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Tri(L-isoleucinium) sulfate bisulfate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
R factor = 0.047
wR factor = 0.125
Data-to-parameter ratio = 11.1

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 compound, $3C_6H_{14}NO_2^+\cdot HSO_4^-\cdot SO_4^{2-}$, comprises three cationic isoleucinium molecules, and sulfate and bisulfate anions (1:1). The molecules are held together by strong N—H···O and O—H···O hydrogen bonds.

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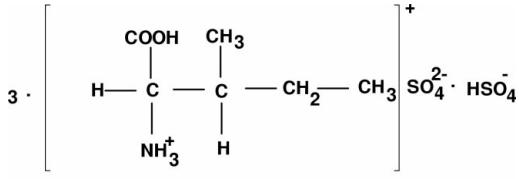
Comment

Isoleucine is one of the essential constituents of proteins. The crystal structures of L-isoleucine (Torii & Iitaka, 1971), D-(–)-isoleucine (Trommel & Bijvoet, 1954), and D-alloisoleucine hydrochloride monohydrate (Varughese & Srinivasan, 1976) are available in the literature. In the present study, the structure of isoleucine recrystallized from sulfuric acid (I) was investigated.



(I)

The crystal structures of amino acids and their complexes have provided a wealth of interesting information pertaining to the patterns of their aggregation, and the effect of other molecules and ions on their interaction and molecular properties (Vijayan, 1988; Prasad & Vijayan, 1993). The structure analysis (Fig. 1 and Table 1) of the present structure has been carried out as a contribution to this body of information.

In the crystallization process, one of the sulfuric acid molecules has donated both protons to isoleucine molecules and thereby exists as a sulfate anion in the structure. The other sulfuric acid molecule has donated one of its H atoms to an isoleucine molecule and exists as bisulfate anion in the solid state. The bond distance of 1.537 (5) Å between S1 and O2 confirms the presence of the H atom in the bisulfate. This H atom links both the sulfate groups through a short hydrogen bond [O2···O6 is 2.502 (7) Å].

The geometries of the three crystallographically independent isoleucinium ions are similar. The arrangement of the γ and γ' atoms about the C^{α}–C^{β} bond are found to be *gauche* I in molecule (I) and *gauche* II in molecules (II) and (III) (Torii & Iitaka, 1971). The C^{δ} atom is *trans* to C^{α} in the molecules (I) & (III), whereas in molecule (II) this atom is *trans* to $C^{\gamma'}$ (Lakshiminarayanan *et al.* (1967).

The carboxyl and the amino group of the isoleucinium molecules and the O atoms of the sulfate anions are involved in hydrogen bonding (see Table 2). In isoleucinium molecule

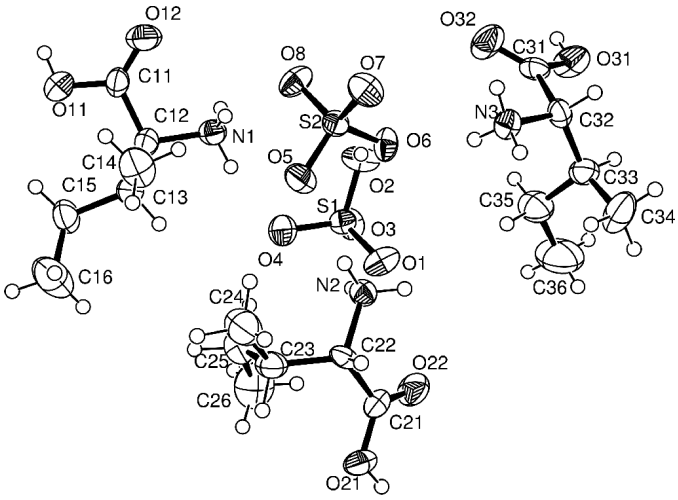


Figure 1
The molecular structures of the three independent isoleucinium cations and the two anions, showing the atomic numbering scheme and 50% probability displacement ellipsoids. (Johnson, 1976)

(III), the amino group links with the symmetry-related carboxyl group of the same molecule through a zigzag head-to-tail *Z*2 sequence (Vijayan, 1988). The sulfate-bound O atoms O1, O7 and O8, as acceptors, link the isoleucinium molecules (I), (II) & (III) through rather strong hydrogen bonds (Table 2) with a three-dimensional network of hydrogen bonding. A chelated three-centre hydrogen bond is present in isoleucinium molecule (III) (Jeffrey & Saenger, 1991).

Experimental

The title compound was crystallized in aqueous solution from a 3:2 stoichiometric ratio of L-isoleucine and sulfuric acid. Colorless, needle-shaped crystals elongated along the *b* axis were formed.

Crystal data

$3C_6H_{14}NO_2^+\cdot HSO_4^-\cdot SO_4^{2-}$
M_r = 589.67
Orthorhombic, $P2_12_12_1$
a = 6.743 (5) Å
b = 19.418 (5) Å
c = 22.095 (5) Å
V = 2893 (2) Å^3
Z = 4
D_x = 1.354 Mg m^{-3}
D_m = 1.35 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
θ = 9.9–14.1°
μ = 0.25 mm^{-1}
T = 293 (2) K
Needles, colorless
0.33 × 0.13 × 0.10 mm

Data collection

Enraf–Nonius sealed tube diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.945, T_{max} = 0.970
4192 measured reflections
3764 independent reflections
1902 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 25.0°
$h = -1 \rightarrow 8$
$k = -2 \rightarrow 23$
$l = -2 \rightarrow 26$
3 standard reflections every 60 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.125
S = 0.99
3764 reflections
339 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Absolute structure: (Flack, 1983)
Flack parameter = −0.15 (15)

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.537 (5)	O22—C21	1.190 (8)
O11—C11	1.316 (7)	O31—C31	1.303 (7)
O12—C11	1.191 (7)	O32—C31	1.203 (8)
O21—C21	1.330 (8)		
N1—C12—C13—C15	−162.5 (5)	C24—C23—C25—C26	−171.1 (7)
N1—C12—C13—C14	71.7 (7)	C22—C23—C25—C26	63.7 (10)
C12—C13—C15—C16	164.5 (7)	N3—C32—C33—C35	59.7 (9)
C14—C13—C15—C16	−69.4 (8)	N3—C32—C33—C34	−67.5 (8)
N2—C22—C23—C24	−71.1 (8)	C32—C33—C35—C36	169.3 (8)
N2—C22—C23—C25	54.1 (8)	C34—C33—C35—C36	−64.4 (10)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O6	0.82	1.71	2.502 (7)	163
O11—H11···O1^{i}	0.82	1.87	2.671 (6)	167
N1—H1A···O4	0.89	1.92	2.802 (6)	169
N1—H1B···O8	0.89	2.09	2.900 (8)	152
N1—H1C···O7^{ii}	0.89	2.02	2.887 (7)	163
O21—H21···O8^{iii}	0.82	1.83	2.631 (6)	167
N2—H2A···O5	0.89	2.03	2.864 (6)	155
N2—H2B···O1	0.89	2.07	2.828 (7)	143
N2—H2C···O3^{iv}	0.89	2.06	2.819 (7)	143
O31—H31···O7^{v}	0.82	1.80	2.588 (7)	161
N3—H3A···O2^{iv}	0.89	2.26	3.002 (7)	141
N3—H3A···O3^{iv}	0.89	2.40	3.033 (7)	129
N3—H3B···O6	0.89	1.97	2.797 (7)	154
N3—H3C···O32^{vi}	0.89	1.97	2.786 (7)	152

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

All the H atoms were fixed by geometric constraints and were allowed to ride on the parent 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; molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Johnson, C. K. (1976). *ORTEP*II. Oak Ridge National Laboratory, Tennessee, USA.

Jeffrey, G. A. & Saenger, W. (1991). In *Hydrogen Bonding in Biological Structures*. Berlin, Heidelberg, New York: Springer-Verlag.
Lakshiminarayanan, A. V., Sashisekharan, V. & Ramachandran, G. N. (1967). In *Conformation of Biopolymers*, edited by G. N. Ramachandran. London: Academic Press.
Prasad, G. S. & Vijayan, M. (1993). *Acta Cryst.* B**49**, 348–356.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1999). *PLATON for Windows*. Utrecht University, The Netherlands.
Torii, K. & Iitaka, Y. (1971). *Acta Cryst.* B**27**, 2237–2246.
Trommel, J. & Bijvoet, J. M. (1954). *Acta Cryst.* **7**, 703–708.
Varughese, K. I. & Srinivasan, R. (1976). *Acta Cryst.* B**32**, 994–997.
Vijayan, M. (1988). *Prog. Biophys. Mol. Biol.* **52**, 71–99.