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#### Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}—\text{C}) = 0.004\text{ Å}$   
 $R$  factor = 0.036  
 $wR$  factor = 0.090  
Data-to-parameter ratio = 7.4

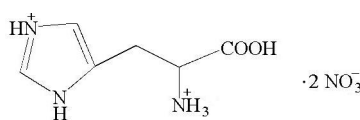
For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

## L-Histidinium dinitrate

The title salt,  $\text{L-HisH}_2^{2+} \cdot 2\text{NO}_3^-$ , 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 deoxy-hemoglobin by 2,3-diphosphoglycerate (Perutz *et al.*, 1972).



(I)

In the present study, the  $\alpha$ -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  $\text{L-HisH}_2^{2+}$ . Indeed, atoms N2 and N3 are involved in intramolecular  $[\text{N2}—\text{H1N2} \cdots \text{O7 } 2.767(3)\text{ Å}]$  and intermolecular  $[\text{N3}—\text{H1N3} \cdots \text{O6 } 2.836(3)\text{ Å}$  and  $\text{N3}—\text{H1N3} \cdots \text{O8 } 2.940(3)\text{ Å}]$  hydrogen bonds with nitrate anions. As found in crystals of  $\text{L-HisH}^+ \cdot \text{H}_2\text{PO}_4^- \cdot \text{H}_3\text{PO}_4$  (Blessing, 1986), the  $\text{L-HisH}_2^{2+}$  cation in the title compound has a fully extended *trans*  $\text{C1}—\text{C2}—\text{C3}—\text{C4}$  conformation; torsion angles around atom C2 show this clearly  $[\text{N1}—\text{C2}—\text{C3}—\text{C4} -60.2(3)^\circ$  and  $\text{O2}—\text{C1}—\text{C2}—\text{C3} 111.7(3)^\circ]$ . This is in contrast to the bent *gauche* conformation in the structure of  $\text{L-HisH}^+ \cdot \text{Cl}^- \cdot \text{H}_2\text{O}$  (Donohue *et al.*, 1956; Donohue & Caron,

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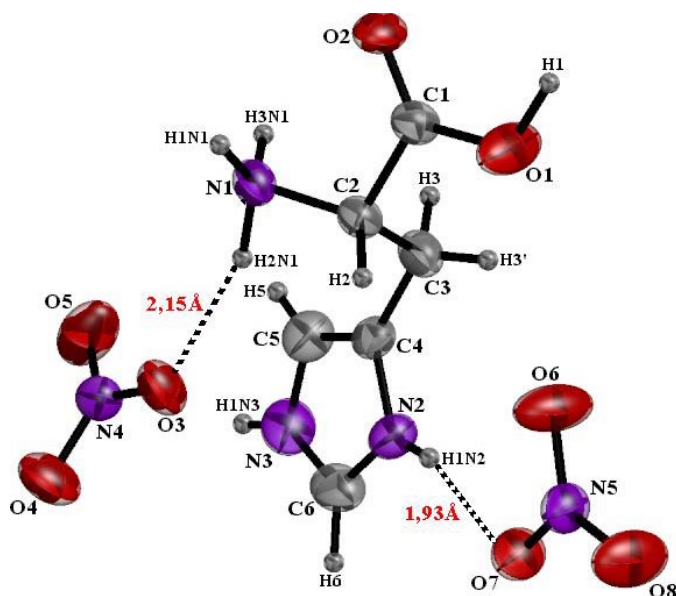


Figure 1

A Raster3D (Merritt & Bacon, 1997) view of the title compound, with the atomic labelling scheme, showing the *trans* conformation of L-HisH<sub>2</sub><sup>2+</sup>. Displacement ellipsoids are drawn at the 50% probability level.

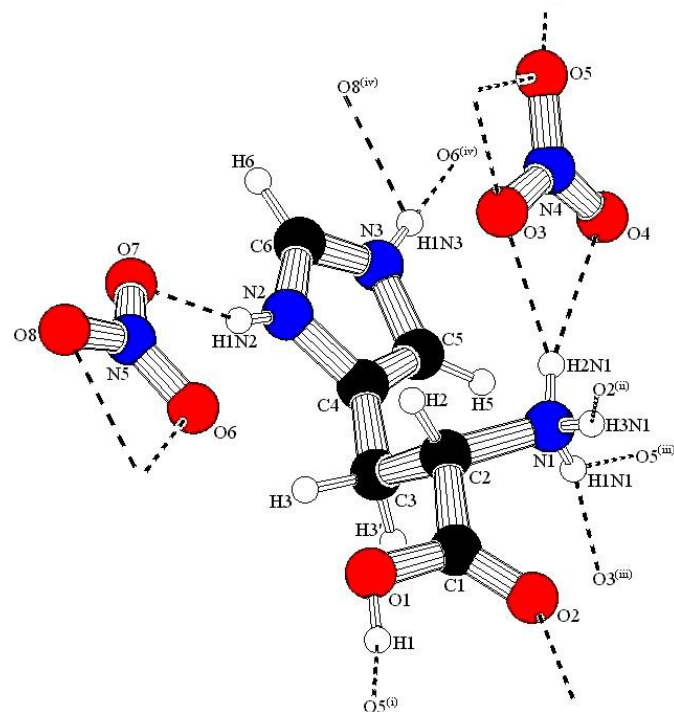
1964; Hohlwein, 1977), but similar to the *trans* conformation observed in DL-HisH<sup>+</sup>·Cl<sup>−</sup>·2H<sub>2</sub>O (Bennett *et al.*, 1970). In L-HisH<sup>+</sup>·H<sub>2</sub>PO<sub>4</sub><sup>−</sup>·H<sub>3</sub>PO<sub>4</sub> and L-HisH<sup>+</sup>·Cl<sup>−</sup>·H<sub>2</sub>O, the C1–C2–C3–C4 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<sub>2</sub><sup>2+</sup>, the imidazolylum 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<sub>2</sub><sup>2+</sup>·2NO<sub>3</sub><sup>−</sup> structure there is one type of O–H donor and three types 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 <sub>6</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> <sup>2+</sup> ·2NO <sub>3</sub> <sup>−</sup>	Mo Kα radiation
<i>M<sub>r</sub></i> = 281.20	Cell parameters from 8658 reflections
Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>θ</i> = 1.6–26.4°
<i>a</i> = 5.4810 (2) Å	<i>μ</i> = 0.15 mm <sup>−1</sup>
<i>b</i> = 8.2860 (5) Å	<i>T</i> = 293 K
<i>c</i> = 25.5350 (1) Å	Needle, colorless
<i>V</i> = 1159.69 (8) Å <sup>3</sup>	0.4 × 0.2 × 0.1 mm
<i>Z</i> = 4	
<i>D<sub>x</sub></i> = 1.611 Mg m <sup>−3</sup>	



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: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (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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## supporting information

*Acta Cryst.* (2002). E58, o822–o824 [https://doi.org/10.1107/S1600536802011625]

## L-Histidinium dinitrate

Nourredine Benali-Cherif, Lamia Benguedouar, Aouatef Cherouana, Lamia Bendjeddou and Hocine Merazig

(I)

*Crystal data*

$\text{C}_6\text{H}_{11}\text{N}_3\text{O}_2^{2+} \cdot 2\text{NO}_3^-$

$M_r = 281.20$

Orthorhombic,  $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.4810$  (2) Å

$b = 8.2860$  (5) Å

$c = 25.5350$  (1) Å

$V = 1159.69$  (8) Å<sup>3</sup>

$Z = 4$

$F(000) = 584.39$

$D_x = 1.611$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 8658 reflections

$\theta = 1.6$ – $26.4^\circ$

$\mu = 0.15$  mm<sup>-1</sup>

$T = 293$  K

Needle, colorless

$0.4 \times 0.2 \times 0.1$  mm

*Data collection*

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  scans

8658 measured reflections

1286 independent reflections

1186 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

$\theta_{\text{max}} = 26.4^\circ$ ,  $\theta_{\text{min}} = 1.6^\circ$

$h = -6 \rightarrow 6$

$k = -9 \rightarrow 10$

$l = -28 \rightarrow 31$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.091$

$S = 1.09$

1286 reflections

174 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 0.3591P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.16$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.14$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1369 (5)	0.2147 (3)	0.06582 (10)	0.0413 (6)
C2	0.2991 (5)	0.3515 (3)	0.08398 (9)	0.0367 (5)
H2	0.4687	0.3141	0.0847	0.044*
C3	0.2266 (5)	0.4075 (3)	0.13888 (9)	0.0441 (6)
H3	0.0568	0.4405	0.1383	0.053*
H3'	0.2403	0.3169	0.1627	0.053*
C4	0.3760 (5)	0.5431 (3)	0.15945 (8)	0.0371 (5)
C6	0.6786 (6)	0.6688 (3)	0.19920 (10)	0.0514 (7)
H6	0.8198	0.6887	0.2183	0.062*
C5	0.3488 (6)	0.7038 (3)	0.15433 (10)	0.0477 (6)
H5	0.2214	0.7556	0.1371	0.057*
N1	0.2764 (4)	0.4850 (2)	0.04518 (7)	0.0397 (5)
H3N1	0.3032	0.4467	0.0131	0.060*
H2N1	0.3856	0.5613	0.0524	0.060*
H1N1	0.1270	0.5267	0.0468	0.060*
N2	0.5858 (4)	0.5227 (3)	0.18842 (7)	0.0438 (5)
H1N2	0.6469	0.4317	0.1980	0.053*
N3	0.5389 (5)	0.7774 (3)	0.17855 (9)	0.0550 (7)
H1N3	0.5628	0.8799	0.1800	0.066*
N4	0.7818 (4)	0.7487 (3)	0.05698 (8)	0.0431 (5)
N5	0.7913 (5)	0.1268 (3)	0.20650 (9)	0.0509 (6)
O1	0.1698 (6)	0.0859 (2)	0.09366 (10)	0.0888 (10)
H1	0.0791	0.0141	0.0832	0.133*
O2	−0.0073 (4)	0.2273 (2)	0.03089 (7)	0.0536 (5)
O3	0.7709 (4)	0.5988 (2)	0.06161 (8)	0.0580 (5)
O4	0.5985 (5)	0.8287 (3)	0.04941 (9)	0.0765 (8)
O5	0.9865 (4)	0.8132 (3)	0.05967 (10)	0.0684 (7)
O6	0.6101 (5)	0.1164 (3)	0.17807 (11)	0.0849 (9)
O7	0.8534 (4)	0.2613 (2)	0.22367 (8)	0.0578 (6)
O8	0.9039 (5)	0.0055 (3)	0.21913 (11)	0.0886 (9)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0430 (14)	0.0341 (12)	0.0470 (12)	−0.0036 (10)	−0.0046 (11)	−0.0044 (10)
C2	0.0340 (13)	0.0324 (11)	0.0437 (12)	−0.0043 (10)	−0.0013 (10)	−0.0033 (9)
C3	0.0462 (16)	0.0465 (13)	0.0395 (12)	−0.0111 (12)	0.0014 (11)	−0.0018 (10)
C4	0.0417 (14)	0.0390 (12)	0.0307 (10)	−0.0006 (11)	−0.0012 (10)	−0.0028 (9)
C6	0.0537 (17)	0.0581 (16)	0.0424 (13)	−0.0099 (14)	−0.0068 (12)	−0.0133 (12)
C5	0.0569 (17)	0.0395 (13)	0.0467 (13)	0.0019 (12)	−0.0051 (12)	−0.0039 (11)

N1	0.0430 (13)	0.0371 (10)	0.0389 (9)	−0.0071 (9)	0.0031 (8)	−0.0042 (8)
N2	0.0481 (13)	0.0445 (11)	0.0389 (10)	0.0034 (10)	−0.0046 (9)	0.0001 (8)
N3	0.0727 (18)	0.0383 (11)	0.0541 (13)	−0.0055 (12)	−0.0039 (13)	−0.0101 (10)
N4	0.0403 (13)	0.0460 (11)	0.0429 (10)	−0.0016 (10)	−0.0001 (9)	0.0014 (9)
N5	0.0614 (16)	0.0371 (11)	0.0542 (12)	−0.0025 (11)	−0.0097 (12)	0.0032 (10)
O1	0.120 (2)	0.0402 (11)	0.1058 (18)	−0.0276 (13)	−0.0673 (18)	0.0180 (11)
O2	0.0605 (13)	0.0431 (10)	0.0573 (10)	−0.0117 (10)	−0.0231 (10)	−0.0006 (8)
O3	0.0515 (13)	0.0424 (10)	0.0802 (13)	−0.0109 (9)	0.0032 (11)	0.0076 (10)
O4	0.0617 (16)	0.0956 (18)	0.0724 (14)	0.0309 (15)	0.0023 (11)	0.0190 (13)
O5	0.0569 (14)	0.0527 (11)	0.0956 (17)	−0.0201 (11)	−0.0097 (13)	−0.0077 (12)
O6	0.088 (2)	0.0532 (12)	0.1138 (19)	0.0048 (13)	−0.0577 (17)	−0.0092 (13)
O7	0.0743 (15)	0.0362 (9)	0.0627 (11)	−0.0078 (10)	−0.0138 (11)	−0.0017 (8)
O8	0.101 (2)	0.0389 (11)	0.126 (2)	0.0063 (13)	−0.0512 (18)	0.0048 (12)

*Geometric parameters (Å, °)*

C1—O2	1.196 (3)	C6—N2	1.342 (3)
C1—O1	1.295 (3)	C5—N3	1.356 (4)
C1—C2	1.513 (3)	N4—O4	1.219 (3)
C2—N1	1.490 (3)	N4—O5	1.244 (3)
C2—C3	1.529 (3)	N4—O3	1.249 (3)
C3—C4	1.486 (3)	N5—O8	1.223 (3)
C4—C5	1.346 (3)	N5—O6	1.233 (3)
C4—N2	1.378 (3)	N5—O7	1.245 (3)
C6—N3	1.294 (4)		
O2—C1—O1	125.0 (2)	N3—C6—N2	108.6 (2)
O2—C1—C2	123.4 (2)	C4—C5—N3	108.4 (3)
O1—C1—C2	111.5 (2)	C6—N2—C4	108.4 (2)
N1—C2—C1	107.67 (18)	C6—N3—C5	109.1 (2)
N1—C2—C3	111.25 (19)	O4—N4—O5	121.2 (2)
C1—C2—C3	110.8 (2)	O4—N4—O3	121.1 (3)
C4—C3—C2	114.2 (2)	O5—N4—O3	117.7 (2)
C5—C4—N2	105.4 (2)	O8—N5—O6	120.3 (2)
C5—C4—C3	130.7 (3)	O8—N5—O7	120.3 (2)
N2—C4—C3	123.8 (2)	O6—N5—O7	119.3 (2)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H3N1 $\cdots$ O2 <sup>i</sup>	0.89	2.10	2.876 (3)	145
N1—H2N1 $\cdots$ O3	0.89	2.15	2.900 (3)	142
N1—H2N1 $\cdots$ O4	0.89	2.51	3.352 (4)	159
N1—H2N1 $\cdots$ N4	0.89	2.67	3.541 (3)	166
N1—H1N1 $\cdots$ O3 <sup>ii</sup>	0.89	2.08	2.957 (3)	170
N1—H1N1 $\cdots$ O5 <sup>ii</sup>	0.89	2.52	3.171 (3)	131
N1—H1N1 $\cdots$ N4 <sup>ii</sup>	0.89	2.65	3.495 (3)	159
N2—H1N2 $\cdots$ O7	0.86	1.93	2.767 (3)	166

N2—H1N2...N5	0.86	2.66	3.499 (3)	167
N3—H1N3...O6 <sup>iii</sup>	0.86	1.98	2.836 (3)	176
N3—H1N3...O8 <sup>iii</sup>	0.86	2.36	2.940 (3)	125
N3—H1N3...N5 <sup>iii</sup>	0.86	2.49	3.287 (3)	154
O1—H1...O5 <sup>iv</sup>	0.82	1.84	2.621 (3)	158

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