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L-Lysine L-lysinium dichloride nitrate

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Key indicators

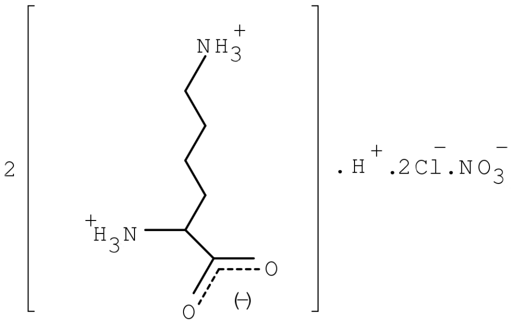
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
Disorder in solvent or counterion
R factor = 0.062
wR factor = 0.190
Data-to-parameter ratio = 10.8

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

In the title compound, $2C_6H_{15}N_2O_2^+ \cdot H^+ \cdot NO_3^- \cdot 2Cl^-$, both the monoprotonated lysinium molecules are bonded through a strong, nearly symmetric, O—H···O hydrogen bond forming a dimer. The O···O distance is 2.425 (8) Å. Molecule I is engaged in a zigzag (Z1) head-to-tail sequence. Both chloride anions link molecules I and II through the α- and ε-amino groups in an infinite chain along the a axis. The nitrate ion shows orientational disorder.

Comment

Lysine is the one of the four amino acids having basic side chains. The crystal structure of L-lysine monohydrochloride dihydrate (Wright & Marsh, 1962; Koetzle *et al.*, 1972), L-lysine sulfate (Capasso *et al.*, 1983), L-lysine semimaleate (Pratap *et al.*, 2000) and hydrogen bis[L-lysinium(+)] dichloride perchlorate (Srinivasan *et al.*, 2001) have been reported. The crystal structure of lysine hydrochloride reacted with nitric acid, (I), was undertaken to study the effects of hydrogen bonding due to the presence of inorganic acids.



(I)

A pseudo-non-crystallographic twofold axis is observed near ($\frac{1}{4}$, y, 0.41) for both the chloride anions and lysinium cations (Fig. 1). The N atom of the nitrate group lies on this pseudo-twofold axis. The existence of pseudosymmetry is responsible for two possible orientation of the nitrate O atom and hence the large deviation from the nearly trigonal symmetry.

The asymmetric unit contains two crystallographically independent lysinium residues (I and II). The lysinium cations are characterized by two planar configurations, *viz*. the carboxylate group and the aliphatic side chain terminating at the ε-amino group. The straight chain conformation angle ψ^1 is −6.1 (8) and −0.1 (9)° for lysinium residues I and II, respectively. This tendency of twisting of the C—N bond is found in various amino acids (Lakshminarayan *et al.*, 1967).

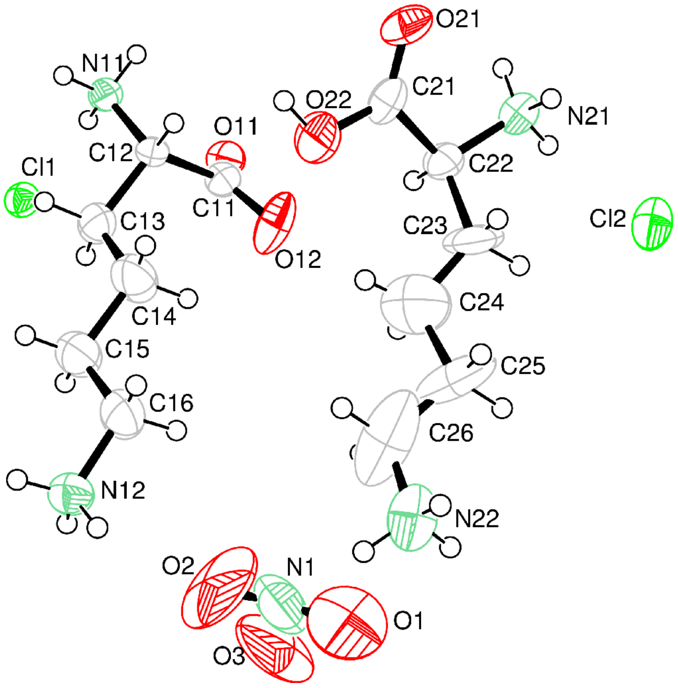


Figure 1
The molecular structure of (I) with the atom-numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

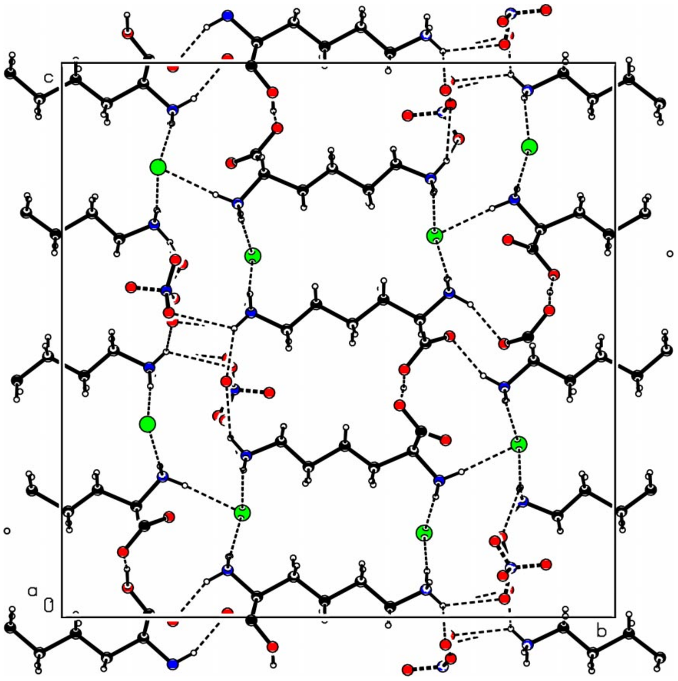


Figure 2
Packing diagram of (I) viewed down the *a* axis.

The average value of the four C—C—C angles for both molecules I and II are 112.4 (6) and 113.3 (11)°, significantly greater than the tetrahedral value. However, the angles C^{α} —C^{β} —C^{γ}, 113.1 (6) and 120.5 (11)° for the molecules I and II, are appreciably larger than the other three. The widening of this angle might be due to the steric effect of an atom hydrogen bonded to the NH_3^+ group, also found in other amino acids and peptides (Leung & Marsh, 1958). Molecules I and II have a fully extended side-chain conformation [$\chi^1 = -167.4$ (9) and -168.7 (15)°, $\chi^2 = -178.3$ (9) and -174.6 (12)°, $\chi^3 = 175.1$ (11) and 174.1 (17)°, and $\chi^4 = -178.0$ (9) and 174.3 (14)°, respectively].

Both the lysinium molecules (I and II) are cationic, with ε-amino groups accepting an H atom. The two lysinium molecules are bonded with a strong O—H···O hydrogen bond [O22···O12 2.425 (8) Å]. The equality of the C—O distances of molecules I and II within significant limits [1.223 (7) and 1.217 (9) Å, and 1.267 (8) and 1.274 (9) Å] suggests that the hydrogen linking I and II is equally shared by I and II. Hence, this hydrogen bond may be termed a symmetric hydrogen bond, since the two cations are related by non-crystallographic pseudo-twofold symmetry and the H atom is on the pseudo-axis. The O12—H2 and O22—H2 distances [1.06 (11) and 1.38 (11) Å] are nearly equal within significant limits. Hence, the symmetric hydrogen-bonded lysinium dimer thus formed carries a net positive charge, as found in L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997).

A zigzag (*Z*1) head-to-tail sequence is present in molecule I, since the N11—H11*A*···O11($\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$) bond connects two 2_1-related amino acids (Vijayan, 1988). But in the case of lysinium molecule II, the α-amino group has hydrogen bonds with chloride anions only. The chloride anion (Cl1) links the α-amino nitrogen of lysinium molecule I through a hydrogen bond in an infinite chain running along the *a* axis and chloride anion Cl2 links the ε-amino nitrogen in an infinite chain along the *a* axis. Similarly, in lysinium molecule II, the α-N atom is linked by chloride anion Cl2 through a hydrogen bond in an infinite chain along the *a* axis and the ε-amino nitrogen is linked by chloride anion Cl1 in an infinite chain along the *a* axis. Besides this, the nitrate anion links the ε-amino N atoms of both molecules I and II.

As shown in Fig. 2, the two hydrophilic layers about the $y = \frac{1}{4}$ plane are connected by hydrogen bonds involving nitrate and chloride anions. The aggregation of the hydrophilic double layers is interspersed by the hydrophobic side chain across the $y = \frac{1}{2}$ plane.

Experimental

The title compound was crystallized from an aqueous solution of a 2:1 stoichiometric ratio of L-lysine hydrochloride and nitric acid by slow evaporation.

Crystal data

$2C_6H_{15}N_2O_2^+ \cdot H^+ \cdot NO_3^- \cdot 2Cl^-$
$M_r = 428.32$
Orthorhombic, $P2_12_12_1$
$a = 4.9846$ (2) Å
$b = 20.604$ (2) Å
$c = 20.663$ (2) Å
$V = 2122.1$ (3) Å^3
$Z = 4$
$D_x = 1.341$ Mg m^{-3}
$D_m = 1.333$ Mg m^{-3}

D_m measured by flotation
Mo *Kα* radiation
Cell parameters from 20 reflections
$\theta = 10.2$–14.3°
$\mu = 0.35$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.5 × 0.3 × 0.3 mm

Acta Cryst. (2001). E**57**, o888–o890 N. Srinivasan *et al.* • $2C_6H_{15}N_2O_2^+ \cdot H^+ \cdot NO_3^- \cdot 2Cl^-$ **o889**

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.883$, $T_{\max} = 0.901$
3313 measured reflections
2910 independent reflections
1805 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.046$
$\theta_{\max} = 25.0°$
$h = -1 \rightarrow 5$
$k = -2 \rightarrow 24$
$l = -2 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.190$
$S = 1.03$
2910 reflections
270 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0869P)^2 + 3.2345P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}
Absolute structure: Flack (1983), 714 Friedel pairs
Flack parameter = 0.2 (2)

Table 1
Selected geometric parameters (Å, °).

O11—C11	1.223 (7)	O21—C21	1.217 (9)
O12—C11	1.267 (8)	O22—C21	1.274 (9)
O11—C11—C12—N11	−6.1 (8)	O21—C21—C22—N21	−0.1 (9)
N11—C12—C13—C14	−167.4 (9)	N21—C22—C23—C24	−168.7 (15)
C12—C13—C14—C15	−178.3 (9)	C22—C23—C24—C25	−174.6 (12)
C13—C14—C15—C16	175.1 (11)	C23—C24—C25—C26	174.1 (17)
C14—C15—C16—N12	−178.0 (9)	C24—C25—C26—N22	174.3 (14)

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

D—H···A	D—H	H···A	D···A	D—H···A
O22—H2···O12$^{\rm i}$	1.06 (11)	1.38 (11)	2.425 (8)	169 (9)
N11—H11*A*···O11$^{\rm ii}$	0.89	1.98	2.821 (7)	157
N11—H11*B*···Cl1$^{\rm i}$	0.89	2.40	3.283 (6)	171
N11—H11*C*···Cl1	0.89	2.49	3.367 (6)	168
N12—H12*A*···Cl2$^{\rm iii}$	0.89	2.37	3.237 (7)	164
N12—H12*B*···O3$^{\rm i}$	0.89	2.24	2.994 (18)	142
N12—H12*B*···O2$'^{\rm iv}$	0.89	2.32	2.945 (14)	127
N12—H12*B*···O2$'^{\rm i}$	0.89	2.52	3.124 (14)	125
N12—H12*B*···O2$^{\rm iv}$	0.89	2.56	3.16 (3)	125
N12—H12*C*···Cl2$^{\rm v}$	0.89	2.51	3.298 (7)	149
N21—H21*A*···Cl1$^{\rm ii}$	0.89	2.38	3.260 (5)	172
N21—H21*B*···Cl2	0.89	2.36	3.221 (6)	163
N21—H21*C*···Cl2$^{\rm i}$	0.89	2.33	3.215 (6)	173
N22—H22*A*···Cl1$^{\rm vi}$	0.89	2.40	3.268 (8)	166
N22—H22*B*···O3$^{\rm i}$	0.89	2.42	3.12 (3)	136
N22—H22*B*···O1$^{\rm i}$	0.89	2.71	3.08 (3)	106
N22—H22*C*···Cl1$^{\rm vii}$	0.89	2.42	3.302 (8)	173

Symmetry codes: (i) $1+x, y, z$; (ii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$; (iii) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (v) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (vi) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (vii) $\frac{3}{2}-x, 1-y, z-\frac{1}{2}$.

The nitrate O atoms are disordered due to the presence of pseudo-twofold symmetry. The site-occupation factors for O1/O2/O3 and O1′/O2′/O3′ are 0.54 (1) and 0.46 (1). Since the geometry of these disordered atoms differ significantly from expected values, the *DFIX* constraint was used to fix the geometry of the nitrate anion as a free variable. In the case of lysinium molecule II, atoms C23, C24, C25 and C26 showed large displacement amplitudes with unusual C—C distances, indicating disorder. Since this disorder cannot be explained satisfactorily, these atoms were refined using *DFIX* constraints. The H2 atom involved in the symmetric hydrogen bond was located and refined while all the other H atoms were fixed by geometric constraints using *HFIX* and were allowed to ride on the attached 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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o890 N. Srinivasan *et al.* • $2C_6H_{15}N_2O_2^+ \cdot H^+ \cdot NO_3^- \cdot 2Cl^-$ *Acta Cryst.* (2001). E**57**, o888–o890