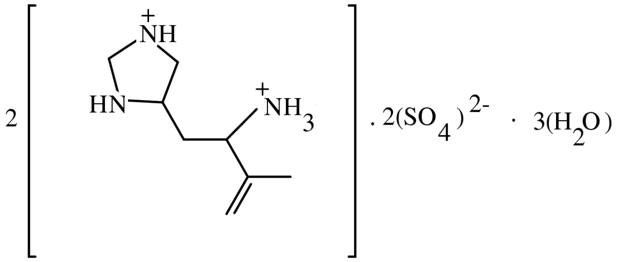
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $2C_6H_{11}N_3O_2^{2+}\cdot 2SO_4^{2-}\cdot 3H_2O$, both diprotonated histidinium cations are linked by strong hydrogen bonds by water molecules and normal hydrogen bonds by sulfate anions. The C^{γ} atom has a *gauche* II conformation with respect to the amino N atom and it is *trans* to the C' atom for both molecules. The imidazolinium rings are normal to the carbon skeletal plane, as expected.

Comment

The crystal structures of L-histidine (Madden *et al.*, 1972), L-histidine hydrochloride monohydrate (Fuess *et al.*, 1977), DL-histidine hydrochloride dihydrate (Bennett *et al.*, 1970), L-histidinium dinitrate (Asath Bahadur, 1992), DL-histidinium dinitrate (Asath Bahadur, 1992), DL-histidinium sulfamate (Asath Bahadur, 1992) and DL-histidine perchlorate (Asath Bahadur, 1992) have been reported earlier. In the present study, the crystal structure determination of bis(L-histidinium sulfate) trihydrate, (I), was undertaken.

The two crystallographically independent diprotonated histidinium molecules (*A* and *B*) have similar geometries. The histidinium molecule consists of two groups of nearly coplanar atoms. The chain has a straight conformation in molecules *A* and *B* which adopts the open form, as is present in L-histidine (Madden *et al.*, 1972) and DL-histidine hydrochloride (Bennett *et al.*, 1970). The conformation angles are such that χ^1 is in the *gauche* II conformation [−61.9 (7) and −53.8 (7)°] for both molecules having a closed conformation (Pratap *et al.*, 2000) (Table 1).



(I)

The sulfate anion links the amino N atom and the imidazolinium group of both molecules *A* and *B* and the water molecules through hydrogen bonds and stabilizes the structure (Table 2). The sulfate anion links the imidazolinium rings of both molecules, extending as a chain along the *a* axis (N12—H12*A*···O3^{i}, N13—H13···O1^{iv}, N22—H22*A*···O8$'^{v}$ and N22—H23···O6^{vii}). A three-centered (bifurcated) hydrogen

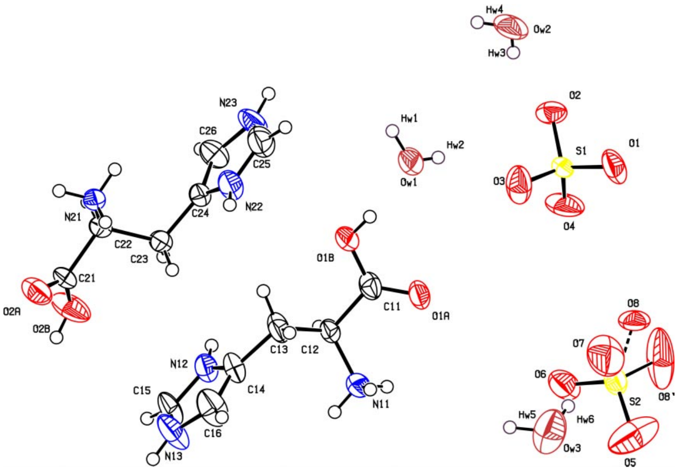


Figure 1
The molecular structures of the two independent cations showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

bond is observed in the case of the amino N atom of molecule *A* with sulfate O atoms (Jeffrey & Saenger, 1991). The water molecules O*W*1 and O*W*2, as acceptors, link the carboxyl O atom of both molecules through strong hydrogen bonds. Both crystallographically independent sulfate anions are linked to the three water molecules by hydrogen bonds. Molecules *A* and *B* are engaged in a straight (S1) head-to-tail sequence since the hydrogen bonds, *viz*. N11—H11*C*···O2*A*^{iii} and N21—H21*C*···O1*A*^{v}, connect the amino acids along the (101) plane (Vijayan, 1988), as a closed dimer (Jeffrey & Saenger, 1991).

Experimental

The title compound, (I), was crystallized from an aqueous solution of DL-histidine and sulfuric acid by slow evaporation.

Crystal data

$2C_6H_{11}N_3O_2^{2+}\cdot 2SO_4^{2-}\cdot 3H_2O$
$M_r = 280.26$
Triclinic, $P1$
$a = 8.3400\ (13)$ Å
$b = 8.9291\ (11)$ Å
$c = 10.724\ (2)$ Å
$\alpha = 102.576\ (13)°$
$\beta = 107.704\ (15)°$
$\gamma = 119.667\ (11)°$
$V = 592.03\ (16)$ Å^3
$Z = 2$
$D_x = 1.572$ Mg m^{-3}
$D_m = 1.568$ Mg m^{-3}
D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Cu *Kα* radiation
Cell parameters from 25 reflections
$\theta = 15.2–23.8°$
$\mu = 2.81$ mm^{-1}
$T = 293\ (2)$ K
Needle, colorless
0.50 × 0.30 × 0.15 mm

Data collection

Enraf–Nonius sealed-tube diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.418$, $T_{max} = 0.656$
2303 measured reflections
2303 independent reflections
2280 reflections with $I > 2\sigma(I)$
$\theta_{max} = 68.0°$
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 9$
$l = -12 \rightarrow 12$
25 standard reflections every 3 reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.148$
$S = 1.05$
2303 reflections
346 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1061P)^2 + 0.4470P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.014$
$\Delta\rho_{max} = 0.79$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.042 (4)
Absolute structure: Flack (1983)
Flack parameter = 0.03 (3)

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.218 (7)	O2*A*—C21	1.217 (7)
O1*B*—C11	1.286 (8)	O2*B*—C21	1.303 (7)
O1*A*—C11—C12—N11	11.9 (8)	O2*A*—C21—C22—N21	0.4 (8)
N11—C12—C13—C14	−61.9 (7)	N21—C22—C23—C24	−53.8 (7)
C11—C12—C13—C14	175.6 (6)	C21—C22—C23—C24	−173.8 (5)
C12—C13—C14—C16	118.4 (9)	C22—C23—C24—C26	−82.1 (8)
C12—C13—C14—N12	−64.2 (9)	C22—C23—C24—N22	97.2 (7)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1*B*···O*W*1	0.82	1.68	2.474 (6)	162
N11—H11*A*···O7^{i}	0.89	1.92	2.795 (8)	169
N11—H11*B*···O2^{ii}	0.89	2.23	3.046 (6)	153
N11—H11*B*···O4^{ii}	0.89	2.32	3.055 (8)	140
N11—H11*C*···O2*A*^{iii}	0.89	2.12	2.989 (6)	164
N12—H12*A*···O3^{i}	0.86	1.82	2.662 (7)	166
N13—H13···O1^{iv}	0.86	1.98	2.794 (8)	156
O2*B*—H2*B*···O*W*2^{iv}	0.82	1.67	2.485 (7)	172
N21—H21*A*···O4^{v}	0.89	1.86	2.714 (6)	161
N21—H21*B*···O6^{v}	0.89	1.89	2.767 (7)	170
N21—H21*C*···O1*A*^{v}	0.89	2.09	2.895 (6)	149
N22—H22*A*···O8^{v}	0.86	1.81	2.665 (11)	175
N22—H22*A*···O8′^{v}	0.86	1.95	2.713 (19)	148
N23—H23···O6^{vi}	0.86	2.05	2.821 (7)	150
O*W*1—H*W*1···O5^{vi}	0.88 (9)	1.87 (9)	2.629 (9)	144 (7)
O*W*1—H*W*2···O3	0.68 (8)	2.08 (8)	2.684 (8)	148 (8)
O*W*2—H*W*3···O2	0.65 (8)	2.09 (8)	2.666 (7)	149 (8)
O*W*2—H*W*4···O8^{vi}	0.82 (12)	1.79 (12)	2.588 (14)	162 (10)
O*W*3—H*W*5···O1^{ii}	0.98	1.80	2.775 (13)	180
O*W*3—H*W*6···O7	0.98	1.93	2.909 (15)	179

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

One of the O atoms (O8) of the sulfate anion is disordered and the site-occupation factors of O8 and O8′ are 0.74 (2) and 0.29 (2), respectively. The H atoms of the water molecules were located from difference Fourier maps and refined, leading to short O—H bonds, since the H atoms of the water molecules cannot be fixed by *HFIX* constraints, while all other H atoms were fixed by geometric constraints using *HFIX* and were allowed to ride on the carrier atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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