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Bis(L-tyrosinium) sulfate monohydrate

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Key indicators

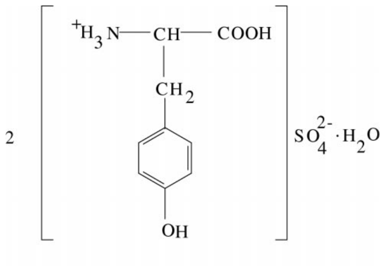
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.030
wR factor = 0.084
Data-to-parameter ratio = 8.1

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

In the title compound, $2C_9H_{12}NO_3^+ \cdot SO_4^{2-} \cdot H_2O$, the sulfate anion is linked to the tyrosinium residue 1 by a strong O—H···O hydrogen bond, while tyrosinium residue 2 forms a relatively strong O—H···O hydrogen bond with the terminal hydroxyl O atom, O^η, resulting in a hydrogen-bonded helical structure around the *b* axis. A zigzag (*Z*1) head-to-tail sequence is observed in residue 2. Ribbons of tyrosinium residues parallel to the *a* axis are interconnected by sulfate anions and disordered water molecules in a three-dimensional network. The disordered water molecule links the sulfate anion and tyrosinium residue as a chain running along the *b* axis.

Comment

The crystal structures of L-tyrosine hydrobromide (Srinivasan, 1956), L-3,4-dihydroxyphenylalanine (Mostad *et al.*, 1971), L-tyrosine (Mostad *et al.*, 1972), DL-tyrosine (Mostad & Rømming, 1973), L-tyrosine hydrochloride (Frey *et al.*, 1973) and *O*-tyrosine (Mostad *et al.*, 1975) have been reported. In the present study, the crystal structure of L-tyrosine recrystallized from sulfuric acid was determined, namely bis(L-tyrosinium) sulfate monohydrate, (I).



(I)

The asymmetric unit of the crystal structure contains two cystallographically independent tyrosinium residues, one sulfate anion and a water molecule. The backbone conformation angles ψ^1 for tyrosinium residues 1 and 2 are −2.0 (4) and −28.2 (4)°, respectively. This tendency for the C—N bond to twist is found in various amino acids (Lakshminarayanan *et al.*, 1967). The branched side-chain conformation angle χ^1 is in the *gauche*-II form [−71.6 (3)°] for residue 1, while residue 2 is in the *trans* form [176.4 (3)°]. Interestingly, residue 1 adopts the sterically most favourable 'open conformation I', while residue 2 adopts 'open conformation II' (Bhat & Vijayan, 1978).

The conformation angles χ^{21} and χ^{22} are 133.1 (3) and −53.4 (3)° and −110.1 (3) and 67.1 (4)° for residues 1 and 2,

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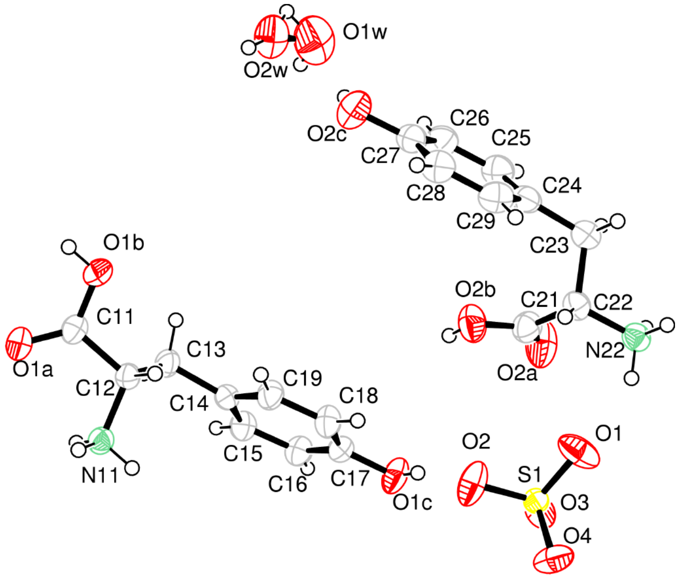

Figure 1
*ORTEP*II (Johnson, 1976) drawing of the title compound, with the atomic numbering scheme and 50% probability displacement ellipsoids.

respectively. These χ^{21} values lie within the expected range of 90±30° (Cotrait *et al.*, 1984). In the case of tyrosinium residue 1, the χ^{21} value deviates slightly from the expected value.

The carboxyl group of residue 1 has the normal C—O dimensions expected for a non-ionized carboxyl group (Table 1), while residue 2 has C—O distances of 1.233 (4) and 1.274 (3) Å. These do not correspond to a delocalized sysytem, since the O—C—C angles are different [119.7 (3) and 114.6 (3)°]. In the zwitterionic amino acid form, the O—C—C angles will be nearly the same, as found in L-leucine [118.03 (10) and 117.27 (9)°] (Görbitz & Dalhus, 1996). The cationic form of residue 2 is further confirmed by a relatively strong hydrogen bond.

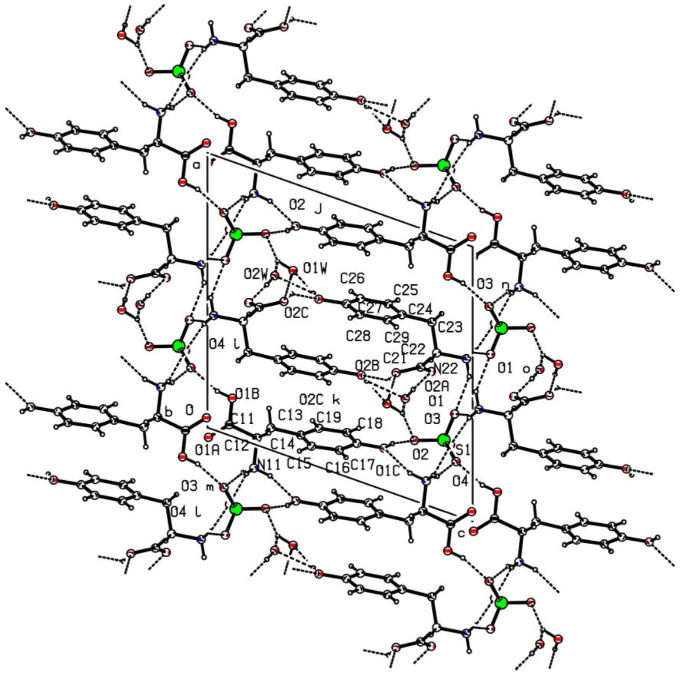

Figure 2
Packing diagram of the title structure, viewed down the *b* axis.

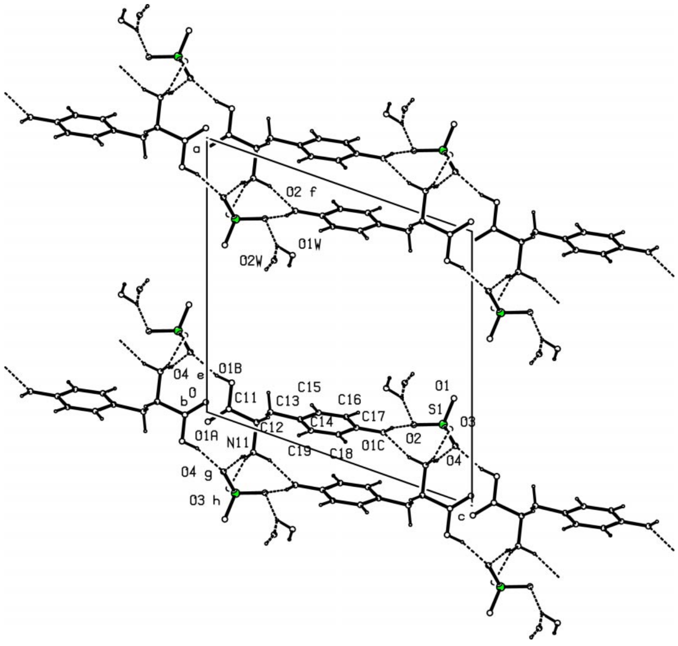

Figure 3
Packing diagram of the title structure, viewed down the *b* axis. For clarity, only tyrosinium residue 1, the sulfate anion and the water molecule are shown.

All O atoms of sulfate anions are involved in hydrogen bonding with tyrosinium residues and the water molecule (Table 2). The latter plays a vital role in stabilizing the structure (Fig. 2). The amino N atom of both the cation residues forms a normal N—H···O bond with the sulfate anion (Table 2). Intermolecular hydrogen bonding is observed in residue 1 involving the N atom and the 2_1 screw symmetry-related terminal hydroxyl O atom, O$^{\eta}$. A bifurcated hydrogen bond is observed in residue 2 involving nitrogen with an O atom of the sulfate anion and a carboxyl O atom. In the case of residue 1, a class I hydrogen-bonding structure is observed, while in the case of residue 2, a class II hydrogen-bonding structure (Jeffrey & Saenger, 1991) is present.

A zigzag ($Z1$) head-to-tail sequence is observed in tyrosinium residue 2, connecting the residues related by a 2_1 screw parallel to *b* and its symmetry equivalents (Vijayan, 1988).

The O and one of the H atoms of the water molecule are disordered, with site-occupancy factors of 0.61(1) and 0.39(1). Besides the acceptor role, the disordered water molecule forms hydrogen bonds with the sulfate anion through the ordered H1*W* atom. The other disordered H atoms, H2*W*1 and H2*W*2, link the carboxyl O atoms of residue 2 into an infinite chain running along the *b* axis.

In the present study, the tyrosinium layers are interconnected, as an infinite chain, by interactions involving the sulfate ion and the disordered water molecule. Residue 1 runs as a ribbon along the *a* axis. These ribbons are interconnected,

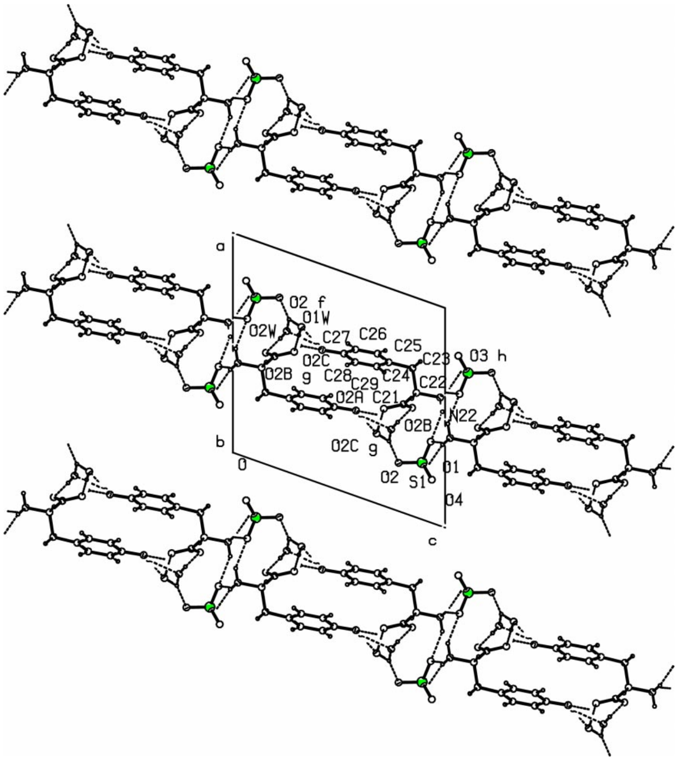

Figure 4
Packing diagram of the title structure, viewed down the *b* axis. For clarity, only tyrosinium residue 2, the sulfate anion and the water molecule are shown.

as an infinite chain, by the sulfate anion along the *b* axis through the amino N atom (Fig. 3). Residue 2, also as a ribbon in the $x = 1/2$ plane, is linked through an O—H···O [O2*B*—H2*B*···O2*C*(1−*x*, *y*−1/2, 1−*z*)] hydrogen-bonded interaction and runs as a helical structure along the *b* axis (Fig. 4). These ribbons [O2*B*—H2*B*···O2*C*—H2*C*···O1*W*—H2*W*1···O2*B*(*x*, 1−*y*, *z*)] are connected in a three-dimensional network by the disordered water molecule and by sulfate anions. The aggregation of the hydrophilic carboxyl, amino and sulfate groups are about the $z = 0$ plane with the phenyl rings about the $z = 1/2$ plane (Fig. 2).

Experimental

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

Crystal data

$2C_9H_{12}NO_3^+\cdot O_4S^{2-}\cdot H_2O$
$M_r = 478.47$
Monoclinic, $P2_1$
$a = 13.473$ (2) Å
$b = 6.134$ (1) Å
$c = 13.785$ (3) Å
$\beta = 109.51$ (2)°
$V = 1073.8$ (3) Å^3
$Z = 2$
$D_x = 1.480$ Mg m^{-3}
$D_m = 1.478$ Mg m^{-3}
D_m measured by flotation using a mixture of carbon tetrachloride and xylene
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 11.3$–14.2°
$\mu = 0.22$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.5 × 0.4 × 0.3 mm

Data collection

Enraf–Nonis CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.862$, $T_{\max} = 0.939$
3011 measured reflections
2455 independent reflections
2322 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$
$\theta_{\max} = 25.0°$
$h = -2 \rightarrow 16$
$k = -1 \rightarrow 7$
$l = -16 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.084$
$S = 1.07$
2459 reflections
304 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.1816P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.011 (2)
Absolute structure: Flack (1983); 488 Friedel pairs
Flack parameter = 0.04 (8)

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.203 (3)	O2*A*—C21	1.233 (4)
O1*B*—C11	1.309 (3)	O2*B*—C21	1.274 (3)
O1*A*—C11—O1*B*	126.8 (2)	O2*A*—C21—O2*B*	125.7 (3)
O1*A*—C11—C12	123.5 (2)	O2*A*—C21—C22	119.7 (3)
O1*B*—C11—C12	109.74 (18)	O2*B*—C21—C22	114.6 (3)
O1*A*—C11—C12—N11	−2.0 (4)	O2*A*—C21—C22—N22	−28.2 (4)
N11—C12—C13—C14	−71.6 (3)	N22—C22—C23—C24	176.4 (3)
C12—C13—C14—C15	133.1 (3)	C22—C23—C24—C25	−110.1 (3)
C12—C13—C14—C19	−53.4 (3)	C22—C23—C24—C29	67.1 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1*B*···O4$^{\rm i}$	0.82	1.81	2.600 (2)	161
N11—H11*A*···O1C$^{\rm ii}$	0.89	2.19	2.875 (3)	133
N11—H11*B*···O4$^{\rm iii}$	0.89	1.85	2.727 (3)	170
N11—H11*C*···O3$^{\rm ii}$	0.89	2.00	2.791 (3)	147
O1*C*—H1*C*···O2	0.82	1.89	2.695 (3)	168
O2*B*—H2*B*···O2*C*$^{\rm iv}$	0.82	1.95	2.644 (3)	142
N22—H22*A*···O3$^{\rm v}$	0.89	1.93	2.792 (3)	163
N22—H22*B*···O1$^{\rm vi}$	0.89	2.02	2.860 (4)	156
N22—H22*C*···O1	0.89	2.01	2.810 (3)	148
N22—H22*C*···O2*A*$^{\rm v}$	0.89	2.61	3.170 (3)	121
O2*C*—H2*C*···O1*W*	0.82	1.77	2.514 (6)	151
O2*C*—H2*C*···O2*W*	0.82	2.14	2.728 (7)	129
O1*W*—H2*W*1···O2*B*$^{\rm iv}$	0.95	1.98	2.926 (7)	179
O2*W*—H2*W*2···O2*A*$^{\rm vii}$	0.84	1.74	2.577 (10)	177
O1*W*—H1*W*···O2$^{\rm iv}$	0.91	2.08	2.788 (6)	134
O2*W*—H1*W*···O2$^{\rm iv}$	0.96	2.08	2.975 (8)	154

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

The water molecule is disordered with site-occupation factors for O1*W* and O2*W* of 0.61 (1) and 0.39 (1), respectively, and these components were refined anisotropically. One of the H atoms, H1*W*, links the two disordered O atoms, while the other H atom is also disordered, H2*W*1 and H2*W*2 with site-occupation factors of 0.61 (1) and 0.39 (1). These water H atoms were located but were not refined. Other H atoms were fixed by geometric constraints and were allowed to ride on the attached atom.

Acta Cryst. (2002). E**58**, o211–o214 B. Sridhar *et al.* • $2C_9H_{12}NO_3^+\cdot O_4S^{2-}\cdot H_2O$ **o213**

214 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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