

meric in crystals and dissociates into monomers in benzene (Lawton, 1971).

Since the stereochemistry of a metal complex undoubtedly depends not only on the intramolecular metal-ligand interactions but also on the effect of the molecular environment, the appearance of different molecular shapes in solution and in the solid should be possible in some cases. In the description of the structure of coordination compounds, however, we frequently encounter a statement such as 'monomers and dimers are coexistent in solutions but the complex is monomeric in crystals'. Although it is doubtful whether both types of stable crystals corresponding to the monomeric and dimeric forms could always be obtained, such a conclusion may sometimes be misleading unless a careful examination of the polymorphism of the grown crystals is made. The crystal structure of the ' $\gamma$  form',  $\text{Hg}_3\text{Cl}_2\text{dtc}_4$ , will appear shortly in a separate paper.

The calculations in this study were carried out on FACOM 270-30 Computer installed in this Institute. Figs. 2 and 4 were drawn by *ORTEP* (Johnson, 1965). Other computations were made with the programs *ANSFR-32* (Fourier synthesis) and *RBDLS-32* (least-squares refinement) written by the author, and with the universal crystallographic computation system UNICS (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

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## Structure and Conformation of Orthorhombic L-Cysteine

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The crystal structure of an orthorhombic form of L-cysteine has been determined by X-ray diffraction. The molecule crystallizes in the space group  $P2_12_12_1$  with four molecules in a unit cell of dimensions  $a = 8.116 \pm 3$ ,  $b = 12.185 \pm 4$ ,  $c = 5.426 \pm 2$  Å; density  $D_x = 1.50$ ,  $D_{\text{meas}} = 1.47$  g cm<sup>-3</sup>. After full-matrix refinement, the  $R$  value was 3.75% for the 1062 observed reflexions. The molecule exists as a zwitterion with a three-dimensional network of hydrogen bonds. Conformational angles are close to those observed in other cysteinyl residues. The thiol hydrogen was not located.

### Introduction

Although the crystal structures of monoclinic cysteine and several closely related compounds have been determined by X-ray diffraction (Lakshminarayanan, Sasi-sekhara & Ramachandran, 1967; Harding & Long, 1968; Hendrickson & Karle, 1971) hydrogen atoms

were not located; hence, details of hydrogen bonding are not available for this class of compounds. Since such interactions are likely to be of importance in the biological activity we have attempted to provide details of the hydrogen-bond geometry as well as accurate bond distances and conformational parameters in our study of the orthorhombic form of L-cysteine.

### Experimental

Data were collected on a Picker automatic diffractometer equipped with a graphite monochromator and operated in the  $\theta$ - $2\theta$  scan mode with a scan rate of  $2^\circ \text{ min}^{-1}$  and a scan range of  $(2.0 + 0.692 \tan \theta)^\circ$ . Background was measured for 40 sec at either end of the scan. In order to minimize the occurrence of simultaneous reflexions, the crystal was oriented with its  $c$  axis about  $10^\circ$  from the  $\phi$  axis of the goniometer (Young, 1969). The orientation matrix and the cell dimensions were refined by a least-squares method (Busing & Levy, 1967) involving the parameters of 12 high-angle reflexions. Lorentz and polarization corrections were applied assuming that both the monochromator crystal and the sample crystal had ideal mosaic structure. No correction was made for absorption. Crystal data are given in Table 1.

Table 1. *Crystal data*

Molecular formula	$\text{C}_3\text{H}_7\text{NO}_2\text{S}$
Molecular weight	121.16
Habit	Prismatic $c$
Crystal size	$0.10 \times 0.12 \times 0.30$ mm
Space group	$P2_12_12_1$
$Z$	4 molecules/unit cell
$a$	$8.1156 \pm 0.0026$ Å
$b$	$12.1849 \pm 0.0042$
$c$	$5.4258 \pm 0.0020$
$V$	$536.54$ Å <sup>3</sup>
Density, density gradient	$1.47 \pm 0.02$ g cm <sup>-3</sup>
Density, calculated	$1.50$ g cm <sup>-3</sup>
Radiation	Mo $K\alpha$ , $0.7107$ Å,
Linear absorption coefficient, $\mu$	$4.78$ cm <sup>-1</sup>
Temperature	$23^\circ\text{C}$ , ambient
Number of independent reflexions	1383
Number of observed reflexions	1062
Maximum $\sin \theta/\lambda$	0.807

### Structure analysis

The location of the sulphur atom was determined from a sharpened Patterson function and used to calculate phases for the observed structure amplitudes. A subsequent Fourier synthesis revealed the locations of all the non-hydrogen atoms in the molecule. Refinement was achieved by full-matrix least-squares minimization of  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1.0/(1.0 + 0.02 F_o^2)$ . Scattering functions were provided in exponential form with coefficients for the heavy atoms as tabulated by Cromer & Mann (1968), and those appropriate to

bonded hydrogen from *International Tables for X-ray Crystallography* (1973). Values for the real and imaginary parts of the anomalous contribution were taken from *International Tables for X-ray Crystallography* (1962).

All hydrogen atoms other than the one attached to sulphur were clearly visible in a difference Fourier calculated at the end of isotropic refinement. Positions and isotropic thermal parameters of the hydrogen atoms were held constant in the first few cycles of anisotropic refinement of the heavy atoms, but were allowed to refine without constraints in subsequent cycles. When refinement had converged at  $R = 0.394$ , it was apparent that the data were affected by extinction. For a further two cycles an isotropic extinction parameter was included with the correction applied to the calculated structure factors in the manner suggested by Larson (1967, 1970). Although the value of the extinction parameter,  $g = 4.7(5) \times 10^{-4}$ , and the  $R$  value ratio (Hamilton, 1965) both indicate extinction to be important, the only parameter to show a change larger than twice the estimated standard deviation was the scale factor. A summary of the changes produced by introduction of the extinction parameter is given in Table 2. The final  $R$  value for the 1062 reflexions with  $F_o \geq 2.5\sigma(F_o)$  was 0.0375. The largest shift/error for any non-hydrogen parameter was 0.056. The standard deviation of an observation of unit weight was 0.8905. Although the effects of anomalous dispersion were included in the model, the  $D$  and  $L$  configurations refined to the same  $R$  value. The atomic parameters listed in Table 3 refer to the  $L$  configuration. Their standard deviations have been estimated from the full least-squares matrix. No corrections have been made for thermal motion.

A table of observed and calculated structure factors is available.\*

### Discussion

Bond lengths in the molecule are listed in Table 4, short contacts are in Table 5, and details of the geometry of the hydrogen bonds are given in Table 6. Figs. 1 and 2 are stereoscopic drawings of the molecule and the unit-cell contents, respectively.

\* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30147 (7pp.). Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Comparison of parameters with and without extinction correction*

Refinement parameters	No correction	Extinction correction
$R = \sum ( F_o  -  F_c ) / \sum  F_o $	0.0394	0.0375
$R(H) = \sum w( F_o  -  F_c ) / \sum w F_o^2$	0.0565	0.0548
$\{\sum w \Delta^2 / (m-n)\}^{1/2}$	0.9179	0.8905
Extinction parameter, $g$	0.0	$4.7(5) \times 10^{-4}$
Largest change in $\Delta F$ (002) reflexion	-6.6	-1.1
Largest parameter shift (scale, $\Delta/\sigma = 3.82$ )	4.690 (16)	4.755 (18)
$R$ -value ratio, $\mathcal{R} = 1.031$	$\mathcal{R}_{(1.973, 0.005)} = 1.0046$	

Table 3. Atomic parameters

Coordinates and their standard deviations are expressed as fractions of the cell edge. Fractional coordinates are  $\times 10^3$  for hydrogen atoms,  $\times 10^4$  for other atoms. Anisotropic temperature factors have been multiplied by  $10^5$ . They have the form  $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$  where  $\beta_{11} = 2\pi^2 a^{*2} U_{11}$ . IUPAC designation has been incorporated to facilitate comparison with other amino acids (IUPAC-IUB Commission on Biochemical Nomenclature, 1970).

IUPAC		<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
S $\gamma$	S(1)	4137.3 (9)	10256.7 (6)	6370 (2)	1092 (9)	422 (4)	5319 (40)	366 (9)	-877 (35)	-33 (21)
C $\beta$	C(1)	4244 (3)	8850 (2)	7431 (4)	852 (27)	505 (14)	1973 (67)	157 (35)	590 (73)	-14 (53)
C $\alpha$	C(2)	5797 (3)	8240 (2)	6655 (3)	822 (23)	293 (9)	1254 (45)	20 (27)	365 (62)	202 (36)
C	C(3)	5984 (3)	8218 (2)	3838 (4)	862 (25)	343 (10)	1270 (46)	-39 (28)	18 (61)	-46 (40)
N	N(1)	7282 (2)	8739 (2)	7831 (3)	812 (21)	399 (10)	1139 (41)	125 (26)	-84 (53)	17 (39)
O $^2$	O(1)	5042 (3)	7606 (2)	2685 (4)	1430 (31)	757 (16)	1980 (54)	-1021 (40)	-339 (70)	-380 (50)
O $^1$	O(2)	7068 (3)	8827 (2)	2912 (3)	1280 (28)	579 (13)	1153 (39)	-672 (33)	440 (58)	-69 (39)
H $\beta^2$	H(2)	418 (5)	849 (3)	927 (8)	3.84 (84)					
H $\beta^1$	H(3)	338 (5)	846 (3)	684 (7)	2.95 (69)					
H $\alpha$	H(4)	569 (5)	748 (3)	720 (7)	2.71 (67)					
H $^1$	H(5)	813 (7)	835 (4)	739 (10)	5.95 (1.23)					
H $^2$	H(6)	743 (5)	954 (3)	730 (9)	4.57 (94)					
H $^3$	H(7)	711 (5)	881 (3)	947 (8)	3.02 (79)					

Table 4. Molecular dimensions

Bond lengths (Å)		Bond angles (°)	
S(1)-C(1)	1.811 (3)	S(1)-C(1)-C(2)	114.4 (2)
C(1)-C(2)	1.522 (3)	S(1)-C(1)-H(2)	102 (2)
C(2)-C(3)	1.537 (3)	S(1)-C(1)-H(3)	110 (2)
C(2)-N(1)	1.493 (3)	H(2)-C(1)-H(3)	112 (3)
C(3)-O(1)	1.238 (3)	C(2)-C(1)-H(2)	112 (2)
C(3)-O(2)	1.256 (3)	C(2)-C(1)-H(3)	107 (2)
		C(1)-C(2)-C(3)	111.4 (2)
C(1)-H(2)	1.01 (4)	C(1)-C(2)-N(1)	110.6 (2)
C(1)-H(3)	0.91 (4)	C(3)-C(2)-N(1)	110.6 (2)
C(2)-H(4)	0.97 (4)	C(1)-C(2)-H(4)	108 (2)
N(1)-H(5)	0.87 (6)	C(3)-C(2)-H(4)	107 (2)
N(1)-H(6)	1.02 (4)	N(1)-C(2)-H(4)	109 (2)
N(1)-H(7)	0.91 (4)		
		C(2)-N(1)-H(7)	110 (2)
		C(2)-N(1)-H(6)	111 (3)
		C(2)-N(1)-H(5)	107 (3)
		H(7)-N(1)-H(5)	117 (4)
		H(6)-N(1)-H(5)	111 (4)
		H(7)-N(1)-H(6)	101 (4)
		O(2)-C(3)-O(1)	125.9 (2)
		O(2)-C(3)-C(2)	116.9 (2)
		O(1)-C(3)-C(2)	117.2 (2)

Torsional angles  
 $\psi_1 = -16.5^\circ$   
 $\psi_2 = 163.0$   
 $\chi_1 = 65.3$

Table 5. Short contact distances between non-hydrogen atoms

Symmetry operations with necessary translation components are defined relative to the central molecule in Fig. 2.

	Symmetry operation	A...B	$\angle C-A...B$
S(1)...O(2)	$(\frac{1}{2}-x, 2-y, \frac{1}{2}+z)$	3.381 Å	101.0°
S(1)...O(2)	$(x, y, z)$	3.495	70.5
S(1)...O(1)	$(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3.671	157.0
S(1)...S(1)	$(\frac{1}{2}-x, 2-y, -\frac{1}{2}+z)$	3.849	95.9
N(1)...O(2)	$(x, y, z)$	2.677	62.5
N(1)...O(2)	$(x, y, 1+z)$	2.764	113.0
N(1)...O(1)	$(\frac{1}{2}+x, 1\frac{1}{2}-y, 1-z)$	2.790	115.0
N(1)...O(2)	$(\frac{1}{2}-x, 1-y, \frac{1}{2}+z)$	3.013	123.3
N(1)...S(1)	$(x, y, z)$	3.250	65.2

Table 6. Geometry of hydrogen bonds

	N-H	N-H...O	H...O	$\angle N-H...O$	$\angle C-N...O$
H(5)...O(1)	0.87 Å	2.790 Å	1.94 Å	165°	115.0°
H(6)...O(2)	1.03	3.013	2.06	154	123.3
H(7)...O(2)	0.91	2.764	1.86	170	113.0

In its orthorhombic form, cysteine exists as a zwitterion, with the three hydrogens from the nitrogen forming distinct hydrogen bonds with oxygen atoms on neighbouring molecules, thus binding the structure together in three dimensions. The short intramolecular contact of 2.677 Å between O(2) and N(1) has not been interpreted as a hydrogen bond because the disposition of the hydrogens is unfavourable. The lengthening of the C(3)-O(2) bond relative to C(3)-O(1) can be attributed to the fact that O(2) acts as an acceptor in two hydrogen bonds while O(1) is involved only in one.

The sulphur atom makes several short contacts with atoms that could be acceptor atoms for S-H...B hydrogen bonds. These are detailed in Fig. 3. In order for hydrogen bonding of this type to occur, the C-S...B angle would have to be similar to the H-S-H angle of 92° observed in H<sub>2</sub>S (Srinivasan & Chacko, 1967). This suggests that the thiol group could form a hydrogen bond with S(1) at  $(\frac{1}{2}-x, 2-y, -\frac{1}{2}+z)$  or with O(2) at  $(1\frac{1}{2}-x, 2-y, \frac{1}{2}+z)$ . The corresponding S...S and S...O distances of 3.849 and 3.381 Å are shorter than expected for non-bonded contacts and

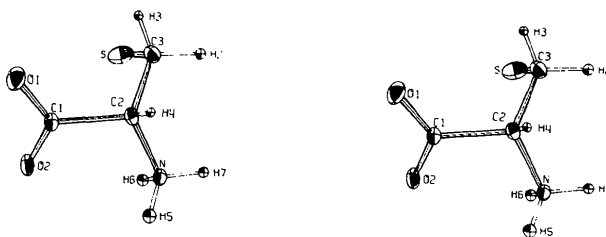


Fig. 1. Stereoscopic view of L-cysteine molecule showing 50% probability vibration ellipsoids. The  $U_{33}$  parameter on sulphur is high relative to other thermal parameters in the molecule.

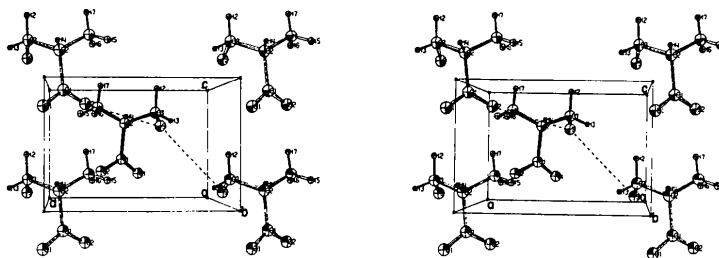


Fig. 2. Stereoscopic view of unit cell contents. Dotted lines indicate possible hydrogen bonds involving sulphur as donor.

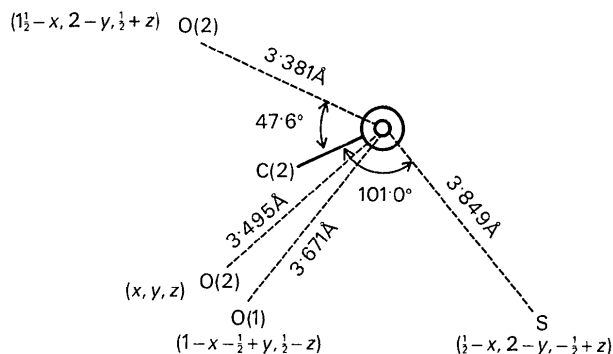


Fig. 3. Environment of sulphur atom viewed along S-C bond. Symmetry operations and orientation are defined relative to the central molecule in Fig. 2.  $B \cdots S-C$  projection angles shown for possible hydrogen bonds.

the corresponding  $C-S \cdots B$  angles of  $95.9$  and  $101.0^\circ$  would appear favourable. However, our results are not conclusive since we did not locate the thiol hydrogen. Difference maps computed with refined data are featureless except for two peaks of about  $0.4 \text{ \AA}^{-3}$  which lie within  $0.6 \text{ \AA}$  of the sulphur position in a line roughly parallel to the major axis of the vibration ellipsoid. This, coupled with the fact that the  $U_{33}$  parameter for sulphur is much higher than any other anisotropic vibration parameter in the structure (Fig. 1) suggests that the sulphur atom is disordered. We hope to investigate this matter more fully in a neutron diffraction study in the near future.

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Calculations were carried out on a CDC 6400 computer at The University of Calgary with programs supplied by A. C. Larson and modified by the authors to meet the constraints of the local installation. Particular thanks are due to Dr Iain C. Paul who produced the stereo diagrams used in this paper.

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