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L-Histidinium dinitrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.036
wR factor = 0.090
Data-to-parameter ratio = 7.4

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

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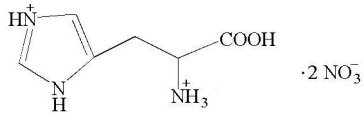
The title salt, L-$HisH_2^{2+}\cdot 2NO_3^-$, contains two nitrate anions and one L-histidinium dication. The anions and cations are linked to each other through strong hydrogen bonds, formed by all H atoms covalently bonded to the N and O atoms of the L-histidinium dications. This three-dimensional complex network of hydrogen bonds ensures the cohesion of the ionic structure.

Comment

The present work is part of a systematic investigation of interactions between amino acids and various phosphoric acids or nitric acid (Benali-Cherif, Cherouana *et al.*, 2002; Benali-Cherif, Abouimrane *et al.*, 2002; Benali-Cherif, Bendheif *et al.*, 2002). Organic–inorganic hybrid materials have received increasing attention during the past few decades (Mazeaud *et al.*, 2000; Soghomonian *et al.*, 1995; Mayer *et al.*, 1999). In addition of their great interest in the field of new materials chemistry (Siegel *et al.*, 1998; Baker *et al.*, 1992), and their electrical, magnetic and optical properties (Kagan *et al.*, 1999; Hill, 1998), hydrogen bonds of hybrid compounds are of interest because of their widespread biological occurrence; for example, hydrogen bonds between phosphate groups and histidine imidazolyl groups are involved in the active-site substrate-binding mechanism of ribonuclease (Richards *et al.*, 1972) and in the regulation of the oxygen affinity of deoxyhemoglobin by 2,3-diphosphoglycerate (Perutz *et al.*, 1972).



(I)

In the present study, the α-amino and imino groups of L-histidine are protonated, but the carboxylic acid group is not deprotonated. Imidazolyl N atoms of the iminium and amine groups are involved in the strongest hydrogen bonds and block the free rotation of this group, thus imposing a *trans* conformation on L-$HisH_2^{2+}$. Indeed, atoms N2 and N3 are involved in intramolecular [N2—H1N2···O7 2.767 (3) Å] and intermolecular [N3—H1N3···O6 2.836 (3) Å and N3—H1N3···O8 2.940 (3) Å] hydrogen bonds with nitrate anions. As found in crystals of L-$HisH^+\cdot H_2PO_4^-\cdot H_3PO_4$ (Blessing, 1986), the L-$HisH_2^{2+}$ cation in the title compound has a fully extended *trans* C1—C2—C3—C4 conformation; torsion angles around atom C2 show this clearly [N1—C2—C3—C4 −60.2 (3)° and O2—C1—C2—C3 111.7 (3)°]. This is in contrast to the bent *gauche* conformation in the structure of L-$HisH^+\cdot Cl^-\cdot H_2O$ (Donohue *et al.*, 1956; Donohue & Caron,

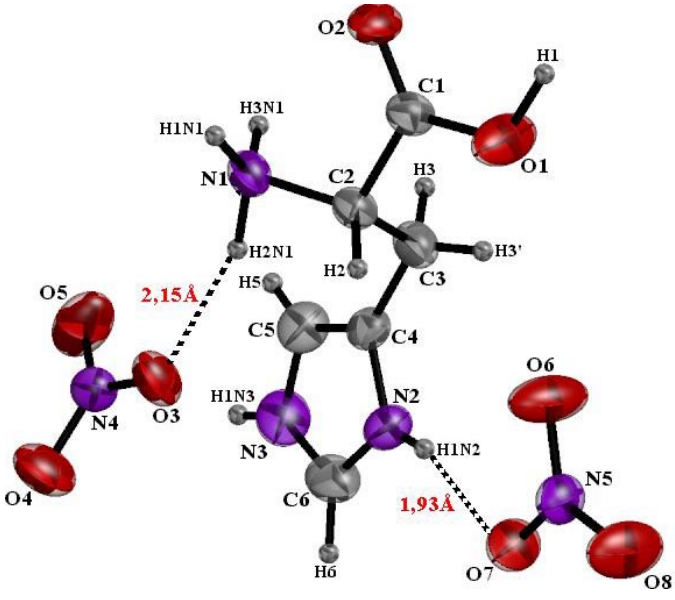


Figure 1
A *Raster3D* (Merritt & Bacon, 1997) view of the title compound, with the atomic labelling scheme, showing the *trans* conformation of L-$HisH_2^{2+}$. Displacement ellipsoids are drawn at the 50% probability level.

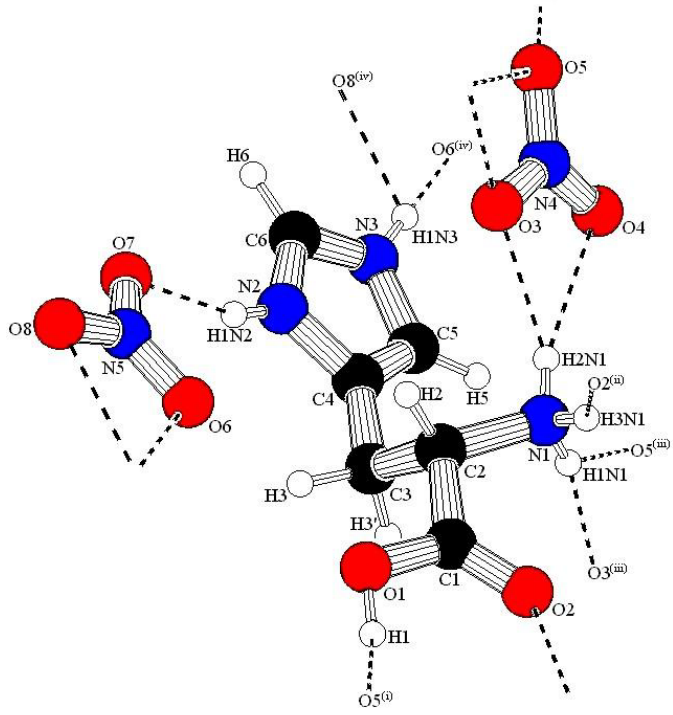


Figure 2
PLUTON (Spek, 1990) view of (I), showing the immediate hydrogen-bonded surroundings of the cation and anions.

1964; Hohlwein, 1977), but similar to the *trans* conformation observed in DL-$HisH^+\cdot Cl^-\cdot 2H_2O$ (Bennett *et al.*, 1970). In L-$HisH^+\cdot H_2PO_4^-\cdot H_3PO_4$ and L-$HisH^+\cdot Cl^-\cdot H_2O$, the C1—C2—C3—C4 conformation is also *trans*, but the imidazolyl group is rotated to accept an intramolecular hydrogen bond from the ammonium group to the imidazolyl atom N2. In our dication, L-$HisH_2^{2+}$, the imidazolylium orientation is fixed by strong hydrogen bonds and does not accept another intramolecular hydrogen bond from the ammonium group. The crystal structure contains N—H(ammonium)···O—N, N—H(ammonium)···O═C, N—H(iminium)···O—N, N—H(amine)···O—N and O—H···O—N hydrogen bonds. In this L-$HisH_2^{2+}\cdot 2NO_3^-$ structure there is one type of O—H donor and three types of N—H donors; the range of N···O distances is broad (2.767–3.171 Å) and the strongest hydrogen bonds are observed with carboxylic acid and iminium donors [2.621 (3) and 2.767 (3) Å].

Experimental

The title compound was prepared from a solution of 1 mmol L-histidine and 2 mmol nitric acid in 10 ml water. The product salt crystallized on slow evaporation of the solution and crystals of the resulting salt were thin colorless needles.

Crystal data

$C_6H_{11}N_3O_2^{2+}\cdot 2NO_3^-$
M_r = 281.20
Orthorhombic, $P2_12_12_1$
a = 5.4810 (2) Å
b = 8.2860 (5) Å
c = 25.5350 (1) Å
V = 1159.69 (8) Å^3
Z = 4
D_x = 1.611 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8658 reflections
θ = 1.6–26.4°
μ = 0.15 mm^{-1}
T = 293 K
Needle, colorless
0.4 × 0.2 × 0.1 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: none
8658 measured reflections
1286 independent reflections
1186 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 26.4°
$h = -6 \rightarrow 6$
$k = -9 \rightarrow 10$
$l = -28 \rightarrow 31$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.091
S = 1.09
1286 reflections
174 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.3591P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H3N1···O2^{i}	0.89	2.10	2.876 (3)	145
N1—H2N1···O3	0.89	2.15	2.900 (3)	142
N1—H2N1···O4	0.89	2.51	3.352 (4)	159
N1—H2N1···N4	0.89	2.67	3.541 (3)	166
N1—H1N1···O3^{ii}	0.89	2.08	2.957 (3)	170
N1—H1N1···O5^{ii}	0.89	2.52	3.171 (3)	131
N1—H1N1···N4^{ii}	0.89	2.65	3.495 (3)	159
N2—H1N2···O7	0.86	1.93	2.767 (3)	166
N2—H1N2···N5	0.86	2.66	3.499 (3)	167
N3—H1N3···O6^{iii}	0.86	1.98	2.836 (3)	176
N3—H1N3···O8^{iii}	0.86	2.36	2.940 (3)	125
N3—H1N3···N5^{iii}	0.86	2.49	3.287 (3)	154
O1—H1···O5^{iv}	0.82	1.84	2.621 (3)	158

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

All H atoms were placed at idealized positions and constrained with a riding model; a riding isotropic displacement parameter was used. Owing to the absence of atoms heavier than O, the Friedel opposites were merged. The absolute configuration was known from the starting L-histidine materials.

Data collection: *KappaCCD Reference Manual* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Raster3D* (Merritt & Bacon, 1997) and *PLUTON* (Spek, 1990); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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