

S-Carboxymethyl-L-cysteine

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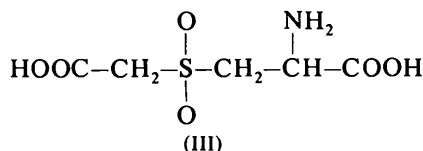
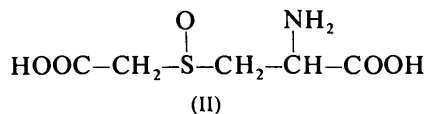
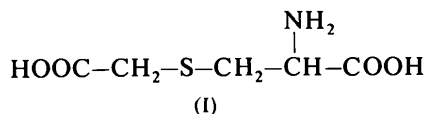
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Abstract. $C_5H_9NO_4S$, monoclinic, $P2_1$, $a = 10.290$ (4), $b = 7.039$ (1), $c = 5.093$ (1) Å, $\beta = 95.09$ (2)°, $Z = 2$, $\rho_c = 1.62$, $\rho_o = 1.60$ Mg m⁻³ (floatation). The structure has been determined by direct methods and refined to $R = 0.021$ for 720 independent reflections. The compound exists as a zwitterion. Two carboxyl groups in adjacent molecules are involved in a hydrogen bond with $O-H \cdots O = 2.548$ (2) Å. The H atom in this bond was found to be covalently bonded to the carboxyl group in the carboxymethyl moiety. The $-NH_3^+$ group is involved in three hydrogen bonds.

Introduction. Carboxymethylation of sulfhydryl ($-SH$) groups is commonly used in protein studies (Bradbury & Smyth, 1973). Carboxymethylation of the sulfhydryl group in cysteine yields (I). *S*-Carboxymethyl-L-cysteine can then be oxidized to the corresponding sulfoxides (one O atom bonded to the S atom) and further to the sulfone (two O atoms bonded to the S atom). The X-ray structure determinations of one of the epimeric sulfoxides (II) and of the sulfone (III) have been reported by Staffa, Zervos, Mighell & Hubbard (1976) and Hubbard, Mighell, Staffa, Zervos & Konopelski (1976) respectively. The structure determination of (I) was carried out to ascertain the structural relationships between this compound and its oxidation products for the correlation of chemistry with structure.



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Reagent-grade *S*-carboxymethyl-L-cysteine (I) was recrystallized from water several times to grow crystals suitable for X-ray diffraction studies. A powder diffraction pattern indicated that the recrystallized material was single phase. Density (floatation) and chemical analysis were consistent with the formula $C_5H_9NO_4S$. The results of the chemical analysis are: (a) found: 18.29% S, 33.65% C, 7.87% N, 5.02% H; and (b) calculated for $C_5H_9NO_4S$: 17.89% S, 33.51% C, 7.82% N, 5.06% H. Precession photographs showed $2/m$ symmetry. Systematic absences ($0k0$, $k = 2n + 1$), observed on the films and verified on the diffractometer, indicated that the space group is $P2_1$.

A colorless crystal formed as a plate ($0.05 \times 0.20 \times 0.20$ mm) was mounted for data collection. 883 reflections were measured on an automated four-circle diffractometer out to $\theta = 76.5^\circ$ using the bisecting and parallel modes, $\theta/2\theta$ scans, and $\text{Cu } K\alpha$ X-radiation ($\lambda = 1.54178$ Å) which was monochromated with a pyrolytic-graphite crystal. Three reflections, measured periodically, showed no significant decrease in intensity during the course of data collection. The observed intensities were corrected for absorption ($\mu = 3.63$ mm⁻¹). The maximum and minimum correction factors were 1.85 and 1.20 respectively. The equivalent data were averaged ($wR = 0.022$, average deviation = 1.02σ), resulting in 720 unique reflections. The intensities were corrected for Lorentz and polarization effects. The estimated standard deviation was calculated as $\sigma(I) = (\text{TC} + 0.00019\text{TC}^2)^{1/2}$, where TC represents the total counts and the 'instability' constant was derived from the distribution of standards. For the averaged reflections $\sigma(I_{\text{avg}})$ was obtained as the average of the mean $\sigma(I)$ and the r.m.s. deviation from the average.

The trial model was obtained using the program *MULTAN* (Germain, Main & Woolfson, 1971). After preliminary refinement, a difference synthesis was calculated and all eight H atoms were located. The final refinement of the model was carried out by full-matrix anisotropic least-squares analysis including a correction for isotropic extinction (Larson, 1967). The © 1979 International Union of Crystallography

constant G refined to $2.15(0.12) \times 10^{-3}$. The maximum correction in F^2 was about 20%. The scattering factors for H were taken from Stewart, Davidson & Simpson (1965); the scattering factors for C, N, and S were computed from the numerical Hartree-Fock wave functions (Cromer & Mann, 1968). Anomalous-dispersion factors f' and f'' for S, O, N, and C atoms were from *International Tables for X-ray Crystallography* (1974).

The model was refined to a conventional R , based on F^2 , of 0.021 and $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2} =$

0.029; * the function minimized was $\sum w(F_o^2 - F_c^2)^2$ with $w = 1/[\sigma(I)(1/Lp)]$. In the final cycle, the average and the maximum shift/error for the atomic parameters were 0.02 and 0.10 respectively. A final difference electron-density synthesis showed no peak greater than $0.1 \text{ e } \text{Å}^{-3}$, except for a peak of $0.2 \text{ e } \text{Å}^{-3}$ near the S position. An analysis of the weighted ΔF values versus F and $\sin \theta/\lambda$ revealed that the data set was free of common systematic errors. Table 1 lists the atomic parameters, while the labeling scheme for the atoms is given in Fig. 1. Computer programs used in the refinement were from XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976).

Table 1. Atomic parameters

The standard deviations are given in parentheses.

	x	y	z
S	0.85111 (4)	1.000	0.0458 (1)
N	0.6350 (2)	0.6956 (3)	0.1155 (4)
C(1)	0.5224 (2)	0.8835 (3)	0.4356 (4)
C(2)	0.6547 (2)	0.8363 (3)	0.3327 (5)
C(3)	0.7114 (2)	1.0223 (4)	0.2351 (6)
C(4)	0.9713 (2)	0.9133 (4)	0.2967 (6)
C(5)	1.1072 (2)	0.9525 (3)	0.2191 (5)
O(1)	0.5203 (2)	0.9094 (3)	0.6758 (3)
O(2)	0.4280 (1)	0.8968 (3)	0.2651 (3)
O(3)	1.1287 (1)	1.0183 (3)	0.0082 (4)
O(4)	1.1964 (1)	0.9053 (3)	0.4065 (4)
H(O4)	0.281 (3)	0.910 (5)	0.333 (6)
H(C2)	0.709 (3)	0.778 (5)	0.459 (6)
H1(C3)	0.642 (3)	1.094 (5)	0.119 (6)
H2(C3)	0.745 (3)	1.096 (5)	0.388 (6)
H1(C4)	0.961 (3)	0.965 (5)	0.456 (7)
H2(C4)	0.964 (3)	0.768 (5)	0.317 (7)
H1(N)	0.587 (3)	0.597 (5)	0.165 (6)
H2(N)	0.595 (3)	0.761 (5)	-0.041 (6)
H3(N)	0.710 (3)	0.646 (4)	0.069 (6)

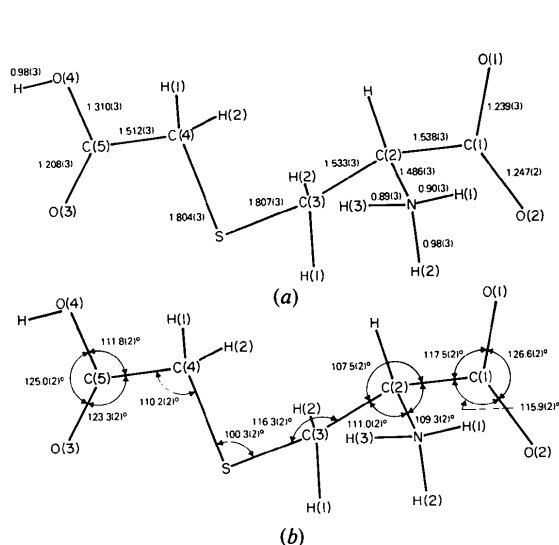


Fig. 1. (a) Bond lengths (Å) and (b) bond angles in *S*-carboxymethyl-L-cysteine.

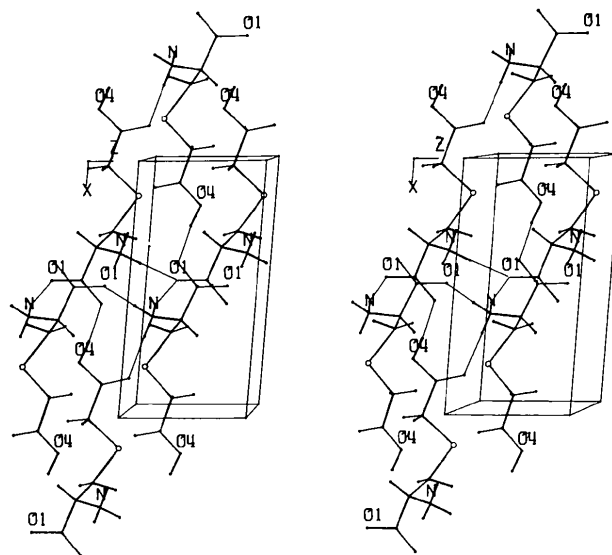


Fig. 2. Stereoscopic view of the packing of *S*-carboxymethyl-L-cysteine (ORTEP: Johnson, 1965).

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34173 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Hydrogen-bond distances and angles for S-carboxymethyl-L-cysteine*

$A-H \cdots B-C$	d_{A-H}	$d_{H \cdots B}$	$d_{A \cdots B}$	$\angle A-H \cdots B$	$\angle H \cdots B-C$
O(4)-H ⁱ ...O(2) ^l -C(1) ^j	0.98 (3) Å	1.58 (3) Å	2.548 (2) Å	169 (3)°	124 (1)°
N-H(1)...O(1) ^{ll} -C(1) ^{ll}	0.90 (3)	1.94 (3)	2.836 (3)	171 (3)	125 (1)
N-H(2)...O(1) ^{lll} -C(1) ^{lll}	0.98 (3)	1.89 (3)	2.864 (3)	175 (3)	129 (1)
N-H(3)...O(3) ^{lv} -C(5) ^{lv}	0.89 (3)	1.96 (3)	2.853 (3)	174 (3)	125 (2)

Symmetry code

(i) $1 + x, y, z$ (ii) $1 - x, y - \frac{1}{2}, 1 - z$ (iii) $x, y, z - 1$ (iv) $2 - x, y - \frac{1}{2}, -z$ Table 3. *Dicarboxylic amino-acid zwitterions: correlation of the O-H...O hydrogen-bond distance with the C-O bond distance in each of the carboxylic acid groups*

	O-H...O	C(1)* carboxyl	$\Delta 1$ †	C(5)‡ carboxyl	$\Delta 2$ †	$\Delta 3$ ($\Delta 2 - \Delta 1$)
(I)	2.548 Å	1.247 Å 1.239	0.008 Å	1.310 Å 1.208	0.102 Å	0.094 Å
Glutamic acid	2.519	1.263 1.243	0.020	1.312 1.219	0.093	0.073
(III)	2.504	1.267 1.219	0.048	1.316 1.218	0.098	0.050
(II)	2.449	1.262 1.230	0.032	1.284 1.226	0.058	0.026

* C(1): zwitterion carboxyl.

† $\Delta 1$ and $\Delta 2$: difference in the two C-O bond distances in the C(1) and C(5) carboxyl groups respectively.

‡ C(5): terminal carboxyl.

[1.218 (6) and 1.316 (5) Å]. For the C(1) carboxyl group of (I) the C(1)-O distances are 1.239 (3) and 1.247 (2) Å. The approximate equality clearly indicates that the C(1) carboxyl is unprotonated.

The packing is shown in Fig. 2. Each molecule of (I) is hydrogen bonded [via O(1)...H-O(4)] to two molecules to form chains. As in (II) and (III), the chains are interlinked by three (N-H...O) hydrogen bonds between ammonium and the carboxyl groups of adjacent molecules. The N-H...O distances ($d_{A \cdots B}$ in Table 2) compare closely with those of the sulfone (III). The three H atoms on the N are also involved in three hydrogen bonds in the sulfoxide (II) and in glutamic acid. Thus the ammonium group, in these four dicarboxylic acid amino-acid zwitterions, provides three H atoms, each of which is involved in a N-H...O hydrogen bond.

In (I), (II), and (III) the O-H...O hydrogen bonds range between 2.548 and 2.449 Å (here and subsequently the distance refers to the separation between the two O atoms). When comparing (I) with the closely related sulfone and sulfoxide, we note that the hydrogen-bond distance (O-H...O) influences the C-O bond distances in both the C(1) and the C(5) carboxyl groups (Table 3). In (I) (Fig. 1) the O-H...O hydrogen bond is 2.548 (2) Å, and both carboxyl groups have 'normal' distances. By normal we mean a

C-O single bond (~1.31 Å) and a C=O double bond (~1.21 Å) at the C(5) carboxyl and approximately equal C-O distances (~1.24 Å) at the C(1) carboxyl. Distortion occurs with a shortening of this hydrogen-bond distance. In the sulfoxide (II) the O-H...O hydrogen bond is very short [2.449 (3) Å] and the H atom appears to be at the center of the bond. However, O-H...O bonds considerably shorter than 2.45 Å have been shown to be significantly asymmetric in several other compounds. In (II) this short distance is presumed to be responsible for the unusual C-O distances in both the C(1) and the C(5) carboxyl groups [these distances are: C(1) carboxyl, 1.230 (4) and 1.262 (3) Å; C(5) carboxyl, 1.284 (4) and 1.226 (3) Å]. In the sulfone (III), the O-H...O hydrogen-bond distance is 2.504 (5) Å which is between the corresponding distances in the other two structures. The C(5) distances are 'normal' but the C(1) distances are not [C(1) carboxyl, 1.219 (5) and 1.267 (5) Å; C(5) carboxyl, 1.218 (6) and 1.316 (5) Å].

Thus, in all three compounds, the carboxyl bond distances appear to be influenced principally by the O-H...O hydrogen bond and to a lesser extent by the three N-H...O hydrogen bonds. The last column in Table 3 shows that as the strength of the O-H...O hydrogen bond increases (as indicated by decreasing

O—O distance), there is a tendency for both the C(1) and C(5) carboxyl groups in these dicarboxylic acid zwitterions to become more nearly alike ($\Delta 3$ approaches zero). A fundamental question still remains: why in such similar compounds does the O—H...O hydrogen-bond distance vary so much?

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Triphenylphosphine Selenide*

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Abstract. $C_{18}H_{15}PSe$, monoclinic, $P2_1/c$, $a = 18.471$ (3), $b = 9.667$ (1), $c = 18.120$ (3) Å, $\beta = 106.87$ (1)°, $Z = 8$, $\rho_c = 1.46$ Mg m⁻³. The dimensions of the two molecules in the asymmetric unit are the same within the error of the determination. The coordination geometry of the P atom is nearly tetrahedral with an average P=Se distance of 2.106 (1) Å and an average P—C distance of 1.826 (13) Å. The bond angles around the P atom range from 103.4 (4) to 113.8 (3)° with an average Se—P—C angle of 113.1 (8)° and average C—P—C angle of 106 (2)°.

Introduction. This study is a continuation of the investigation of an isostructural series of chalcogenide ligands of the type $(C_6H_5)_3M=Y$. The triphenylphosphine sulfide (TPPS) structure ($M = P$, $Y = S$) has been reported (Coddling & Kerr, 1978) and the determinations of the arsine sulfide and stibine sulfide structures are in progress.

Crystals were obtained as colorless laths from acetone. Weissenberg photographs indicated that they

were isostructural with TPPS and that the space group was $P2_1/c$ (systematic absences of the type $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$). A crystal of dimensions 0.20 × 0.16 × 0.27 mm was coated with epoxy resin to prevent the loss of elemental Se and used for intensity data collection on a Picker FACS-1 diffractometer with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). The data were collected in the θ - 2θ scan mode at a scan rate of 1° min⁻¹ with a scan width of $\Delta 2\theta = (1.6 + 0.285 \tan \theta)$ °. Background counts were measured for 20 s at either end of the scan. The data were measured to a maximum $\sin \theta/\lambda$ of 0.562 Å⁻¹; of the 4119 reflections measured, 2481 had intensities greater than $3\sigma(I)$ where $\sigma(I) = [T + k^2B + (0.02I)^2]^{1/2}$ and T is the total peak count, B is the total background count, and k is the time factor to normalize B to the time interval of the scan.

Data were corrected for absorption [$\mu(\text{Cu } K\alpha) = 4.498$ mm⁻¹] by analytical methods. The value of the correction ranged from 1.77–2.96. Since the structure is isomorphous with TPPS, the TPPS coordinates were used to start the refinement. The positions and thermal parameters of the heavy atoms were refined in large blocks (1 molecule/block). Positions of the H atoms

* Crystal Structure Studies of Group V Chalcogenide Compounds. III.