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The Crystal and Molecular Structure of Glycyl-L-histidyl-glycinatocopper(II) Dihemihydrate

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The crystal and molecular structure of glycyl-L-histidyl-glycinatocopper(II) dihemihydrate [CuGHG.2($\frac{1}{2}H_2O$)], $C_{10}H_{13}O_4N_5Cu.2(\frac{1}{2}H_2O)$, has been determined from three-dimensional X-ray counter data by Patterson and Fourier methods. The compound crystallizes in the monoclinic space group $C2$ with four formula units per cell. The cell dimensions are $a = 19{\cdot}040$ (6), $b = 6{\cdot}943$ (4), $c = 12{\cdot}201$ (4) Å and $\beta = 103{\cdot}89$ (2)°. Full-matrix least-squares refinement using 1948 independent reflections reached $R = 0{\cdot}035$. The Cu atom is six-coordinate. The four closest donor atoms, which form an approximate square plane about the Cu, are the amino, peptide and imidazole N atoms of one ligand and a carboxyl O of another. The distances Cu–N(amino), Cu–N(peptide), Cu–N(imidazole) and Cu–O(carboxyl) are 1·997 (3), 1·951 (3), 1·957 (3) and 1·996 (3) Å respectively. The distorted octahedral geometry about the Cu atom is completed, at much longer distances, by the second O atom of the carboxyl group, and by a water molecule. The distances Cu–O and Cu–*W* are 2·817 (4) and 2·784 (4) Å respectively. Each tripeptide binds two Cu atoms and, therefore, produces a polymeric chain of Cu–tripeptide–Cu–tripeptide units extending approximately along the crystallographic *a* axis. The crystal arrangement is stabilized by an extensive network of hydrogen bonds of the types N–H···O, N–H···*W*, *W*–H···O, and *W*–H···*W*. The structure of this monoclinic form of CuGHG is very similar to that of the orthorhombic modification, but quite different from that of the tetragonal form.

Introduction

There is an increasing interest in Cu complexes with peptides because of their potential use as models in the study of the interactions of this metal with proteins (Osterberg, 1974). Up to now, only a limited number of X-ray structural determinations of Cu–peptide complexes are available. Among histidine-containing peptide complexes, the structure of Cu–glycyl-L-histidine (Blount, Frazer, Freeman, Szymanski & Wang, 1967) and, more recently, that of copper glycyl-glycyl-L-histidine-*N*-methylamide (Camerman, Camerman & Sarkar, 1976) have been reported. In this laboratory we have recently determined the structure of the product of the reaction of copper hydroxide with glycyl-glycyl-L-histidine and found that the peptide underwent an oxidative decarboxylation upon coordinating to the metal (de Meester & Hodgson, 1976).

The crystal structures of two forms of glycyl-L-histidyl-glycinatocopper(II) have been investigated by Osterberg, Sjoberg & Soderquist (1972*a*,*b*). In the orthorhombic modification, $CuGHG.NaClO_4.H_2O$, each tripeptide binds strongly to one Cu center through N(amino), N(peptide), and N(imidazole) and to a second Cu center through O(carboxylate). In addition, the other terminal carboxylate O atom also binds weakly to this second Cu atom. The sixth site of the distorted (4 + 2) octahedral geometry at Cu is occupied by a water molecule. The structure, therefore, consists of infinite chains of Cu–peptide–Cu linkages containing six-coordinated Cu centers. In the tetragonal modification, $CuGHG.nH_2O$, the three N donors of one residue again coordinate to a single Cu atom, but in this case the structure is dimeric, the two Cu centers being linked by carboxylate O atoms from two other ligands. The Cu atoms in this modification are five-coordinated.

We have recently obtained excellent crystals of a third (monoclinic) form, formulation CuGHG.2($\frac{1}{2}H_2O$), in this system. In view of the great differences between the two earlier forms, and the relative lack of precision in one of those two structures as a result of high water content, we felt it worthwhile to undertake an accurate structural determination of this new modification. The results of our investigation are reported here.

Experimental

Crystals of the title compound are blue rectangular plates. Preliminary Weissenberg and precession photographs indicated a monoclinic lattice, whose systematic absences ($h + k = 2n + 1$) are consistent with space groups $C2$, Cm and $C2/m$. The centrosymmetric space group $C2/m$ was disregarded because of the chirality of the ligand, as was the noncentrosymmetric space group Cm. The space group $C2$ was assigned and, later, the successful structure analysis in this space group proved this choice to be correct. Accurate unit-cell dimensions were obtained by least-squares procedures described previously (Busing & Levy, 1967) from the 2θ values of

12 reflections centered on an automatic diffractometer (Mo $K\alpha_1$). These parameters and other crystal data are listed in Table 1.

A crystal of approximate dimensions 0·5 × 0·6 × 0·1 mm was mounted on an automatic Picker four-circle diffractometer with its b axis parallel to the φ axis. Intensity data were collected at a take-off angle of 1·0°. At this angle, the peak intensity of a typical strong reflection was approximately 90% of the maximum value as a function of the take-off angle. The data were collected by the θ–2θ scan technique at a scan rate of 1° min^{-1}. Allowance was made for the presence of both $K\alpha_1$ and $K\alpha_2$ radiations, the peaks being scanned from −0·80° in 2θ below the calculated $K\alpha_1$ position to 0·80° above the calculated $K\alpha_2$ position. Stationary-counter, stationary-crystal background counts of 20 s were taken at each end of the scan. A unique data set having $3 \leq 2\theta \leq 60°$ was gathered. The intensities of three standard reflections, measured after every 100 reflections, showed no decline other than that predicted by counting statistics.

Data processing was carried out as described by Corfield, Doedens & Ibers (1966). After correction for background, the intensities were assigned standard deviations according to the formula $\sigma(I) = [C + 0{\cdot}25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$ and the value of p was selected as 0·040. The intensities were corrected for Lorentz–polarization effects. The intensities were not corrected for absorption because the crystal was lost soon after data collection. The absorption coefficient for this compound for Mo $K\alpha$ radiation is 14·9 cm^{-1}, and a trial calculation suggested that the maximum effect on any reflection of neglecting absorption effects would be approximately 5% (as a function of F^2). 1948 reflections had intensities greater than 2·6 times their estimated standard deviations, and only these were used in this analysis. The programs used in this study have been described elsewhere (Estes & Hodgson, 1973).

Solution and refinement of the structure

The position of the Cu atom was determined from a three-dimensional Patterson function, and two cycles of least-squares refinement of this position were run. All least-squares refinements in this structure were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o^2/\sigma^2(F_o^2)$. In calculations of F_c, the atomic scattering factors for Cu, C, N and O were from *International Tables for X-ray Crystallography* (1974) and those for H were from Stewart, Davidson & Simpson (1965). The effects of the anomalous dispersion of Cu were included in the calculation of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from *International Tables*. The remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Isotropic least-squares refinement of these atoms led to values of the conventional agreement

Table 1. *Crystal data*

$C_{10}H_{13}O_4N_5Cu \cdot 2(\frac{1}{2}H_2O)$, FW 375·8
Monoclinic $C2$
a = 19·040 (6) Å
b = 6·943 (4)
c = 12·201 (4)
β = 103·89 (2)°
V = 1565·7 Å^3
D_m = 1·58 g cm^{-3}
D_c = 1·594
Z = 4
μ(Mo $K\alpha$) = 14·9 cm^{-1}

Table 2. *Fractional coordinates for nonhydrogen atoms in* $CuGHG \cdot 2(\frac{1}{2}H_2O)$

	x	y	z
Cu	0·20362 (2)	½	0·22525 (3)
O(1)	0·3165 (2)	0·4187 (5)	−0·0097 (3)
O(2)	0·3591 (2)	0·1656 (5)	0·2710 (3)
O(3)	0·6147 (1)	−0·0248 (6)	0·2836 (2)
O(4)	0·5986 (2)	0·2810 (5)	0·2353 (3)
N(1)	0·1482 (1)	0·5212 (9)	0·0646 (2)
N(2)	0·2863 (1)	0·4867 (8)	0·1572 (2)
N(3)	0·2641 (2)	0·5332 (7)	0·3782 (2)
N(4)	0·3060 (2)	0·5243 (9)	0·5612 (3)
N(5)	0·4669 (2)	0·2988 (7)	0·2777 (4)
C(1)	0·1910 (2)	0·4370 (7)	−0·0088 (3)
C(2)	0·2718 (2)	0·4483 (6)	0·0479 (3)
C(3)	0·3629 (2)	0·4998 (10)	0·2159 (3)
C(4)	0·3730 (2)	0·6433 (7)	0·3139 (3)
C(5)	0·3366 (2)	0·5838 (7)	0·4034 (3)
C(6)	0·3621 (2)	0·5752 (8)	0·5184 (4)
C(7)	0·2482 (2)	0·4988 (11)	0·4769 (3)
C(8)	0·3950 (2)	0·3048 (7)	0·2559 (3)
C(9)	0·5083 (3)	0·1240 (9)	0·3084 (5)
C(10)	0·5786 (2)	0·1313 (7)	0·2710 (3)
$W(1)$	0·2115 (2)	0·0996 (6)	0·2237 (2)
$W(2)$	0	0·3359 (9)	0
$W(3)$	0·0389 (2)	0·1466 (6)	0·2084 (3)

Table 3. *Fractional coordinates of the hydrogen atoms*

	Bonded	x	y	z
H(1)	N(1)	0·154	0·646	0·053
H(2)	N(1)	0·109	0·471	0·045
H(3)	C(1)	0·201	0·443	−0·084
H(4)	C(1)	0·183	0·288	0·018
H(5)	C(3)	0·388	0·542	0·180
H(6)	C(4)	0·360	0·767	0·291
H(7)	C(4)	0·423	0·662	0·354
H(8)	C(6)	0·409	0·616	0·568
H(9)	N(4)	0·300	0·533	0·629
H(10)	C(7)	0·200	0·446	0·483
H(11)	N(5)	0·490	0·422	0·263
H(12)	C(9)	0·488	0·035	0·272
H(13)	C(9)	0·519	0·070	0·372
H(14)	$W(1)$	0·205	0·014	0·169
H(15)	$W(1)$	0·267	0·120	0·235
H(16)	$W(3)$	0·075	0·269	0·239
H(17)	$W(3)$	0·066	0·047	0·193
H(18)	$W(2)$	0·016	0·261	0·075

indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ of 0·107 and 0·157 respectively. Anisotropic refinement of these atoms gave $R_1 = 0{\cdot}045$ and $R_2 = 0{\cdot}058$. At this stage we checked our model and found that the histidine was the L isomer, *i.e.* we had chosen the correct enantiomer. The positions of the 18 H atoms were located in a difference Fourier map. In the next refinement, all nonhydrogen atoms were refined anisotropically with all H atoms (with B's set at 4·0 Å^2) as a fixed atom contribution. This refinement gave the final values of F_o and F_c which suggested that no correction for secondary extinction was necessary. In the final cycle of least-squares refinement, no parameter underwent a shift in excess of 55% of its estimated standard deviation, which is taken as evidence that the refinement had converged. A final difference Fourier was featureless, with no peak higher than 0·41 e Å^{-3}, except for two (of heights 0·55 and 0·50 e Å^{-3}) in the vicinity of the Cu atom; the value of R_2 showed no unusual dependence on sin θ or on $|F_c|$. The atom positional parameters are listed in Tables 2 and 3.*

Discussion

The title complex consists of polymeric chains of $(CuGHG)_n$ running approximately parallel to the crystallographic a axis. There are also water molecules: one of these is in the coordination sphere of the metal atom, the others being molecules of solvation in the lattice. The polymeric nature of the compound may be seen in the stereoscopic view shown in Fig. 1. A fragment of the chain is shown in Fig. 2. One can see that each individual ligand donates three N atoms to one Cu atom and a terminal carboxy O atom from a glycyl group to a neighbouring Cu atom. Consequently, the structure of this monoclinic form of the complex is very similar to that of the orthorhombic modification (Osterberg *et al.*, 1972*a*).

Copper coordination

Each metal atom has a distorted octahedral coordination with four short and two long metal–ligand bond distances. The four nearest Cu-coordinated atoms, N(1), N(2), N(3) and O(3)^i, are arranged in an

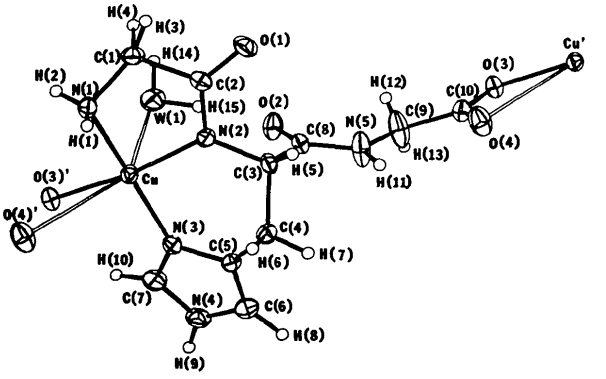

Fig. 2. A fragment of the chain of CuGHG. Thermal ellipsoids are scaled to enclose 40% probability. Hydrogen atoms are represented as circles of arbitrary size. Atom numbering is consistent with the text and tables.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32745 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

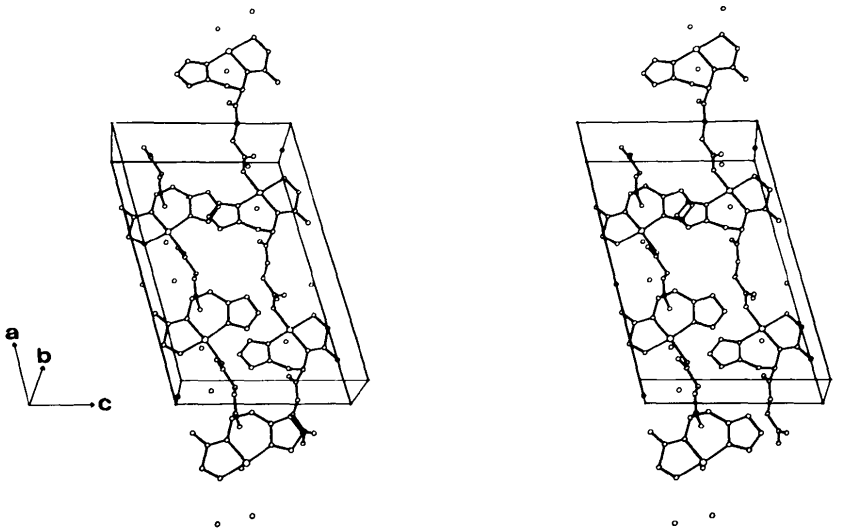

Fig. 1. Stereoscopic pair of drawings showing two chains of CuGHG and the water molecules.

Table 4. *Comparison of the copper coordination in* CuGHG.2($\frac{1}{2}H_2O$) *with that in other complexes*

Distances in Å.

Complex	Cu–N (amino)	Cu–N (peptide)(5,5)*	Cu–N (peptide)(5,6)	Cu–N (imidazole)	Cu–O (carboxy)
CuGHG.2($\frac{1}{2}H_2O$)	1·997 (3)	–	1·951 (3)	1·957 (3)	1·996 (3)
CuGHG.$NaClO_4$	2·01	–	1·93	1·93	2·03
CuGH	2·043 (7)	–	1·991 (8)	1·977 (8)	2·007 (6)
CuGGHa	2·047 (4)	1·904 (4)	1·950 (4)	1·962 (4)	–
CuGGHd	2·028 (4)	1·898 (3)	1·960 (3)	1·941 (3)	–

* The numbers indicate the sizes of the rings shared by the N atoms.

† Abbreviations used here, in Table 6, and in the text are CuGHG.2($\frac{1}{2}H_2O$): glycyl-histidyl-glycinatocopper(II).2($\frac{1}{2}H_2O$) (this work); CuGHG.$NaClO_4$: glycyl-L-histidyl-glycinatocopper(II).$NaClO_4$.H_2O (Osterberg, Sjoberg & Soderquist, 1972*a*,*b*); CuGH: glycyl-L-histidinatocopper(II) (Blount, Frazer, Freeman, Szymanski & Wang, 1967); CuGGHa: copper(II) glycyl-glycyl-L-histidine-*N*-methylamide (Camerman, Camerman & Sarkar, 1976); CuGGHd: the dihydrate copper(II) complex with glycyl-glycyl-L-histidine, where the histidine residue underwent an oxidative decarboxylation (de Meester & Hodgson, 1976).

approximately square-planar coordination. Their distances to the metal atom are compared in Table 4 with those found in other relevant complexes. From this table it can be seen that these bond lengths are normal. The Cu–N(2) peptide distance of 1·951 (3) Å in the title complex is in the range anticipated for a Cu peptide complex in which the N atom is shared by a five- and a six-membered ring, and is in good agreement with the corresponding distances in CuGGHa (Camerman, Camerman & Sarkar, 1976) and CuGGHd (de Meester & Hodgson, 1976). Normally, the Cu–N(peptide) distance is shorter (about 1·91 Å, Blount, Freeman, Holland & Milburn, 1970) when the N atom is shared by two five-membered rings (see also Table 4). Any apparent discrepancy between the present structure and those of CuGHG.$NaClO_4$ and CuGH is probably a measure of the inherent standard deviations in these structures (no standard deviations are reported for the former and the latter has been refined from visually estimated data).

The square plane formed by N(1), N(2), N(3), and O(3)^i is only approximate (Table 5) and may be considered as a very flattened tetrahedron. The same trend has been reported for CuGH (Blount *et al.*, 1967).

The two other atoms in the coordination sphere of the Cu atom are $W(1)$ and O(4)^i, at much longer distances. The vector $W(1)$–Cu is almost perpendicular to the plane N(1), N(2), N(3) and O(3)^i, with angles $W(1)$–Cu–X [X = N(1), N(2), N(3) or O(3)^i] ranging from 84·2 (1) to 96·0 (2)°. The atom O(4)^i, belonging to the carboxyl group of an adjacent unit, makes a vector O(4)^i–Cu which is severely displaced from the normal octahedral geometry, with O(4)^i–Cu–X angles ranging from 51·1 (1) to 134·9 (2)°, the *trans* angle O(4)^i–Cu–$W(1)$ being 137·0 (2)°. Similar geometries have been reported to occur in the structures of copper glutamate (Gramaccioli & Marsh, 1966), CuGGG (Freeman, Robinson & Schoone, 1964) and CuGH (Blount *et al.*, 1967). The Cu–$W(1)$ distance of 2·784 (4) Å and the Cu–O(4)^i distance of 2·817 (4) Å represent weak interactions with the metal. It is interesting to note that in CuGH (Blount *et al.*, 1967) the corresponding distances are 2·458 (9) and 2·943 (8) Å, while in CuGHG.$NaClO_4$ (Osterberg, Sjoberg & Soderquist, 1972*a*) they are 2·74 and 2·76 Å respectively. Therefore, it seems that such variations in Cu–axial atom distances are mainly a consequence of the crystal packing.

Table 5. *Deviations* (Å) *of atoms from least-squares planes of interest in* CuGHG.2($\frac{1}{2}H_2O$)

Superscript (i) refers to an atom in the symmetry position ($\frac{1}{2} - x$, $\frac{1}{2} + y$, z).

Copper environment			
N(1)	0·153	O(3)^i	−0·058
N(2)	−0·191	Cu*	−0·064
N(3)	0·096		
Imidazole ring			
N(3)	0·003	N(4)	−0·004
C(5)	−0·005	C(7)	0·001
C(6)	0·006		
Peptide 1			
C(1)	0·000	N(2)	0·006
C(2)	0·005	C(3)	0·003
O(1)	−0·003		
Peptide 2			
C(3)	0·021	N(5)	−0·047
C(8)	0·003	C(8)	0·032
O(2)	−0·010		

* Atom not used in defining the plane.

Angles at the N donor atoms

In Table 6, the Cu–N–C angles found in this structure are compared with those reported in the related

Table 6. *Comparison between* Cu–N–C *angles* (°) *in* CuGHG.2($\frac{1}{2}H_2O$) *and other structures*

Complex	N (amino)(5)*	N (peptide)(5,5)	N (peptide)(5,6)	N (peptide)(5,6)	N (imidazole)(6)
CuGHG.2($\frac{1}{2}H_2O$)†	109·2 (2)	–	116·3 (2)	126·8 (2)	124·7 (3)
CuGH	110·7 (6)	–	115·9 (7)	127·1 (6)	122·6 (8)
CuGGHa	110·0 (3)	117–119·0 (3)	116·0 (3)	126·0 (3)	–
CuGGHd	110·2 (2)	117·2–120·8 (3)	115·8 (3)	125·9 (3)	123·8 (3)

* The numbers indicate the sizes of the rings at the N atoms. The ring concerned is underlined.
† For abbreviations and references see Table 4.

structures. One can see that the values found for the title complex are very similar to those found for corresponding angles in other structures and confirm the observation (Blount *et al.*, 1967) that the angles at the N atoms depend on the nature of that N atom (amino, peptide or imidazole) and the sizes of the rings in which it is involved (five- and five- or five- and six-membered rings).

The glycyl-L-histidyl-glycyl ligand

Within the ligand all bond lengths and angles are normal (bond lengths and angles are given in Table 7). The peptide bonds C(2)–N(2) and C(8)–N(5) of 1·323 (5) and 1·332 (5) Å, respectively, are in good agreement with the value of 1·32 Å cited by Pauling (1960). Further, the length of this bond is virtually unaffected upon metal coordination, since N(2) is bonded to the metal atom while N(5) is not. The planarity of the two peptide groups can be estimated from Table 5.

In the imidazole ring, the two shortest bonds are centered on C(7): the distances C(7)–N(3) and C(7)–N(4) of 1·332 (5) and 1·326 (5) Å, respectively, are suggestive of greater double-bond character in these two bonds than for the other three. It is interesting to note that the same trend has been observed in CuGGHa (Camerman, Camerman & Sarkar, 1976), and in CuGGHd (de Meester & Hodgson, 1976), where the corresponding distances are 1·328 (6) and 1·330 (6) Å, and 1·335 (5) and 1·329 (5) Å respectively. The angle at C(7) is also the largest exhibited in the imidazole moiety in these three accurate structures: 110·5 (4) in the title compound, 111·0 (3) in CuGGHa and 111·4 (4)° in CuGGHd (de Meester & Hodgson, 1976). The imidazole ring is quite planar (Table 5). The imidazole ring and the square 'plane' formed by N(1), N(2), N(3) and O(3)^i are not coplanar, but are inclined to each other at an angle of 15°.

Hydrogen bonding

The structure exhibits a complex network of hydrogen bonds. The terminal amino group is involved in two hydrogen bonds of lengths 2·955 (7) and 3·028 (5) Å

Table 7. *Bond distances* (Å) *and bond angles* (°)

Cu–N(1)	1·997 (3)	Cu–O(3)^i	1·996 (3)
Cu–N(2)	1·951 (3)	Cu···O(4)^i	2·817 (4)
Cu–N(3)	1·957 (3)	Cu···*W*(1)	2·784 (4)
N(1)–C(1)	1·469 (5)	C(7)–N(3)	1·332 (5)
C(1)–C(2)	1·530 (6)	N(3)–C(5)	1·385 (5)
C(2)–N(2)	1·323 (5)	C(3)–C(8)	1·517 (8)
C(2)–O(1)	1·245 (5)		
N(2)–C(3)	1·464 (4)	C(8)–O(2)	1·223 (5)
C(3)–C(4)	1·533 (7)	C(8)–N(5)	1·332 (5)
C(4)–C(5)	1·486 (6)	N(5)–C(9)	1·456 (7)
C(5)–C(6)	1·371 (6)	C(9)–C(10)	1·515 (6)
C(6)–N(4)	1·345 (6)	C(10)–O(3)	1·272 (6)
N(4)–C(7)	1·326 (5)	C(10)–O(4)	1·223 (6)
N(1)–Cu–N(2)	82·9 (1)	N(2)–Cu–O(4)^i	134·9 (2)
N(2)–Cu–N(3)	93·5 (1)	N(3)–Cu–O(4)^i	98·0 (1)
N(3)–Cu–O(3)^i	91·5 (1)	N(1)–Cu–*W*(1)	94·8 (1)
N(1)–Cu–O(3)^i	93·6 (1)	N(2)–Cu–*W*(1)	84·2 (1)
N(2)–Cu–O(3)^i	171·3 (2)	N(3)–Cu–*W*(1)	96·0 (2)
N(1)–Cu–N(3)	168·2 (2)	O(3)^i–Cu–*W*(1)	88·2 (1)
O(3)^i–Cu–O(4)^i	51·1 (1)	O(4)^i–Cu–*W*(1)	137·0 (2)
N(1)–Cu–O(4)^i	77·2 (2)		
Cu–N(1)–C(1)	109·2 (2)	C(7)–N(3)–C(5)	106·0 (3)
N(1)–C(1)–C(2)	110·4 (3)	C(7)–N(3)–Cu	129·1 (3)
C(1)–C(2)–N(2)	114·3 (3)	C(5)–N(3)–Cu	124·7 (3)
C(1)–C(2)–O(1)	119·1 (4)	N(2)–C(2)–O(1)	126·6 (4)
C(2)–N(2)–Cu	116·3 (2)	N(2)–C(3)–C(8)	112·2 (5)
C(2)–N(2)–C(3)	116·7 (3)	C(4)–C(3)–C(8)	111·3 (3)
C(3)–N(2)–Cu	126·8 (2)	C(3)–C(8)–O(2)	123·9 (3)
N(2)–C(3)–C(4)	110·2 (4)	C(3)–C(8)–N(5)	114·1 (4)
C(3)–C(4)–C(5)	113·5 (4)	N(5)–C(8)–O(2)	120·0 (4)
C(4)–C(5)–N(3)	121·5 (3)	C(8)–N(5)–C(9)	123·3 (4)
C(4)–C(5)–C(6)	130·5 (4)	N(5)–C(9)–C(10)	111·1 (4)
N(3)–C(5)–C(6)	107·9 (4)		
C(5)–C(6)–N(4)	106·7 (4)	C(9)–C(10)–O(3)	115·2 (4)
C(6)–N(4)–C(7)	108·9 (3)	C(9)–C(10)–O(4)	120·6 (4)
N(4)–C(7)–N(3)	110·5 (4)	O(3)–C(10)–O(4)	124·2 (4)

Hydrogen bonding

A H *B*	*A*···*B*	*B*···H	∠*A*–H–*B*
N(1)–H(1)···O(1)^{ii}	2·955 (7)	2·079	168
N(1)–H(2)···*W*(2)	3·028 (5)	2·223	177
N(4)–H(9)···*W*(1)^{iii}	2·774 (4)	1·918	170
N(5)–H(11)···*W*(3)	2·997 (6)	2·010	170
W(1)–H(14)···O(1)^{iv}	2·831 (5)	2·000	157
W(1)–H(15)···O(2)	2·767 (4)	1·731	173
W(2)–H(18)···*W*(3)	2·800 (5)	1·769	175
W(3)–H(16)···O(3)^i	2·737 (5)	1·649	169
W(3)–H(17)···O(4)^i	2·768 (5)	1·977	145

Superscripts refer to atoms in the following positions: (i) $\frac{1}{2}-x$, $\frac{1}{2}+y$, z; (ii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $-z$; (iii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $1-z$; (iv) $\frac{1}{2}-x$, $y-\frac{1}{2}$, $-z$.

with a carboxy O atom of an adjacent molecule and a water molecule respectively. The protonated, uncoordinated imidazole atom N(4) forms a hydrogen bond of length 2·774 (4) Å with the coordinated $W(1)$. The protonated N(5) on the glycyl group participates in a hydrogen bond of length 2·997 (6) Å with $W(3)$. All H atoms belonging to the water molecules are also involved in hydrogen bonding. $W(1)$ and $W(3)$ form hydrogen bonds with all carboxy oxygens, O(1), O(2), O(3) and O(4), with respective lengths of 2·831 (5), 2·767 (4), 2·737 (5) and 2·768 (5) Å. The water molecule $W(2)$, in a special position on a diad axis, is hydrogen-bonded to $W(3)$ with an associated length of 2·800 (5) Å. In this structure, therefore, all available sites participate in hydrogen bonding.

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A Neutron Diffraction Study of the Crystal Structure of β-D-Fructopyranose*

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β-D-Fructopyranose, $C_6H_{12}O_6$, crystallizes in space group $P2_12_12_1$, $Z = 4$, with $a = 9{\cdot}191\ (2)$, $b = 10{\cdot}046\ (2)$, $c = 8{\cdot}095\ (2)$ Å. The neutron diffraction refinement was based on an earlier X-ray study by Rosenstein (Amer. Cryst. Assoc. Meet., Abstract *KK*2, Buffalo, NY, August, 1968). The hydrogen-bonding consists of an infinite chain with a single-link side chain. Two of the hydrogen bonds involve an unusual *asymmetric bifurcated* interaction, the weak component of which is to the ring oxygen. Although this molecule is a β-ketopyranose, the C–O hemi-acetal bond lengths and valence angles are characteristic of an α-D-aldopyranose or methyl α-D-pyranoside molecule.

Introduction

This work forms part of a neutron diffraction study of simple carbohydrates, aimed at providing the accurate data relating to H atom positions which are necessary to obtain a better understanding of the rules which govern the stereochemistry of hydrogen-bonding in carbohydrate structures. Other investigations in this series are as follows: methyl α-D-altropyranoside (Poppleton, Jeffrey & Williams, 1975), methyl α-D-glucopyranoside and methyl α-D-mannopyranoside (Jeffrey, McMullan & Takagi, 1977), β-maltose monohydrate (Gress & Jeffrey, 1977), β-L-arabinose and methyl β-D-xylopyranoside (Takagi & Jeffrey, 1977), 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranose (Noordik & Jeffrey, 1977).

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