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An Assessment of Ionic and Hydrogen Bonding in the Crystal Structure of (DL-Serine.H⁺)₂.SO₄²⁻.H₂O

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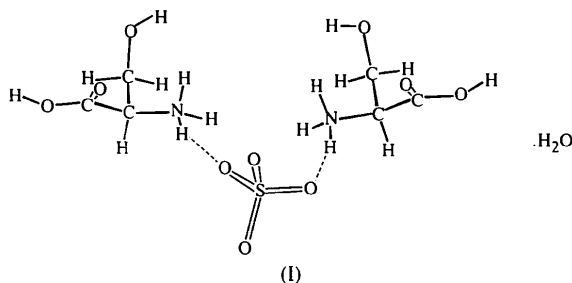
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Abstract

The crystal structure of DL-diserinium sulfate hydrate, 2C₃H₈NO₃⁺·SO₄²⁻·H₂O, consists of sulfate-containing 'ionic complexes' interconnected by extensive hydrogen bonds to form a complex network, creating channels which are filled by water molecules.

Comment

In its fully protonated form, the amino acid serine, 2-amino-3-hydroxypropionic acid, is a dibasic acid with p*K*_a values of 2.21 and 9.15 for the α-COOH and the α-NH₃⁺ moieties, respectively (Lehninger, 1975). Under normal conditions, the hydroxy side chain (β-OH) of serine is not active during titration since it is both weakly acidic and weakly basic (p*K*_a = 16). All three functional groups in serine in its fully protonated form, however, can function as proton donors in hydrogen bonding. Judging from the p*K*_a values, the proton-donating power of the three functional groups follows the trend α-COOH ≫ α-NH₃⁺ ≫ β-OH. In addition, the charged α-NH₃⁺ group is expected to be involved in electrostatic interactions (ionic bonding). In order to assess the relative effects of ionic and hydrogen bonding on the crystal packing (Aakeroy *et al.*, 1995; Kinbara, Hashimoto, Sukegawa, Nohira & Saigo, 1996), we have determined the molecular and crystal structure of (DL-serine.H⁺)₂.SO₄²⁻.H₂O, (I). The crystal structure is dictated by strong ionic and/or hydrogen-bonding interactions among the charged (α-NH₃⁺ and SO₄²⁻) and uncharged (α-COOH and β-OH) groups, forming channels which are filled by the solvated H₂O molecules.



The asymmetric unit of the crystal structure of the title compound, (I), consists of two serine.H⁺ monocations, one sulfate anion and one water molecule (Fig. 1). The two crystallographically independent serine.H⁺ ions exist as a DL racemic mixture. The O atom of the water molecule in the asymmetric unit is disordered in two positions, O1W and O2W, each with an occupancy factor of 0.5. The O1W...O2W distance is 0.7 Å. It is interesting to note that, despite the coexistence of a racemic mixture of D and L serine.H⁺ ions in the crystal, the compound crystallizes in a non-centrosymmetric space group. We believe this is caused by strong ionic and hydrogen-bonding interactions between the tetrahedral SO₄²⁻ anion and the serine.H⁺ cations.

All intramolecular bond lengths and angles are normal (Table 1). The two serine.H⁺ (one D and one L) cations are related by a pseudo-mirror containing S1, O3s and O4s of the sulfate ion. The crystal lattice is held together by strong ionic interactions between the

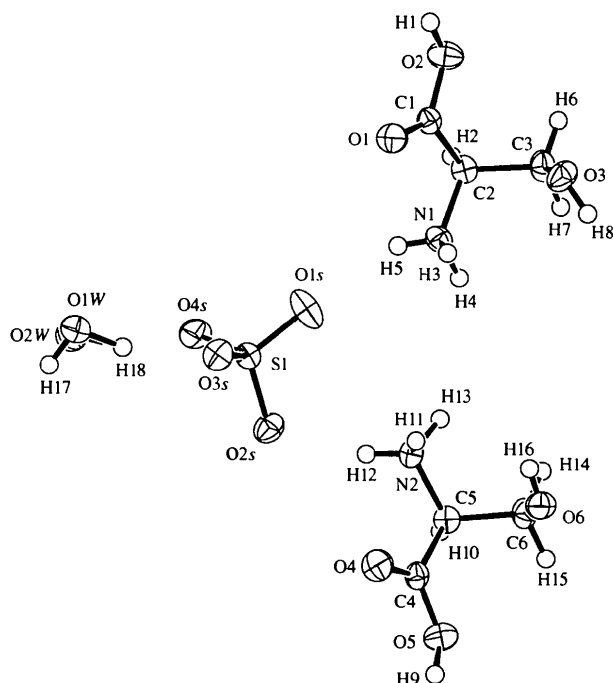


Fig. 1. Molecular structure of (I) showing 50% probability ellipsoids.

α -NH₃⁺ groups and the sulfate anions, augmented by extensive hydrogen-bonding interactions. The shortest D—H···A hydrogen-bonding contacts are listed in Table 2. All three H atoms of the two α -NH₃⁺ groups per asymmetric unit are hydrogen bonded to O1s, O2s and O3s atoms of different sulfate anions. Each sulfate anion is surrounded by nine strong hydrogen bonds: six from α -NH₃⁺ groups of six different serine.H⁺ cations (three D and three L, related by 2₁ along *c* at *a/4*), one from the β -OH group (O6—H16 from one of the serine.H⁺), and two from two different water molecules (also related by 2₁ along *c* at *a/4*). The prevalence of hydrogen-bonding networks in which ammonium cations and carboxylate anions are aligned around a 2₁ screw axis can also be found in the crystal structures of the salts of chiral primary amines with achiral carboxylic acids (Kinbara, Hashimoto, Sukegawa, Nohira & Saigo, 1996). As a result, the SO₄²⁻ anion may be considered to be encapsulated in a cage of nine (donor) H atoms (H5···O1s, H11···O1s, H3···O2s, H12···O2s, H4···O3s, H13···O3s, H18···O3s, H16···O4s and H17···O4s), forming a sulfate-centered 'ionic complex'. The hydrogen bonds (D—H···A) range from 1.73 to 2.17 Å in length (H···A) with D—H···A angles from 149 to 177° (see Table 2). An alternative description

of the 'coordination sphere' of the SO₄²⁻ anion is that of a highly distorted cuboctahedron with three 'missing vertices'. This latter description emphasizes the fact that each O atom of the tetrahedral sulfate anion has three lone pairs capable of forming hydrogen bonds (as proton acceptors). The three lone pairs (one each on O1s, O2s and O4s) pointing toward the 'missing vertices' form three weak and highly bent hydrogen bonds (N2—H13···O1s 2.54 Å and 121°, N1—H4···O2s 2.64 Å and 116°, and N2—H11···O4s 2.38 Å and 127°; see Table 2).

The sulfate-centered 'ionic complexes' are linked by α -COOH··· β -OH and β -OH···SO₄²⁻ hydrogen bonds into an extensive network (Table 2) (Aakeroy *et al.*, 1995; Feeder & Jones, 1993, 1996; Gorbitz & Gundersen, 1996; Kinbara, Hashimoto, Sukegawa, Nohira & Saigo, 1996; Swenson, Habermann & Murphy, 1996). The result of these strong interactions is the observed layered structure shown in Fig. 2. The network structure (in the *ab* plane) has parallelogram-shaped channels that run along the *c* axis and are filled with water molecules. The water molecules also form strong hydrogen bonds to the sulfate anion and the β -OH groups (Table 2). Work is in progress to further the understanding of the crystal packing forces in amino acids and polypeptides.

Experimental

All reagents were purchased and used without further purification. DL-Serine was of BR grade and H₂SO₄ of AR grade. Water was doubly distilled. Crystals suitable for X-ray measurement were grown from a saturated aqueous solution of a mixture (2:1 molar ratio) of DL-serine and H₂SO₄.

Crystal data

2C₃H₈NO₃·SO₄²⁻·H₂O

M_r = 326.27

Orthorhombic

P2₁2₁2₁

a = 10.597 (2) Å

b = 21.337 (2) Å

c = 5.855 (1) Å

V = 1323.9 (3) Å³

Z = 4

D_x = 1.627 Mg m⁻³

D_m not measured

Mo K α radiation

λ = 0.7107 Å

Cell parameters from 25 reflections

θ = 13.5–15.0°

μ = 0.3041 mm⁻¹

T = 296 K

Prismatic

0.60 × 0.45 × 0.38 mm

Colorless

Data collection

AFC-7R diffractometer with rotating-anode X-ray generator

$\omega/2\theta$ scans

Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)

T_{min} = 0.78, *T_{max}* = 0.89

1618 measured reflections

1557 independent reflections

1495 reflections with

I > $\sigma(I)$

R_{int} = 0.008

θ_{\max} = 26°

h = 0 → 13

k = 0 → 26

l = 0 → 7

3 standard reflections

every 150 reflections

intensity decay: 2.50%

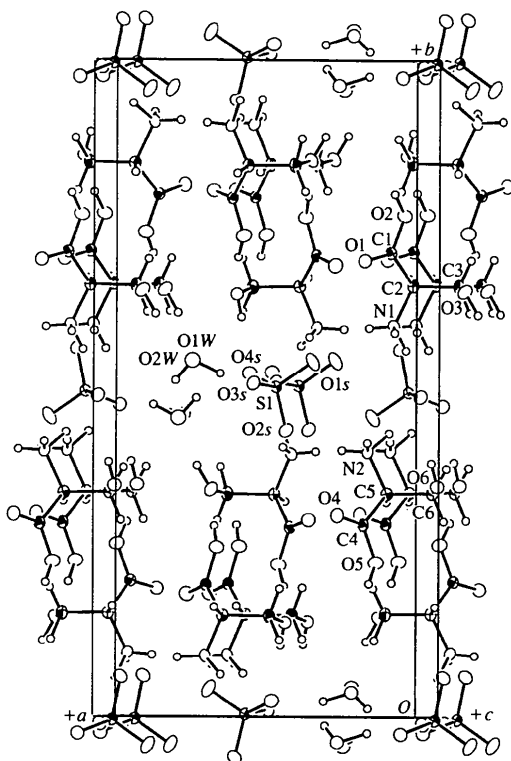


Fig. 2. Unit-cell diagram viewed approximately down the *c* axis. S and C atoms are shown as shaded ellipsoids, with other non-H atoms as boundary ellipsoids (25% probability). Only non-H atoms in the asymmetric unit are labeled.

Refinement

Refinement on *F**R* = 0.034*wR* = 0.032*S* = 1.950

1483 reflections

181 parameters

All H atoms refined

Weighting scheme based on measured e.s.d.'s

 $(\Delta/\sigma)_{\max} = 0.003$ $\Delta\rho_{\max} = 0.296 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.250 \text{ e } \text{Å}^{-3}$

Extinction correction:

Zachariasen (1968) type

2 Gaussian isotropic

Extinction coefficient:

 $1.09(2) \times 10^{-5}$ Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

S1—O1s	1.457(2)	O5—C4	1.322(3)
S1—O2s	1.469(2)	O6—C6	1.432(4)
S1—O3s	1.485(2)	N1—C2	1.480(4)
S1—O4s	1.477(2)	N2—C5	1.493(3)
O1—C1	1.207(3)	C1—C2	1.510(4)
O2—C1	1.324(3)	C2—C3	1.529(4)
O3—C3	1.414(4)	C4—C5	1.513(4)
O4—C4	1.194(4)	C5—C6	1.524(4)
O1s—S1—O2s	111.5(1)	N1—C2—C3	111.2(3)
O1s—S1—O3s	109.9(1)	C1—C2—C3	111.2(3)
O1s—S1—O4s	108.8(1)	O3—C3—C2	110.8(3)
O2s—S1—O3s	108.0(1)	O4—C4—O5	125.6(3)
O2s—S1—O4s	109.1(1)	O4—C4—C5	123.7(3)
O3s—S1—O4s	109.6(1)	O5—C4—C5	110.6(3)
O1—C1—O2	124.8(3)	N2—C5—C4	108.2(2)
O1—C1—C2	124.0(3)	N2—C5—C6	110.8(2)
O2—C1—C2	111.2(3)	C4—C5—C6	111.0(3)
N1—C2—C1	107.7(2)	O6—C6—C5	112.3(3)

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

D—H...A	D—H	H...A	D...A	D—H...A
N1—H5...O1s	0.81	2.17	2.923(4)	155
N2—H11...O1s ⁱ	1.03	2.02	3.02(1)	163
N1—H3...O2s ⁱ	0.97	1.90	2.839(4)	161
N2—H12...O2s	0.89	1.95	2.822(3)	163
N1—H4...O3s ⁱⁱ	1.03	1.85	2.873(4)	172
N2—H13...O3s ⁱⁱ	1.10	1.73	2.831(4)	168
O1W—H18...O3s	1.04	1.84	2.82(1)	154
O6—H16...O4s ⁱ	0.78	1.90	2.683(3)	177
O1W—H17...O4s ⁱⁱⁱ	0.87	1.98	2.76(1)	149
N2—H13...O1s ⁱⁱ	1.10	2.54	3.25(1)	121
N1—H4...O2s ⁱⁱ	1.03	2.64	3.23(1)	116
N2—H11...O4s ⁱ	1.03	2.38	3.110(4)	127
O2—H1...O6 ^{iv}	0.96	1.66	2.613(3)	171
O5—H9...O3 ^v	0.92	1.67	2.589(3)	176
O3—H8...O1W ⁱ	0.89	1.71	2.59(1)	167
O3—H8...O2W ⁱ	0.89	1.75	2.60(1)	159
O1W—H17...O2W ⁱⁱⁱ	0.87	2.68	2.840(4)	134

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

All H atoms were found *via* difference Fourier syntheses and refined. The correct enantiomorph under the non-centrosymmetric space group was determined by inverting the coordinates during the final cycles of least-square refinement. In the final cycles of refinement, non-H atoms were refined anisotropically, while H atoms were fixed. The water molecule was treated as a disordered model with an occupancy factor of 0.5 for both O1W and O2W, and was refined isotropically.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Data reduction: *MSCIAFC Diffractometer Control Software*. Program(s) used to solve structure: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to refine structure: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1155). Services for accessing these data are described at the back of the journal.

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(11*R*,11*aS*-*trans*)-11-Ethylthio-2,3,5,10,11,11*a*-hexahydro-1*H*-pyrrolo-[2,1-*c*][1,4]benzodiazepin-5-one

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Abstract

The pyrrolo ring in the title compound, C₁₄H₁₈N₂O₅, exhibits a flattened envelope conformation, while the benzodiazepine ring exists as a twisted boat. The