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Bis(L-ornithinium) chloride nitrate sulfate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.039
wR factor = 0.098
Data-to-parameter ratio = 9.7

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

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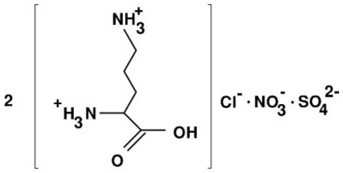
In the title compound, $2C_5H_{14}N_2O_2^{2+}\cdot Cl^-\cdot NO_3^-\cdot SO_4^{2-}$, the three anions all sit on twofold axes. The plane of the ammonioalkyl chain forms a dihedral angle of 87.8 (2)° with the carboxyl plane. In the crystal structure, the ornithine residue is linked to the sulfate anion *via* a strong O—H···O hydrogen bond and the structure is further stabilized by N—H···Cl and N—H···O hydrogen bonds.

Comment

Ornithine, a non-essential amino acid, is abundant in protein foods. It stimulates the growth hormone. The crystal structures of L-ornithine hydrochloride (Chiba *et al.*, 1967) and L-ornithine nitrate (Ramaswamy *et al.*, 2002) have been reported in the literature. In the present work, the structure of bis(L-ornithinium) chloride nitrate sulfate, (I), a reaction product of L-ornithine hydrochloride with nitric acid and sulfuric acid, is reported.



(I)

The asymmetric unit of (I) contains one ornithinium cation, and one-half each of a chloride anion, a nitrate anion and a sulfate anion (Fig. 1). All three anions sit on twofold axes. The bond distances and angles of the nitrate and sulfate anions show nearly ideal trigonal and tetrahedral symmetry, respec-

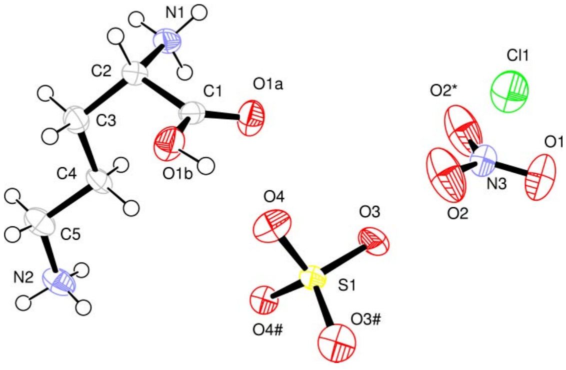


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976). Atoms denoted with a hash (#) are at symmetry postions (1 − *x*, *y*, −*z*) and those denoted with an asterisk (*) are at (2 − *x*, *y*, 1 − *z*).

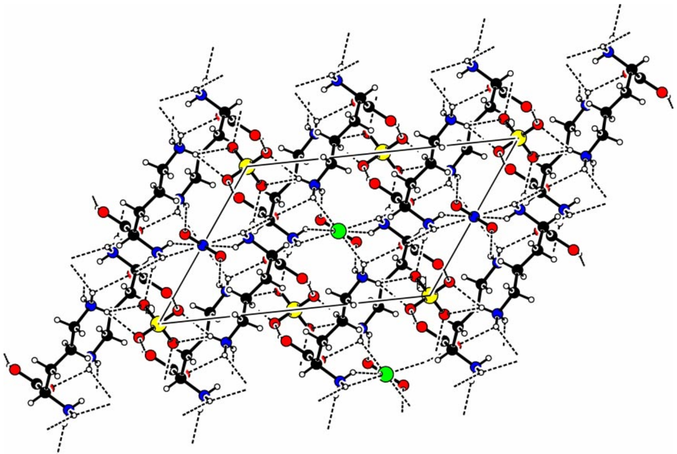


Figure 2
The packing of the ions in the unit cell, viewed down the *b* axis.

tively. The inequality of C—O distances, and of O—C—O and C—C—O angles, clearly indicates the presence of a carboxylic acid group in the ornithine residue. The α-amino N atom deviates from the carboxyl plane by 0.12 (1) Å. This tendency for the C—N bond to twist is found in various amino acids (Lakshiminarayanan *et al.*, 1967). The backbone conformation angle ψ^1 shows a *cis* form. The side-chain conformation angle χ^1 corresponds to *gauche* II, whereas χ^2 and χ^3 shows a *trans* conformation. The plane of the ammonioalkyl chain forms a dihedral angle of 87.8 (2)° with the carboxyl plane.

In the asymmetric unit, the ornithinium cation is linked to the sulfate anion *via* a strong O—H···O hydrogen bond. Both α-amino atom N1 and δ-amino atom N2 form N—H···Cl and N—H···O hydrogen bonds with the symmetry-related O atoms of both nitrate and sulfate anions. Interestingly, δ-amino atom N2 is involved in a three-centered hydrogen bond with sulfate O atoms. A class I hydrogen-bond pattern having three two-centered hydrogen bonds is observed at the α-amino N atom. In the case of the δ-amino N atom, a class II hydrogen-bond pattern involving two two-centered hydrogen bonds and one three-centered hydrogen bond is present. Sulfate atom O3 links both amino atoms N1 and N2 to form an infinite chain [N1—H1C···O3($\frac{3}{2}-x$, $y-\frac{1}{2}$, $1-z$)···N2—H2*B*···O3($\frac{3}{2}-x$, $y-\frac{1}{2}$, $-z$)] along the *c* axis.

Experimental

Equimolar amounts of L-ornithine hydrochloride, nitric acid and sulfuric acid were mixed, and crystals of the title compound were obtained by slow evaporation under natural conditions.

Crystal data

$2C_5H_{14}N_2O_2^{2+}\cdot Cl^-\cdot NO_3^-\cdot SO_4^{2-}$
$M_r = 461.88$
Monoclinic, *C*2
$a = 13.872\ (5)$ Å
$b = 9.578\ (6)$ Å
$c = 9.178\ (1)$ Å
$\beta = 125.350\ (14)°$
$V = 994.6\ (7)$ Å^3
$Z = 2$
$D_x = 1.542$ Mg m^{-3}
$D_m = 1.540$ Mg m^{-3}

D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.2$–$14.3°$
$\mu = 0.36$ mm^{-1}
$T = 293\ (2)$ K
Block, colorless
0.30 × 0.20 × 0.15 mm

Data collection

Nonius MACH3 sealed-tube diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.856$, $T_{\max} = 0.947$
1524 measured reflections
1288 independent reflections
1125 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.021$
$\theta_{\max} = 26.9°$
$h = -17 \rightarrow 15$
$k = -1 \rightarrow 12$
$l = -1 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.098$
$S = 1.19$
1288 reflections
133 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 1.3881P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}
Absolute structure: Flack (1983); 214 Friedel pairs
Flack parameter = 0.01 (13)

Table 1
Selected geometric parameters (Å, °).

O1*A*—C1	1.204 (5)	N3—O2	1.227 (5)
O1*B*—C1	1.325 (5)	S1—O3	1.471 (3)
N3—O1	1.219 (8)	S1—O4	1.475 (3)
O1*A*—C1—O1*B*	123.9 (4)	O1*B*—C1—C2	112.1 (3)
O1*A*—C1—C2	124.0 (3)		
O1*A*—C1—C2—N1	5.3 (5)	C2—C3—C4—C5	−177.8 (3)
N1—C2—C3—C4	−66.7 (4)	C3—C4—C5—N2	173.2 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1···O4	0.88 (6)	1.71 (6)	2.569 (5)	166 (5)
N1—H1*D*···Cl1$^{\rm i}$	0.89	2.39	3.154 (4)	144
N1—H1*B*···O1$^{\rm ii}$	0.89	2.34	2.912 (5)	123
N1—H1*C*···O3$^{\rm iii}$	0.89	2.02	2.788 (4)	144
N2—H2*A*···Cl1$^{\rm iv}$	0.89	2.40	3.152 (4)	142
N2—H2*B*···O4$^{\rm i}$	0.89	2.15	2.951 (5)	150
N2—H2*B*···O3$^{\rm v}$	0.89	2.27	3.036 (5)	145
N2—H2*C*···O2$^{\rm v}$	0.89	2.05	2.838 (6)	147

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

Atom H1 of the carboxyl group was located in a difference Fourier synthesis and its parameters were refined [O—H = 0.88 (6) Å]. All other H atoms were placed in geometrically calculated positions [N—H = 0.89 Å and C—H = 0.97–0.98 Å] and included in the refinement in a riding-model approximation, with $U_{\rm iso}$ values equal to $1.5U_{\rm eq}$ of the carrier atom. Intensities for 214 Friedels pairs were measured.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); 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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