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## A Neutron Diffraction Study of L-Cysteine

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The orthorhombic form of L-cysteine,  $C_3H_7NO_2S$ , crystallizes in space group  $P2_12_12_1$  with four molecules in a unit cell of dimensions  $a = 8.116$  (3),  $b = 12.185$  (4), and  $c = 5.426$  (2) Å. A three-dimensional neutron diffraction study has provided a more precise description of the hydrogen bonds than was possible in the X-ray experiment. In addition, the neutron study has confirmed that the disordered thiol group is involved in two short contacts, one to oxygen and the other to sulphur. The disorder can be modeled as involving only the hydrogen of the thiol group, or as involving both hydrogen and sulphur. Parameters resulting from both models are presented.

### Introduction

There has been some discussion in the literature as to whether sulphur can act as a donor in hydrogen bonding (Srinivasan & Chacko, 1967; Hamilton & Ibers, 1968; Paul, 1974). In our X-ray study of orthorhombic L-cysteine (Kerr & Ashmore, 1973) we found that the sulphur atom was involved in two short intermolecular contacts, one with oxygen and one with a symmetry-related sulphur; but we were not able to locate the thiol hydrogen in difference maps. The present study is part of a series of precision neutron diffraction studies of amino acids and peptides being carried out at Brookhaven National Laboratory.\*

### Experimental

Neutron diffraction data were collected at room temperature on a computer-controlled four-circle diffractometer at the Brookhaven High Flux Beam Reactor using the multi-spectrometer control system (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Norton, 1966). In all, 1960 reflections with  $\sin \theta/\lambda \leq 0.680$  were

measured at a neutron wavelength of 1.012 Å using a  $\theta$ - $2\theta$  step can. A fixed scan range of  $3.0^\circ$  and a step increment of  $0.06^\circ$  were used for low-angle data ( $\sin \theta/\lambda \leq 0.494$ ). For the high-angle data the scan range was determined by the expression  $\Delta 2\theta = 1.0^\circ (1.1 + 8.8 \tan \theta)$  and the step increment was adjusted to give about 40 steps per reflection. In order to minimize the occurrence of simultaneous reflections, the crystal was oriented with its  $c$  axis about  $5^\circ$  from the axis of the goniometer (Young, 1969). The unit-cell constants shown in Table 1 and the orientation matrix were determined by least-squares refinement of setting angles of 25 high-angle reflections. Two standards, measured after every 60 reflections, showed maximum deviations of less than 2.5% from their mean values. Background corrections were made using a method that defines the peak by two points that minimize  $\sigma(I)/I$  (Lehmann & Larsen, 1974).

Squared structure amplitudes were defined as  $F_o^2 = I \sin 2\theta$  and corrected for absorption using Gaussian numerical integration with the crystal shape defined by eight rational planes. The linear absorption coefficient was calculated assuming the incoherent scattering cross section for hydrogen to be 40 barn and using the value of  $(\mu/\rho)$  for C, N, O, S tabulated in *International Tables for X-ray Crystallography* (1968). Resulting transmission factors were in the range 0.76 to 0.88.

\* This paper is regarded as part XVI in the series *Precision Neutron Diffraction Determination of Protein and Nucleic Acid Components*.

Table 1. *Crystal data*

L-Cysteine, C <sub>3</sub> N <sub>7</sub> NO <sub>2</sub> S	F.W. 121.16
Crystal volume: 1.68 mm <sup>3</sup>	
Space group <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>Z</i> = 4
Neutron*	X-ray
<i>a</i> = 8.1159 (32) Å	8.1156 (26) Å
<i>b</i> = 12.1774 (49)	12.1849 (42)
<i>c</i> = 5.4287 (30)	5.4258 (20)
$\lambda = 1.0120$ (7) Å (crystal-monochromatized)	
Linear absorption coefficient: 2.098 cm <sup>-1</sup>	
Temperature: 23°C (ambient)	
Number of independent reflections: 831	
Number of reflections $I \geq 3\sigma(I)$ : 674	
Max. $\sin \theta/\lambda = 0.680$ Å <sup>-1</sup>	

\* Since the neutron wavelength was measured indirectly, the X-ray values for the cell constants are considered to be more precise and have been used throughout.

### Structure determination and refinement

Structure factors were calculated from heavy-atom positions determined in our earlier X-ray study (Kerr & Ashmore, 1973) using scattering lengths as tabulated by the Neutron Diffraction Commission (1969). In addition to the six hydrogens previously located in the X-ray study, a difference map showed two smaller peaks about 1.2 Å from the sulphur atom. In the subsequent full-matrix refinement, population factors for the half-hydrogens were refined along with positional and thermal parameters for all atoms and an isotropic extinction parameter (Zachariasen, 1963). The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $v/w = [\sigma^2(F) + 0.02F^2]^{-1/2}$  and  $\sigma(F)$  was derived from counting statistics. When refinement was terminated the maximum shift/error was less than 0.025. The conventional *R* value was 4.58% and  $wR = \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2$

was 4.12% for the 674 reflections with intensities significantly above background. The standard deviation of an observation of unit weight was 2.20.

A table of observed and calculated structure factors is available.\* These data correspond to refinement with ordered sulphur.

### Disordered model for thiol group

In both the X-ray and neutron experiments the sulphur atom appears to be highly anisotropic. In addition, the only significant peaks on a difference map calculated with refined X-ray data occur within 0.6 Å of the sulphur position on a line roughly parallel to the major axis of the vibration ellipsoid. These features imply that sulphur is disordered and that the two sites overlap.

To a first approximation, the disorder was described with two half-sulphurs separated by a distance of 0.3 Å in the direction parallel to *u*<sub>33</sub>. This model was then refined without constraints but positions were refined separately from thermal and occupancy parameters because of high correlation coefficients. Refined values of the occupancy parameters were 0.55 (3) and 0.43 (3) for S(1*A*) and S(1*B*) which compare with the occupancies of 0.61 (3) and 0.44 (3) for the corresponding hydrogen sites H(1*A*) and H(1*B*). Parameters for both ordered and disordered sulphur are presented in Table 2. Introduction of 11 additional parameters gave agreement values *R* = 4.53% and  $wR$  = 4.07%. Al-

\* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30968 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic parameters*

Coordinates and their standard deviations expressed as fractions of the cell edge. Anisotropic temperature factors have been multiplied by 10<sup>3</sup>. They have the form  $T = \exp \{-2\pi^2(h^2 a^{*2} u_{11} + \dots + 2hka^*b^*u_{12} + \dots)\}$ . IUPAC designation has been incorporated to facilitate comparison with other amino acids (IUPAC-IUB Commission on Biochemical Nomenclature, 1970).

		<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i> <sub>11</sub>	<i>u</i> <sub>22</sub>	<i>u</i> <sub>33</sub>	<i>u</i> <sub>12</sub>	<i>u</i> <sub>13</sub>	<i>u</i> <sub>23</sub>
S <sup>γ</sup>	S(1)	0.4129 (9)	1.0252 (6)	0.6405 (16)	38 (3)	39 (3)	74 (5)	9 (3)	-11 (4)	0 (3)
C <sup>β</sup>	C(1)	0.4238 (3)	0.8850 (2)	0.7418 (5)	28 (1)	37 (1)	36 (1)	3 (1)	8 (1)	-2 (1)
C <sup>α</sup>	C(2)	0.5803 (3)	0.8242 (2)	0.6652 (4)	30 (1)	23 (1)	16 (1)	1 (1)	5 (1)	3 (1)
C	C(3)	0.5984 (3)	0.8217 (2)	0.3844 (4)	28 (1)	25 (1)	18 (1)	-3 (1)	-1 (1)	-3 (1)
N	N(1)	0.7282 (2)	0.8736 (2)	0.7835 (3)	26 (1)	32 (1)	15 (1)	5 (1)	5 (1)	1 (1)
O <sup>2</sup>	O(1)	0.5038 (4)	0.7605 (3)	0.2695 (7)	45 (2)	58 (2)	35 (2)	-25 (2)	-3 (2)	-8 (2)
O <sup>1</sup>	O(2)	0.7063 (4)	0.8820 (3)	0.2910 (6)	43 (2)	45 (2)	22 (1)	-17 (2)	3 (1)	-7 (1)
H <sup>γ</sup>	{ H(1 <i>A</i> )	0.3681 (18)	1.0054 (14)	0.4142 (24)	120 (14)	122 (13)	77 (10)	43 (10)	-11 (9)	32 (9)
	{ H(1 <i>B</i> )	0.5085 (27)	1.0666 (14)	0.7966 (63)	110 (16)	548 (10)	208 (30)	1 (1)	-64 (20)	-28 (15)
H <sup>β1</sup>	H(2)	0.4119 (9)	0.8853 (6)	0.9395 (12)	72 (4)	97 (5)	43 (3)	22 (4)	24 (4)	1 (4)
H <sup>β2</sup>	H(3)	0.3181 (6)	0.8434 (5)	0.6670 (15)	35 (3)	66 (4)	97 (5)	-11 (3)	5 (4)	-9 (4)
H <sup>α</sup>	H(4)	0.5707 (7)	0.7392 (4)	0.7341 (11)	55 (3)	33 (2)	47 (3)	-2 (2)	11 (3)	9 (2)
H <sup>1</sup>	H(5)	0.8337 (6)	0.8305 (4)	0.7352 (11)	32 (2)	66 (3)	40 (3)	9 (2)	4 (2)	-3 (3)
H <sup>2</sup>	H(6)	0.7433 (6)	0.9536 (4)	0.7353 (11)	56 (3)	43 (3)	42 (3)	-12 (3)	1 (3)	7 (2)
H <sup>3</sup>	H(7)	0.7173 (6)	0.8716 (4)	0.9771 (10)	48 (3)	47 (3)	29 (3)	0 (3)	-5 (2)	2 (3)
		Scale = 0.959 (5)	<i>g</i> = 0.38 (15) × 10 <sup>-3</sup>							

### Disordered sulphur

S(1 <i>A</i> )	0.4073 (19)	1.0279 (10)	0.6697 (22)	44 (8)	30 (7)	62 (8)	4 (7)	-2 (7)	-12 (5)
S(1 <i>B</i> )	0.4184 (20)	1.0217 (13)	0.6113 (20)	24 (8)	43 (10)	23 (6)	19 (8)	-4 (6)	-5 (5)
		Scale = 0.958 (2)	<i>g</i> = 0.41 (12) × 10 <sup>-3</sup>						

though the change in  $R$  value is not significant at this level of refinement (Hamilton, 1965), the results are chemically reasonable.

Table 3. *Molecular geometry*

Covalent bond lengths (Å)			
	Neutron	X-ray	Difference
S(1)—C(1)	1.796 (8)	1.811 (3)	-0.015 (9)
C(1)—C(2)	1.529 (4)	1.522 (3)	+0.007 (5)
C(2)—C(3)	1.530 (3)	1.537 (3)	-0.007 (4)
C(2)—N(1)	1.488 (3)	1.493 (3)	-0.005 (4)
C(3)—O(1)	1.239 (4)	1.238 (3)	+0.001 (5)
C(3)—O(2)	1.251 (4)	1.256 (3)	-0.005 (5)
C(1)—H(2)	1.077 (7)	1.01 (4)	0.07 (4)
C(1)—H(3)	1.076 (7)	0.91 (4)	0.17 (4)
C(2)—H(4)	1.104 (5)	0.97 (4)	0.13 (4)
N(1)—H(5)	1.038 (5)	0.87 (6)	0.17 (6)
N(1)—H(6)	1.017 (6)	1.02 (4)	0.00 (5)
N(1)—H(7)	1.055 (5)	0.91 (4)	0.15 (5)
S(1)—H(1A)	1.30 (2)		
S(1)—H(1B)	1.25 (3)		
Disordered S			
S(1A)—H(1A)	1.45 (2)		
S(1B)—H(1B)	1.36 (3)		
S(1A)—C(1)	1.790 (1)		
S(1B)—C(1)	1.810 (1)		
Bond angles (°)			
S(1)—C(1)—C(2)	114.8 (3)	114.4 (2)	
S(1)—C(1)—H(2)	107.3 (5)	102 (2)	
S(1)—C(1)—H(3)	107.1 (5)	110 (2)	
H(2)—C(1)—H(3)	107.8 (6)	112 (2)	
C(2)—C(1)—H(2)	110.3 (5)	112 (2)	
C(2)—C(1)—H(3)	109.3 (4)	107 (2)	
C(1)—C(2)—C(3)	111.1 (2)	111.4 (2)	
C(1)—C(2)—N(1)	110.9 (2)	110.6 (2)	
C(3)—C(2)—N(1)	111.1 (2)	110.6 (2)	
C(1)—C(2)—H(4)	107.7 (3)	108 (2)	
C(3)—C(2)—H(4)	109.0 (4)	107 (2)	
N(1)—C(2)—H(4)	106.9 (3)	109 (2)	
C(2)—N(1)—H(7)	110.6 (3)	110 (2)	
C(2)—N(1)—H(6)	112.0 (3)	111 (3)	
C(2)—N(1)—H(5)	110.6 (3)	107 (3)	
H(7)—N(1)—H(5)	108.0 (4)	117 (4)	
H(6)—N(1)—H(5)	108.7 (4)	111 (4)	
H(7)—N(1)—H(6)	106.8 (4)	101 (4)	
O(2)—C(3)—O(1)	125.7 (3)	125.9 (2)	
O(2)—C(3)—C(2)	117.3 (2)	116.9 (2)	
O(1)—C(3)—C(2)	117.0 (2)	117.2 (2)	
H(1A)—S(1)—C(1)	97 (1)		
H(1B)—S(1)—C(1)	98 (1)		
Disordered sulphur			
H(1A)—S(1A)—C(1)	92 (1)		
H(1B)—S(1B)—C(1)	94 (1)		

### Comparison of neutron and X-ray results

There is very satisfactory agreement between parameters determined in the two experiments. In general, the precision of the heavy atoms is comparable although the  $z$  coordinates tend to be less well determined in the neutron experiment. Although the e.s.d.'s of the sulphur positional parameters appear to have been underestimated in the X-ray experiment, none of the differences in the parameters of the non-hydrogen atoms is significant in terms of the combined standard deviations of the two experiments. In particular, thermal ellipsoids calculated for the 'ordered sulphur' model in the neutron experiment agree in size, shape and orientation with those determined in the X-ray study.

Agreement between the covalent bond lengths and bond angles is shown in Table 3. Neither the neutron nor the X-ray distances have been corrected for thermal motion. The main differences lie in the more precise placement of hydrogens in the neutron experiment, location of the thiol hydrogens and a more realistic estimate of the uncertainty in the C(1)—S bond length. Even the hydrogen distances are in relatively good agreement, although those measured in the X-ray

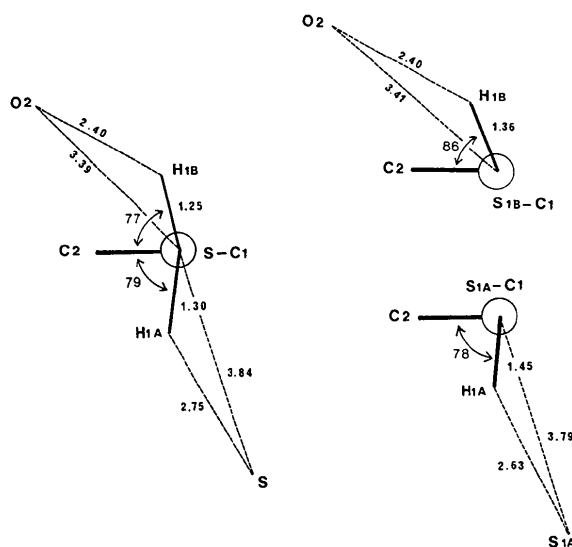


Fig. 1. Environment of sulphur atom for both ordered and disordered models viewed along sulphur-carbon bond.

Table 4. *Geometry of hydrogen bonds*

	A-H	A-H...B	H...B	$\angle$ A-H...B	$\angle$ C-A...B
N(1)—H(5)···O(1)	1.038 (5)	2.784 (4)	1.770 (6)	164.5 (5)	111.5 (2)
N(1)—H(6)···O(2)	1.017 (6)	3.025 (4)	2.066 (6)	156.3 (5)	123.1 (1)
N(1)—H(7)···O(2)	1.065 (5)	2.762 (4)	1.710 (6)	174.1 (5)	113.2 (1)
S(1)—H(1A)···S(1)	1.30 (2)	3.84 (1)	2.75 (2)	140 (4)	95.6 (2)
S(1)—H(1B)···O(2)	1.25 (3)	3.391 (8)	2.40 (2)	134 (2)	101.5 (2)
Disordered sulphur					
S(1A)—H(1A)···S(1A)	1.45 (2)	3.79 (2)	2.63 (2)	134 (1)	91.8 (5)
S(1B)—H(1B)···O(2)	1.36 (3)	3.41 (2)	2.40 (2)	128 (1)	100.6 (5)

experiment are systematically short. The mean N–H distances are 0.93 (6) and 1.037 (7) Å while the mean C–H distances are 0.96 (5) and 1.086 (8) Å for the X-ray and neutron experiments, respectively.

### Discussion

Both the crystal and molecular structure of L-cysteine appear to be strongly influenced by the N–H···O hydrogen bonds whose dimensions are detailed in Table 4. The usual correlations between bond length and bond strength are observed. Stronger hydrogen bonds are characterized by longer N–H distances, shorter O···H distances, NH···O angles near 180° and CN···O angles near tetrahedral. However, the C–N···O angle appears to be less sensitive to bond strength than the N–H···O angle.

These hydrogen bonds provide electrostatic interactions that bind the structure together in three dimensions and dominate the conformation of the molecule by maintaining the 17° torsional angle about the C(2)–C(3) bond (see Table 5). The strongest interaction is between N and O(2) of the molecule related by a translation in the *c* direction; the next strongest involves O(1) of the molecule related by the screw axis parallel to *x* at  $y = \frac{1}{4}$ ; and the third involves O(2) of the molecule related by the screw axis parallel to *z*.

Table 5. *Torsional angles*

A positive number indicates that a clockwise rotation will cause the first-named atom to eclipse the last.

H(1A)–S(1A)–C(1)–C(2)	77.57°
H(1A)–S(1A)–C(1)–H(3)	–47.63
H(1B)–S(1B)–C(1)–H(2)	38.88
H(1B)–S(1B)–C(1)–C(2)	–85.39
S(1A)–C(1)–C(2)–C(3)	–63.87
S(1A)–C(1)–C(2)–N(1)	60.23
S(1B)–C(1)–C(2)–C(3)	–55.09
S(1B)–C(1)–C(2)–N(1)	69.01
H(2)–C(1)–C(2)–H(4)	60.03
H(3)–C(1)–C(2)–H(4)	–58.37
H(2)–C(1)–C(2)–N(1)	–56.57
H(3)–C(1)–C(2)–C(3)	60.93
N(1)–C(2)–C(3)–O(2)	–17.00
C(1)–C(2)–C(3)–O(2)	106.98
C(1)–C(2)–C(3)–O(1)	–72.52
H(4)–C(2)–C(3)–O(1)	46.00
C(3)–C(2)–N(1)–H(5)	–57.67
C(3)–C(2)–N(1)–H(6)	+63.73
C(1)–C(2)–N(1)–H(6)	–60.37
C(1)–C(2)–N(1)–H(7)	58.60
H(4)–C(2)–N(1)–H(5)	61.11
H(4)–C(2)–N(1)–H(7)	–58.52

The difference in length between the two C–O bonds of the carboxyl group is highly significant and arises from the marked difference in the environments of the two atoms. The atom O(1) with the shorter covalent bond to carbon has only one hydrogen-bonding interaction with H(5), while O(2) has weak interactions with H(6) and the ‘half-hydrogen’ H(1B) and a strong

interaction with H(7). Qualitative use of the bond-length bond-valence correlations of Brown & Shannon (1973) suggest that these interactions are important for local minimization of charge.

### Possible hydrogen bonds involving the thiol group

The environment of the sulphur atom is shown in Fig. 1 and Table 4 for both the ordered and disordered refinements. The disordered thiol hydrogen is involved in two intermolecular interactions; one with O(2) at  $1\frac{1}{2} - x, 2 - y, \frac{1}{2} + z$  and one with S at  $\frac{1}{2} - x, 2 - y, -\frac{1}{2} + z$ . Although the S···S and S···O distances suggest these may be hydrogen bonds, the H···O and H···S distances are too close to normal van der Waals distances to warrant such a description (Bondi, 1964). Both models show that the bonded S–H distance is longer in the S–H···S contact than in the S–H···O which would imply that the S–H···S interaction is the stronger of the two. However, the refinement with ordered sulphur does not show the expected correlation in the H···acceptor distances. In the ‘disordered sulphur’ refinement the S(1B)–H(1B) distance in the SH···O contact is close to the value of 1.33 Å reported in H<sub>2</sub>S (Allen & Plyler, 1956). However, the hydrogen position lies more than 25° from the donor–acceptor line and the H···O distance is not shortened below the usual van der Waals distance of 2.40 Å. In the S–H···S contact, the bonded S(1A)–H(1A) distance is lengthened to 1.45 Å and the H···S distance is contracted to 2.65 Å which is significantly less than the sum of the van der Waals radii. These results imply that the interaction with sulphur is stronger than that with oxygen. This is contrary to what would have been expected on the basis of electronegativity of the acceptor atoms. However, it can be noted that O(2) is involved in two other hydrogen bonds. Such interaction would decrease both the conformational mobility of O(2) and its valence requirement thus reducing its availability as an acceptor for the thiol hydrogen.

### Conclusion

Disorder in the thiol group of L-cysteine can be considered to involve both hydrogen and sulphur or just hydrogen. The model with ordered sulphur gives bond length and angles that are somewhat unusual and does not show the expected contraction of the H···S distance below the van der Waals contact distance of 2.75 Å. The model with disordered sulphur gives results that appear to be more meaningful. Bond lengths and angles lie close to expected values, and the dimensions of the hydrogen bonds are consistent with their apparent strength. The S–H···S bond has a longer S–H bond length and a more significant contraction of the H···acceptor distance than the S–H···O bond. Although the model with both sulphur and hydrogen disordered does not significantly improve the *R* value for the refinement, we feel that it is valid.

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## The Crystal Structure of Hopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$

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The structure of hopeite,  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , has been redetermined. It crystallizes in the orthorhombic system with cell dimensions  $a = 10.629$  (2),  $b = 18.339$  (3),  $c = 5.040$  (1) Å. The space group is *Pnma* and there are four molecules in the unit cell. Least-squares refinement has been completed on three-dimensional data (1471 structure factors). The H atoms have been located and included in the refinement with an isotropic temperature factor of 4.0. The final residual is 6.8%. The structure consists of  $\text{ZnO}_2(\text{H}_2\text{O})_4$  octahedra,  $\text{ZnO}_4$  tetrahedra and  $\text{PO}_4$  tetrahedra, none of which are regular; these polyhedra share corners and edges. The mean (uncorrected) bond lengths are 2.099 (3) Å in the  $\text{ZnO}_2(\text{H}_2\text{O})_4$  octahedron, 1.963 (3) Å in the  $\text{ZnO}_4$  tetrahedron and 1.537 (3) Å in the  $\text{PO}_4$  tetrahedron. The thermal vibrations have been analysed and the mean corrected bond length in the  $\text{ZnO}_2(\text{H}_2\text{O})_4$  octahedron is 2.101 Å, assuming riding motion.

### Introduction

The crystal structure of hopeite has been determined twice with different results. In one case the structure reported (Mamedov, Gamidov & Belov, 1961; Gamidov, Golovachev, Mamedov & Belov, 1963) suggests that hopeite is similar to the diaspore  $\text{AlOOH}$ -goethite  $\text{FeOOH}$  structure and the structure factor of the (*hk*0) projection refined to a residual of 24% even without corrections for temperature factors. However, using the same projection, Liebau (1965) reported a completely different structure with certain similarities to the already reported structure of phosphophyllite,  $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  (Kleber, Liebau & Piatkowiak, 1961); in this case a final residual of 14.4% was given.

In view of the completely different structure, it was decided to redetermine the structure with three-dimensional data.

### Experimental

Attempts to grow crystals suitable for investigation failed but finally a naturally occurring specimen was obtained by courtesy of the Keeper of Minerals, Department of Mineralogy, British Museum (Natural History). The original source of the specimen was the Broken Hill Mines, North-Western Rhodesia (specimen number BM 1907, 240). The crystal chosen for the intensity measurements was colourless and of triangular prismatic habit parallel to [001]. The crystal optics and