

N,N'-Ethylenediamedisuccinic Acid Pentahydrate

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Abstract. $C_{10}H_{26}N_2O_{13}$, orthorhombic, $P2_12_12$, $a = 11.299$ (6), $b = 14.271$ (7), $c = 5.462$ (5) Å, $Z = 2$, $D_c = 1.44$ g cm $^{-3}$. The structure was solved by direct methods and was refined by least-squares procedures to a final R of 5.1%. Intermolecular hydrogen bonds between neighboring carboxyl groups organize the title molecules into two-dimensional networks. The water molecules are contained in channels that extend perpendicularly to these networks.

Introduction. EDSS is a hexadentate chelating agent that is isomeric with and chemically quite similar to EDTA. However a major difference between EDSS and EDTA is that the former molecule contains two asymmetric centers. These impose optical activity upon the chelates that EDSS forms. For this reason there has been considerable interest in the coordination chemistry of metal ions using EDSS as a complexing ligand (Babich & Gorelov, 1971; Majer, Springer & Kopecka, 1966; Sunar & Trivedi, 1972; Woodward, 1971; and references contained in these papers).

EDSS was prepared according to the method of Neal & Rose (1968) by J. L. Gabriel and R. C. Davis of the University of Pennsylvania Chemistry Department as part of a program of spectroscopic and theoretical investigations of the properties of optically active

coordination complexes. These workers provided us with tabular crystals of EDSS which they had grown by the slow evaporation of an aqueous solution of EDSS that had been acidified to pH 3 with HCl.

Preliminary X-ray investigations of crystals of EDSS using Weissenberg and precession techniques indicated that these crystals deteriorated upon prolonged exposure to air. This suggested that crystals of EDSS easily lose water of crystallization. Therefore the crystal of EDSS that was selected for data collection ($\sim 0.60 \times 0.28 \times 0.18$ mm) was mounted in a sealed thin-walled glass capillary tube. The systematic absences in the preliminary X-ray photographs of the $h00$ reflections for h odd and the $0k0$ reflections for k odd together with the observed orthorhombic lattice symmetry are consistent with the space group $P2_12_12$.

All subsequent X-ray diffraction measurements were made on a Picker FACS-1 diffractometer equipped with a graphite monochromator and employing Mo $K\alpha$ radiation ($\lambda = 0.7093$ Å). Unit-cell parameters were determined by the least-squares fit of the angular positions of 12 reflections. The X-ray data were measured to the limit $\sin \theta/\lambda = 0.65$ Å $^{-1}$ with the θ - 2θ scan mode and a scan rate of 1° min $^{-1}$. The three reflections that were monitored after every 50th measurement showed no significant decay during the data collection process.

The measured intensities, I , were corrected for Lorentz and polarization effects. No absorption corrections were made due to the small size of μR ($\mu = 1.36$ cm $^{-1}$). Standard deviations, $\sigma(I)$, were calculated according to the method of Stout & Jensen (1968) assuming an instrumental instability factor of 0.03. Of the 1212 measured unique reflections 148 had $I < 2.33\sigma(I)$ and were therefore considered to be unobserved.

All non-hydrogen atoms in the structure were located in an E map based on the phase set with the highest figure of merit as calculated by the program *MULTAN* (Main, Woolfson & Germain, 1971) for the 134 reflections with $|E| \geq 1.5$. The structure was refined by the full matrix least-squares method with the atomic scattering factors of Cromer & Waber (1965) for non-H atoms and those of Stewart, Davidson & Simpson (1965) for H atoms. All non-water H atoms were located in the difference Fourier map based on the structural parameters following isotropic refinement. Least-squares refinement in which the thermal parameters of the non-H atoms were varied

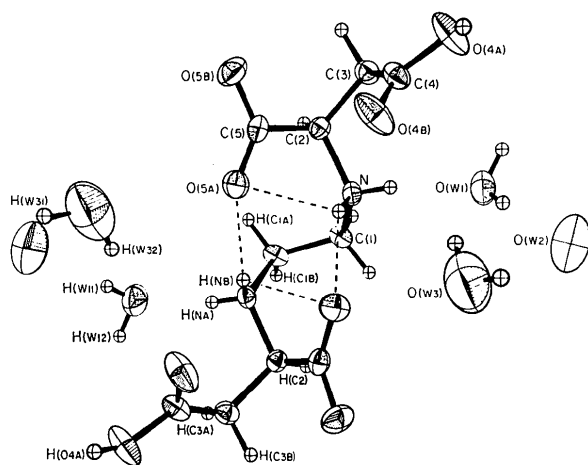


Fig. 1. An ORTEP drawing (Johnson, 1965) of a molecule of EDSS and its waters of hydration together with the atomic numbering scheme used in this report. Non-H atoms are shown as thermal ellipsoids at the 50% level; H atoms are drawn as spheres of an arbitrary radius. Intramolecular hydrogen bonds are represented by dashed lines.

anisotropically and those of the H atoms were varied isotropically led to the location in the subsequent difference Fourier map of the H atoms on the two water molecules not on special positions. These atoms were assigned the isotropic thermal parameter of the O atom to which they were bonded. The parameters describing these water H atoms were not refined. *R* converged to its final value of 0.051 based on the 1064 observed unique reflections. The final difference Fourier map showed no significant features.

Table 1 lists the final positional parameters of the heavy atoms.* The molecular configuration of EDSS in the crystal structure is illustrated in Fig. 1 together with the atomic numbering scheme used in this report. The covalent bond distances and angles of the structure are given in Fig. 2.

Discussion. The EDSS molecules lie with their C(1)–C(1') bond across a crystallographic twofold axis of symmetry. The EDSS was prepared from L-aspartic acid. Therefore, as expected, both asymmetric C atoms of the EDSS molecule exhibit the same configuration. The EDSS molecules exist as zwitterions with the N atoms being protonated by the carboxylic acid groups one atom removed from them.

The EDSS molecule forms two symmetry-related

* Anisotropic thermal parameters for the heavy atoms, positional and thermal parameters for the H atoms, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31775 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional parameters of EDSS* ($\times 10^4$)

Standard deviations, as determined from the variance-covariance matrix of the final cycle of least-squares refinement, are given in parentheses and refer to the least significant digits of their corresponding parameters.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}
C(1)	4354 (3)	138 (2)	7180 (6)	
N	3983 (2)	749 (2)	5094 (4)	
C(2)	4573 (2)	1690 (2)	4876 (5)	
C(3)	3651 (3)	2445 (2)	4404 (6)	
C(4)	2982 (3)	2285 (2)	2071 (6)	
C(5)	5542 (2)	1641 (2)	2916 (5)	
O(4A)	2035 (2)	2812 (2)	1867 (5)	
O(4B)	3275 (2)	1728 (2)	563 (5)	
O(5A)	5890 (2)	861 (1)	2226 (4)	
O(5B)	5927 (2)	2414 (1)	2176 (5)	
O(W1)	1605 (2)	814 (2)	6314 (6)	
O(W2)	0	0	3393 (10)	
O(W3)	3308 (4)	4502 (4)	9760 (9)	

bifurcated intramolecular hydrogen bonds. Each N atom is a donor to both O(5A) atoms in the same molecule as is illustrated in Fig. 1. The four non-H atoms, N, C(2), C(5) and O(5A), comprising one of the hydrogen-bonded rings are coplanar such that the r.m.s. deviation from their least squares plane is 0.060 Å. The H atom involved deviates 0.60 Å from the foregoing least-squares plane. It can be seen from Table 2 that the hydrogen-bond angle of this interaction shows considerable deviation from 180°. Non-H atoms, N, C(1), C(5') and O(5A'), of the other hydrogen-bonded ring are also coplanar, with an r.m.s. deviation from their least-squares plane of 0.021 Å. H(NB) deviates from this plane by 0.25 Å. The hydrogen-

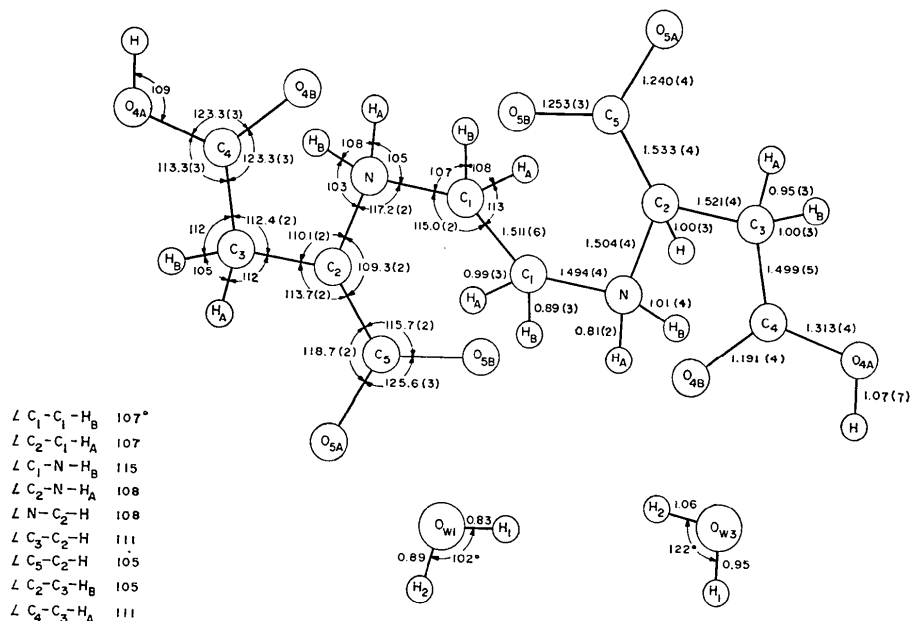


Fig. 2. A schematic drawing indicating the unique bond distances and angles found in the crystal structure of EDSS. The standard deviations, as estimated from the variance-covariance matrix of the final cycle of least-squares refinement, average 0.004 Å and 0.2°, respectively, for distances and angles involving only non-H atoms. The corresponding quantities for distances and angles involving H atoms are 0.04 Å and 3° respectively. H(C2) has been omitted from the drawing for the sake of clarity.

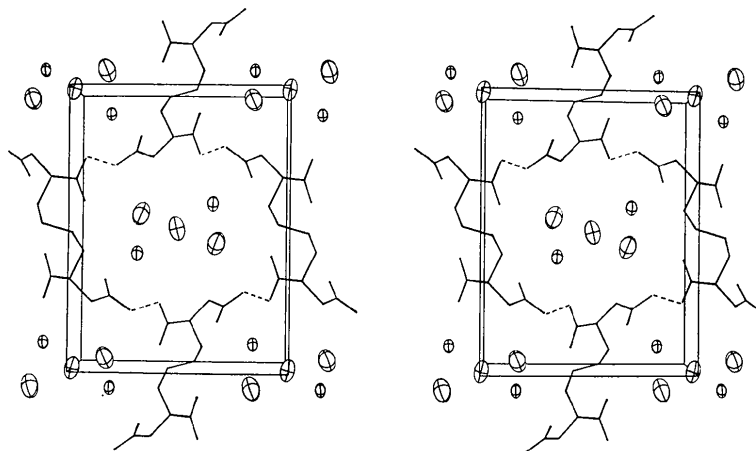


Fig. 3. A stereo drawing illustrating the contents of the unit cell of the crystal structure of EDDS as viewed down the c axis with the a axis horizontal and the b axis vertical. Water O atoms are represented as thermal ellipsoids at the 50% level. Intermolecular hydrogen bonds between EDDS molecules are represented by dashed lines. H atoms have been omitted for the sake of clarity.

Table 2. *Hydrogen-bond data*

Hydrogen bond $D-H \cdots A$	Distance $D \cdots A$	Distance $H \cdots A$	Angle $D-H \cdots A$
$O(4A)-H(O4) \cdots O(5B^i)$	2.559 Å	1.55 Å	156°
$N-H(NA) \cdots O(W1)$	2.770	1.97	168
$O(W1)-H(W12) \cdots O(5B^{ii})$	2.768	1.91	160
$N-H(NB) \cdots O(5A)^*$	2.668	2.20	107
$N-H(NB) \cdots O(5A'')^*$	2.784	2.00	132
$O(W1)-H(W11) \cdots O(W2)$	2.680	1.88	162
$O(W3)-H(W32) \cdots O(W1^{iii})$	2.849	2.28	112
$O(W3) \cdots O(W2^{iv})$	2.669		

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

* Intramolecular hydrogen bond.

bonding angle of this interaction also exhibits considerable deviation from linearity.

Fig. 3 shows the contents of the unit cell as viewed down the c axis. The non-ionized carboxylic acid group forms a hydrogen bond with the carboxylate group of a neighboring molecule. The $O(4A) \cdots O(5B)$ distance in this interaction of 2.559 Å is quite short for a hydrogen bond. However, short (and presumably strong) hydrogen bonds are commonly observed between carboxylic acid groups. Thus, for example, in succinic acid dimers (Broadly, Cruickshank, Morrison, Robertson & Shearer, 1959) the $O \cdots O$ hydrogen-bonding distance is 2.66 Å.

The EDDS molecules are organized through hydrogen bonding into open rectangular networks that extend endlessly in directions normal to the c axis. Adjacent networks, which are symmetry related by the c axis translation, pack in such a manner as to form infinite channels that are centered on twofold axes of rotation parallel to the c axis. The waters of hydration are located within these channels. This structural feature accounts for the ease with which water is lost from the crystal structure.

The positions of the water molecules are fixed in the crystal lattice by a series of hydrogen bonds between the water molecules and the EDDS molecules as well as those between water molecules. These hydrogen bonds are described in Table 2. There are no other intermolecular contacts in the crystal structure that are less than their minimal van der Waals contact distances.

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