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Precision Neutron Diffraction Structure Determination of Protein and Nucleic Acid Components. II.* The Crystal and Molecular Structure of the Dipeptide Glycylglycine Monohydrochloride Monohydrate†

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Glycylglycine monohydrochloride monohydrate, $C_4N_2O_3H_9Cl.H_2O$, crystallizes in the monoclinic system with $a=8{\cdot}813$ (3), $b=9{\cdot}755$ (3), $c=9{\cdot}788$ (3) Å and $\beta=104{\cdot}10$ (2)°, space group $P2_1/c$ and $Z=4$. The crystal structure has been refined by neutron diffraction, and all hydrogen atoms have been located precisely. Average bond distances to hydrogen within the dipeptide molecule are: C–H 1·086, N–H 1·028 and O–H 1·003 Å (all ±0·006 Å). All features involving heavy atoms are nearly identical with those found in the structure determined by X-ray diffraction. The neutron diffraction results indicate the presence of a network of seven distinct hydrogen bonds in the crystal. Three other short N–H···O and N–H···Cl contacts in the crystal structure should probably not be considered as being hydrogen bonds.

Introduction

Interactions involving hydrogen atoms play a large role in determining the configurations of polypeptides and proteins. Detailed information about hydrogen atom stereochemistry in amino acids and small peptides may provide important insights into the action of intramolecular forces in larger systems. A neutron diffraction study of glycylglycine hydrochloride was undertaken in order to determine accurately the positions of hydrogen atoms in this simple dipeptide and to allow a complete examination of hydrogen bonding in the crystal.

Crystal data

Glycylglycine monohydrochloride monohydrate crystalizes in the monoclinic space group $P2_1/c$ with $Z=4$. The earlier X-ray study (Parthasarathy, 1969) established the cell dimensions: $a=8{\cdot}813$ (3), $b=9{\cdot}755$ (5), $c=9{\cdot}788$ (3) Å, and $\beta=104{\cdot}10$ (2)°. The density calculated from this unit cell is 1·513 g.cm^{-3}.

Experimental

Large single crystals grown by slow evaporation from aqueous solution were elongated in the direction of the c axis with major faces {110}. A well-formed sample whose bounding planes are given in Table 1 was mounted on a four-circle neutron diffractometer at the Brookhaven High Flux Beam Reactor. The c^* axis of the crystal was aligned approximately along the diffractometer φ axis. Data were collected automatically using the Brookhaven Multi-Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Norton, 1966) with a crystal-monochromatized neutron beam of wavelength 1·038 Å. The increment between points in the θ–2θ step scan was 0·12°. Data for 3170 reflections having values of $(\sin\theta)/\lambda$ between 0·1 and 0·7 were reduced to integrated intensities and corrected for absorption using programs from the Brookhaven CDC 6600 Crystallographic Computing Library.

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* Part III has already been published (Jönsson & Kvick, *Acta Cryst.* (1972), B**28**, 1827).

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The linear absorption coefficient $\mu = 2{\cdot}19$ cm^{-1}, was calculated from tabulated neutron mass absorption coefficients (*International Tables for X-ray Crystallography*, 1962), except for hydrogen for which the value of $\mu/\varrho = 23{\cdot}16$ cm^{2}g^{-1} includes absorption due to incoherent scattering. Averaging over space-group equivalent reflections yielded intensities for 1807 independent reflections, of which 438 having $F^2 < 2\sigma(F^2)$ were judged too weak to be observed and were omitted from subsequent refinements.

Table 1. *Crystal bounding planes*

Indices	D*
110	0·000 cm
$1\bar{1}0$	0·000
$11\bar{1}$	0·000
$1\bar{1}\bar{1}$	0·000
$\bar{1}\bar{1}0$	0·100
$\bar{1}10$	0·165
$00\bar{1}$	0·056
001	0·446
$\bar{1}\bar{1}1$	0·319
$\bar{1}11$	0·380

* Measured as the perpendicular distance from a given plane to an arbitrary origin fixed at the intersection of (110,) ($1\bar{1}0$), ($11\bar{1}$) and ($1\bar{1}\bar{1}$).

Structure determination and refinement

In order to determine independently the positions of the hydrogen atoms, a structure factor calculation and scale factor refinement were performed using as input the heavy-atom positions determined in the X-ray study. The positions of all 11 hydrogen atoms were clearly revealed in a subsequent difference Fourier synthesis. The structure was refined by full-matrix least-squares methods, using first isotropic and then anisotropic thermal parameters for all atoms. Each reflection was assigned a weight inversely proportional to its

Table 2. *Neutron structure amplitudes with e.s.d.'s used to derive weights for least-squares refinement*

Multiply by 30·0 to place on an absolute scale with $F_{000} = 148{\cdot}6$ fm.

estimated variance:

$$W^{-1}=\sigma^2(F)=\sigma^2(F^2)/4F^2$$

$$\sigma^2(F^2)=\sigma^2_{\text{count}}(F^2)+(0{\cdot}07\ F^2)^2$$

where $\sigma^2_{\text{count}}(F^2)$ was obtained from the Poisson counting statistics.

The quantity minimized in the refinements was

$$\sum_{hkl} w_{hkl}\ (|F^{hkl}_{\text{obs}}-F^{hkl}_{\text{calc}}|)^2.$$

The refinement process was continued until no parameter shifted by more than one per cent of its estimated standard deviation. Neutron scattering lengths were taken from a recent compilation (International Union of Crystallography Neutron Diffraction Commission, 1969). The observed structure amplitudes were corrected for the effects of extinction using an approximation due to Zachariasen (1967), and an extinction parameter was varied throughout the refinement. The crystal used for data collection was apparently subject to quite severe extinction, with the majority of reflections at least somewhat affected. The extinction parameter converged to a value of $g=3{\cdot}5(2)\times10^4$ which gives an apparent mosaic spread of 1·7 sec or a domain size of $3{\cdot}6\times10^{-4}$ cm. The minimum extinction factor was 0·30 for the $\bar{2}02$ reflection. In order to account properly for small changes in extinction among symmetry-equivalent reflections due to different path lengths through the crystal, the final refinement was carried out using the full, unaveraged data set of 2243 reflections. The final unweighted and weighted R values are:

$$R=\sum||F_o|-|F_c||/\sum F_o=0{\cdot}068$$

$$R_w=(\sum w||F_o|-|F_c||^2/\sum wF_o^2)^{1/2}=0{\cdot}076$$

and the standard deviation of an observation of unit weight is 1·55. Table 2 lists observed and calculated structure amplitudes for one asymmetric unit. The final atomic parameters of Table 3 differ insignificantly from those obtained using the averaged data set.

The molecular structure

The asymmetric unit of glycylglycine monohydrochloride monohydrate is drawn in Fig. 1, which shows 2 of the 7 hydrogen bonds in the structure, as well as the short intramolecular van der Waals contact. The complete hydrogen bonding network is displayed in the packing diagram (Fig. 2).

The bond distances and angles are compared with the X-ray results in Tables 4 and 5. All distances and

Table 4. *Bond distances*

	Neutron		X-ray
	Uncorrected	Corrected for thermal motion	
N(1)–C(1)	1·473 (3) Å	1·475 Å	1·478 (6) Å
C(1)–C(2)	1·515 (3)	1·522	1·522 (6)
C(2)–O(1)	1·233 (3)	1·238	1·229 (5)
C(2)–N(2)	1·330 (3)	1·331	1·325 (5)
N(2)–C(3)	1·440 (3)	1·445	1·443 (6)
C(3)–C(4)	1·508 (3)	1·517	1·504 (6)
C(4)–O(2)	1·204 (4)	1·209	1·207 (5)
C(4)–O(3)	1·316 (4)	1·320	1·320 (6)
N(1)–H(1)	1·027 (7)	1·032	0·96
N(1)–H(2)	1·030 (5)	1·034	0·89
N(1)–H(3)	1·022 (6)	1·026	0·92
C(1)–H(4)	1·088 (6)	1·092	0·95
C(1)–H(5)	1·080 (6)	1·086	1·10
N(2)–H(6)	1·034 (5)	1·038	0·79
C(3)–H(7)	1·084 (6)	1·086	1·05
C(3)–H(8)	1·093 (6)	1·098	1·03
O(3)–H(9)	1·003 (7)	1·039	1·08
O(4)–H(10)	0·972 (6)		0·78
O(4)–H(11)	0·954 (8)		0·81
Averages:			
N–H	1·028 (6)	1·033	0·89
C–H	1·086 (6)	1·091	1·03
O–H(water)	0·963 (8)		0·80

Table 3. *Final atomic coordinates* ($\times10^5$) *and thermal parameters* ($\times10^4$)

The temperature factor is of the form

$$\exp[-2\pi^2(u_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$$

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
CL	44232(19)	31356(16)	41408(17)	303(7)	287(8)	297(8)	-9(6)	64(6)	5(6)
O1	84914(29)	36844(27)	36119(27)	238(11)	339(13)	248(12)	71(10)	-14(10)	-33(10)
O2	71744(31)	04273(30)	36504(33)	291(13)	386(15)	381(15)	42(11)	153(12)	29(12)
O3	92737(37)	-07430(34)	34228(38)	389(15)	376(16)	558(19)	153(13)	222(15)	164(15)
O4	86320(38)	71391(32)	48726(33)	282(14)	387(15)	363(15)	61(12)	25(14)	88(13)
N1	61491(19)	55055(16)	28448(17)	277(8)	246(8)	269(8)	48(7)	58(8)	3(7)
N2	76135(20)	23615(16)	16651(18)	365(9)	259(8)	247(8)	49(6)	23(7)	-16(6)
C1	64207(27)	45514(22)	17627(23)	323(12)	285(10)	190(10)	80(9)	23(9)	28(9)
C2	76033(23)	34752(22)	24461(21)	233(9)	240(10)	200(10)	29(8)	35(8)	1(8)
C3	87021(27)	12511(23)	20910(25)	335(12)	250(10)	331(12)	42(9)	144(10)	6(9)
C4	82739(25)	02802(22)	31365(24)	238(9)	265(10)	271(10)	40(8)	76(8)	-8(9)
H1	54959(68)	50296(55)	34431(62)	505(29)	597(32)	532(32)	-46(27)	282(27)	-34(28)
H2	55837(77)	63659(56)	23635(60)	723(35)	372(26)	477(29)	255(26)	41(28)	36(23)
H3	71785(63)	58052(60)	35092(57)	436(28)	540(29)	382(26)	-17(23)	35(24)	-89(23)
H4	53062(67)	40959(62)	12322(67)	450(28)	514(30)	606(35)	86(24)	-158(28)	-162(27)
H5	68651(81)	51120(65)	09912(63)	815(40)	600(33)	440(29)	229(32)	325(29)	240(27)
H6	67608(70)	22699(53)	07351(58)	598(31)	420(25)	360(26)	74(24)	-69(24)	-39(22)
H7	87728(88)	06628(60)	11686(64)	926(45)	460(30)	465(31)	142(30)	344(32)	32(25)
H8	98723(60)	16528(59)	25560(75)	348(24)	454(27)	856(42)	-8(23)	158(26)	60(29)
H9	89365(64)	-14516(57)	40306(61)	504(27)	431(27)	530(30)	122(22)	218(25)	159(25)
H10	96048(60)	68205(55)	54917(60)	358(24)	467(28)	530(30)	53(22)	8(24)	79(24)
H11	78286(64)	71440(60)	53722(60)	391(25)	526(29)	474(28)	90(23)	107(25)	-17(25)

angles not involving hydrogen agree to within two X-ray standard deviations. The X-ray results for the C–H, N–H and O–H bond lengths show the usual systematic shortening and lack of precision. The average C–H distance from our neutron results is 1·086 (6) Å, only 0·016 Å shorter than the value of 1·102 Å

Table 5. *Bond angles*

Angle	Neutron	X-ray
N(1)–C(1)–C(2)	109·6 (2)°	109·6 (4)°
C(1)–C(2)–O(1)	120·5 (2)	120·0 (4)
C(1)–C(2)–N(2)	114·4 (2)	114·6 (4)
O(1)–C(2)–N(2)	125·1 (2)	125·4 (4)
C(2)–N(2)–C(3)	123·1 (2)	123·0 (4)
N(2)–C(3)–C(4)	114·2 (2)	113·7 (4)
C(3)–C(4)–O(2)	124·6 (2)	125·4 (4)
C(3)–C(4)–O(3)	110·8 (2)	110·3 (4)
O(2)–C(4)–O(3)	124·5 (3)	124·2 (4)

Angle	Neutron
C(1)—N(1)–H(1)	109·7 (4)°
C(1)—N(1)–H(2)	109·4 (4)
C(1)—N(1)–H(3)	111·3 (3)
H(1)—N(1)–H(2)	110·7 (5)
H(1)—N(1)–H(3)	107·5 (5)
H(2)—N(1)–H(3)	108·3 (5)
N(1)—C(1)–H(4)	108·4 (4)
N(1)—C(1)–H(5)	109·4 (4)
C(2)—C(1)–H(4)	111·8 (4)
C(2)—C(1)–H(5)	109·4 (4)
H(4)—C(1)–H(5)	108·2 (6)
C(2)—N(2)–H(6)	118·1 (3)
C(3)—N(2)–H(6)	118·7 (3)
N(2)—C(3)–H(7)	109·1 (4)
N(2)—C(3)–H(8)	110·2 (4)
C(4)—C(3)–H(7)	107·9 (4)
C(4)—C(3)–H(8)	108·0 (4)
H(7)—C(3)–H(8)	107·3 (6)
C(4)—O(3)–H(9)	111·7 (4)
H(10)–O(4)–H(11)	109·5 (6)

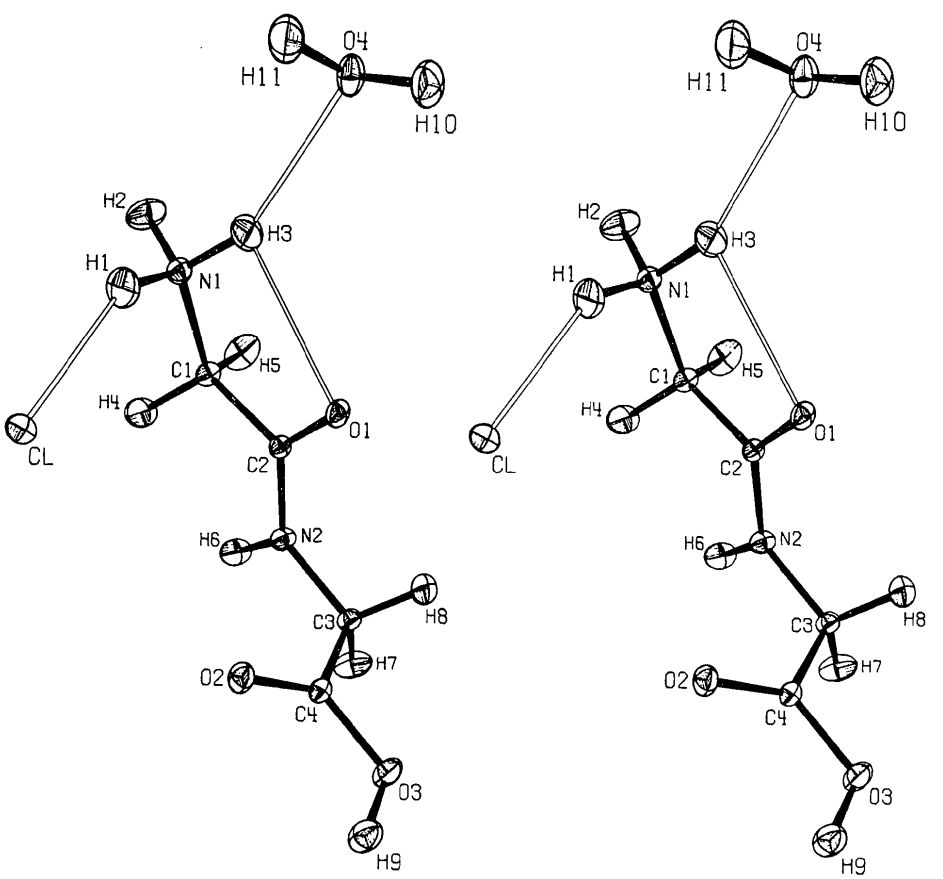

Fig. 1. Stereo view of the asymmetric unit with thermal ellipsoids drawn to enclose 70% probability. The two hydrogen bonds H(1)···Cl and H(3)···O(4), and the short intramolecular van der Waals contact are drawn as open bonds. Illustrations were prepared with the aid of the plotting program *ORTEP* (Johnson, 1965).

found in ethane (Hansen & Dennison, 1952). The average N–H distance of 1·028 (6) Å agrees quite well with values found in two other neutron studies: 1·013 (8) Å in methylglyoxal-bis-guanylhydrazone (Hamilton & La Placa, 1968), and 1·039 (6) Å in L-alanine (Lehmann, Koetzle & Hamilton, 1972*a*). However, these distances are quite sensitive to the strengths of the hydrogen bonds; there is in fact a very good correlation between the N–H and H···B bond lengths in amino acids.

A general property of peptides is that the dimensions of the peptide unit (C^{α}–NH–CO–C^{α}) are remarkably constant and independent of different amino acid constituents. Average dimensions of the peptide unit taken from ten X-ray structures (Marsh & Donohue, 1967) agree quite well with the corresponding bond lengths and angles in glycylglycine hydrochloride determined by neutron diffraction (Table 6).

Table 6. *Dimensions of the peptide unit*

Present work		Marsh & Donohue (1967)	
C(1)–C(2)	1·515 (3) Å	C^{α}–C	1·51 Å
C(2)–O(1)	1·233 (3)	C =O	1·24
C(2)–N(2)	1·330 (3)	C–N	1·325
N(2)–C(3)	1·440 (3)	N–C^{α}	1·455
C(1)–C(2)–O(1)	120·5 (2)°	C^{α}–C =O	120·5°
C(1)–C(2)–N(2)	114·4 (2)	C^{α}–C–N	116
O(1)–C(2)–N(2)	125·1 (2)	O =C–N	123·5
C(2)–N(2)–C(3)	123·1 (2)	C–N–C^{α}	122
N(2)–C(3)–C(4)	114·2 (2)	N–C^{α}–C	111

The conformation of a peptide chain is usually described in terms of torsion angles about the bonds of the chain. The torsion angles φ, ψ, and ω in glycylglycine hydrochloride (Table 7) were calculated according to the latest IUPAC–IUB conventions (IUPAC–IUB(Commission on Biochemical Nomenclature,1970), which differ somewhat from the notation of Edsall *et al.* (1966) used in the paper describing the X-ray study. The X-ray and neutron results differ significantly for the angles φ, involving the hydrogen atoms of the terminal NH_3^+ group.

Atoms O(1), N(2), C(1), C(2), C(3), and H(6) of the peptide unit (Fig. 3) are not strictly planar. The angle ω differs significantly from 180°, the value corresponding to a planar peptide unit (*trans* conformation), and the amide hydrogen H(6) lies 0·104 Å from the least-squares plane through the other 5 atoms of the group. X-ray and neutron studies (Biswas, Hughes, Sharma & Wilson, 1968; Freeman, Paul & Sabine, 1970) have shown that the peptide unit in α-glycylglycine is also somewhat non-planar.

Atom C(3) and the carboxyl group [O(2), O(3) and C(4)] are coplanar to the limit of experimental error. The least-squares plane passes within 0·004 Å of all 4 atoms, and the hydrogen atom H(9) is at a distance of 0·107 Å from this plane.

Hydrogen bonding

The crystal structure contains one hydrogen bond for each hydrogen atom covalently bonded to nitrogen or oxygen. Hydrogen bond distances and angles are summarized in Table 8. For each of the seven hydrogen bonds, the H···B distance is at least 0·5 Å less than the appropriate sum of van der Waals radii. Following Pauling (1960), we have taken the van der Waals radii to be 1·2 for hydrogen, 1·4 for oxygen, and 1·8 Å for Cl^-.

Table 8. *Hydrogen bond distances and angles*

A–H···*B**	Distance *A*···*B*	Distance H···*B*	Angle
N(1)–H(1)···Cl	3·195 (2) Å	2·256 (7) Å	151·4 (5)°
N(1)–H(2)···Cl″	3·184 (2)	2·268 (6)	147·4 (5)
N(1)–H(3)···O(4)	3·025 (4)	2·070 (6)	154·8 (5)
N(2)–H(6)···Cl[I]	3·296 (2)	2·295 (6)	162·4 (5)
O(3)–H(9)···O(4‴)	2·644 (5)	1·658 (6)	166·8 (5)
O(4)–H(10)···O(1[IV])	2·728 (4)	1·764 (6)	170·7 (6)
O(4)–H(11)···Cl′	3·086 (4)	2·168 (6)	161·1 (5)

**A* is the donor and *B* the acceptor atom. The superscript notation for the coordinates of symmetry equivalent atoms is: [unprimed] *x*, *y*, *z*; [′] 1−*x*, 1−*y*, 1−*z*; [″] 1−*x*, ½+*y*, ½−*z*; [‴] *x*, −1+*y*, *z*;
[I] *x*, ½−*y*, −½+*z*; [II] *x*, ½−*y*, ½+*z*; [III] 1−*x*, −½+*y*, ½−*z*; [IV] 2−*x*, 1−*y*, 1−*z*; [V] *x*, 1+*y*, *z*.

The surroundings of the terminal NH_3^+ group are shown in Fig. 4. H(1) and H(2) form hydrogen bonds

Table 7. *Torsion angles*

	Angle	IUPAC-IUB designation	Neutron	X-ray
N-terminal	H(1)–N(1)–C(1)–C(2)	φ_1^1	73·2 (4)°	70·8°
	H(2)–N(1)–C(1)–C(2)	φ_1^2	−165·3 (4)	−169·7
	H(3)–N(1)–C(1)–C(2)	φ_1^3	−45·7 (4)	−51·1
	N(1)–C(1)–C(2)–N(2)	ψ_1	−162·1 (2)	−161·4
Peptide bond	C(1)–C(2)–N(2)–C(3)	ω	−176·8 (2)	−176·6
C-terminal	C(2)–N(2)–C(3)–C(4)	φ_2	−79·6 (3)	−80·0
	N(2)–C(3)–C(4)–O(2)	ψ_T^1	3·8 (4)	3·3
	N(2)–C(3)–C(4)–O(3)	ψ_T^2	−176·8 (2)	−176·2

to Cl and Cl″ respectively. The contacts H(1)···Cl′ and H(2)···O(2″) are only very slightly shorter than van der Waals distances, and should not be called hydrogen bonds, although weak electrostatic interactions may contribute significantly to the stability of the crystal structure. H(3) forms a hydrogen bond N(1)–H(3)···O(4) to the water molecule and is also involved in a short intramolecular contact with the oxygen of the peptide unit. The H(3)···O(1) distance is 2·360 (6) Å. Although such a short intramolecular contact has occasionally been called a hydrogen bond, usually as the weaker member of a bifurcated pair, one may question the utility of this appellation. To be sure, the distance is less than 2·4 Å, the criterion suggested by Hamilton (1968) for an X–H···O hydrogen bond but the N–H···O angle of 97·3 (4)° is at the extreme of the range normally found in hydrogen bonds. Distances between α-amino hydrogen atoms and the adjacent carbonyl oxygen this short are not uncommon in amino acids. We have found, for example, distances of 2·327, 2·291, and 2·467 Å respectively in L-histidine (Lehmann, Koetzle & Hamilton, 1972*b*), L-asparagine monohydrate (Verbist, Lehmann, Koetzle & Hamilton, 1972), and L-arginine dihydrate (Lehmann, Verbist, Koetzle & Hamilton, 1972); and in L-alanine, for which an almost completely staggered configuration is found, the two short distances are 2·496 and 2·522 Å. The H···O distance cannot exceed the sum of the van der Waals radii for any rotation of the ammonium group!

In this structure, there is a short intermolecular contact H(5)···O(2^{I}) with a distance of 2·430 (6) Å. The C(1)–H(5)···O(2^{I}) angle is 113·8 (6)°. Many similarly short C–H···O contacts have been found in amino acids. For example, in glycine (Jönsson & Kvick, 1972) the H···O distances involved are 2·390 and 2·453 Å, while in L-tyrosine (Frey, Koetzle, Lehmann & Hamilton, 1972) we find 2·243 Å. It does not

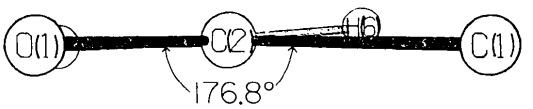

Fig. 3. The peptide unit viewed along the peptide bond C(2)–N(2). Atoms N(2) and C(3) are hidden behind C(2) and O(1) respectively.

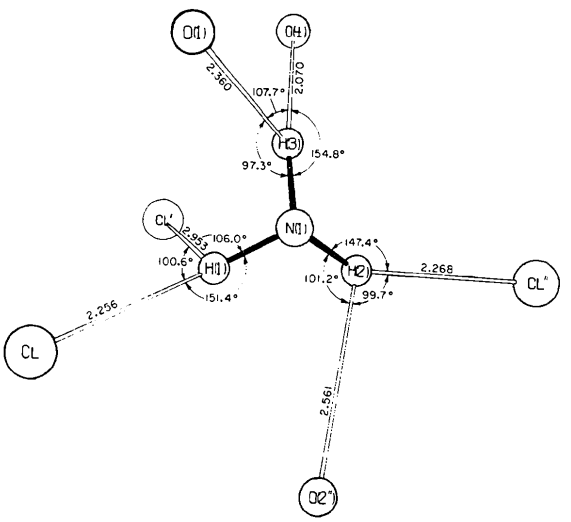

Fig. 4. Environment of the terminal nitrogen atom viewed approximately along C(1)–N(1) with distances in Å.

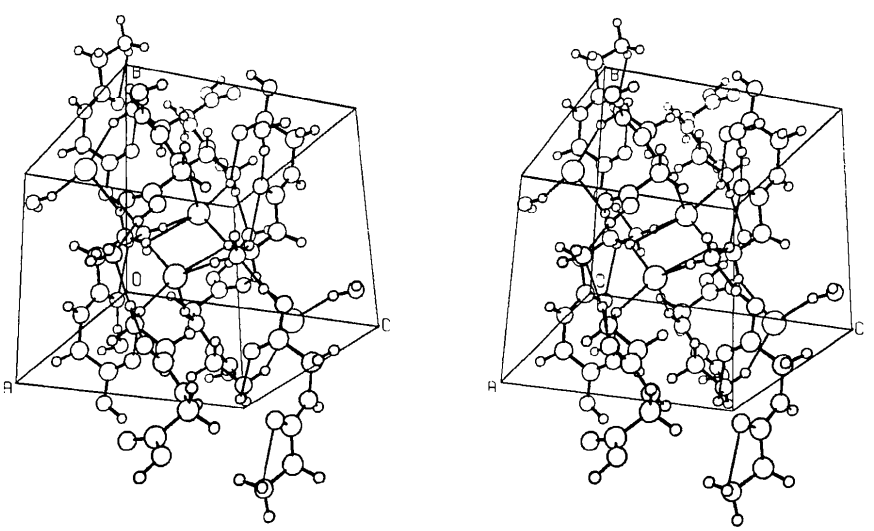

Fig. 2. Stereo view of the packing within one unit cell. Hydrogen bonds are drawn in addition to the van der Waals/electrostatic contacts H(1)···Cl′, H(2)···O(2″), and H(3)···O(1).

seem useful to call all these short contacts weak hydrogen bonds. Baur (1972) has pointed out that there are many H···H contacts of 2·0 Å in crystalline hydrates, and that a van der Waals radius of 1·0 for hydrogen may be more appropriate than the 1·2 Å previously assumed. This would be consistent with the many 2·4 Å H···O contacts found in amino acids and peptides and would suggest that the criterion for hydrogen bonding should be lowered to an H···O distance of 2·2 Å.

Although we may not wish to call the short intramolecular H···O contacts hydrogen bonds, the fact remains that they probably do aid in stabilizing the molecular configurations usually found. *Ab initio* LCAO–MO SCF calculations for alanine using a Gaussian basis set (Lehmann & Newton, 1972) show that the energy minimum does occur for that relative rotation of the carboxyl and ammonium groups which gives the shortest H···O contact. The height of the barrier to rotation of the ammonium group is calculated to be 6·9 kcal.mole^{-1}. Among the amino acid structures we have examined, there is considerable variation in the minimum intramolecular H···O distance and we must conclude that the influence of intramolecular interactions is secondary to the strong external hydrogen bonds in determining molecular configurations. The dominant force arises from the requirements for favorable intermolecular hydrogen bonding, and the weaker internal H···O interaction accommodates itself to the stronger influence. There are also other intramolecular steric constraints which may be important. In the glycylglycine molecule, the NH_3^+ group is rotated only 14° from the configuration which minimizes interactions between it and hydrogens on the adjacent CH_2 group. Furthermore, in most of the amino acid structures we have studied, the H–C–N–H torsion angles are near 60° (with the obvious exception of the prolines).

The Cl^- ion in glycylglycine monohydrochloride monohydrate accepts four quite strong hydrogen bonds (Fig. 5). As noted above, the interaction between Cl^- and H(1′) is certainly very weak.

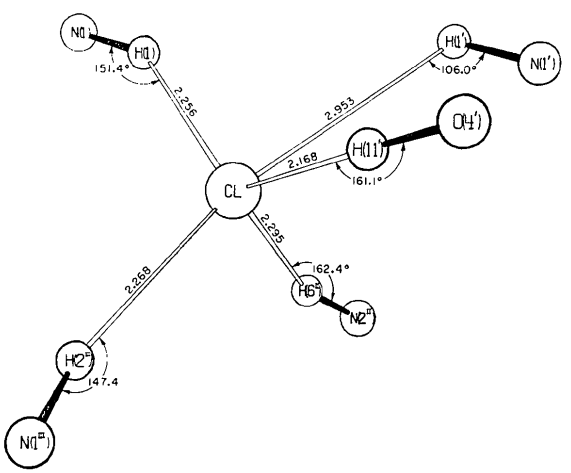

Fig. 5. Surroundings of the Cl^- ion.

The environment of the water molecule is approximately tetrahedral. The oxygen atom O(4) accepts two hydrogen bonds [N(1)–H(3)···O(4) and O(3^{v})–H(9^{v})···O(4)], in addition to donating H(10) to O(1^{iv}) and H(11) to Cl′.

Thermal motion

The thermal parameters U_{ij} of the nonhydrogen atoms in the dipeptide molecule were fitted to a rigid-body model by the method of Schomaker & Trueblood (1968). The axis of maximum libration is approximately aligned along the peptide chain with a calculated r.m.s. amplitude of 5·4°. Corrections to bond lengths were derived from the rigid-body librations and the corrected distances are included in Table 4. The correction increases both the mean N–H and C–H bond distances by 0·005 Å. The value of the r.m.s. deviation of the experimental U_{ij} from those calculated from the rigid-body motions is 0·012 Å^2, which gives an estimate of the magnitude of the non-rigid-body motions present. The U_{ij} are determined to approximately ±0·001 Å^2 from the least-squares refinement.

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The Crystal and Molecular Structure of Bis(glycinato)bis(imidazole)nickel(II)

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The structure of a mixed-ligand complex, bis(glycinato)bis(imidazole)nickel(II), has been determined from three-dimensional counter data. The crystals are monoclinic with $a=10{\cdot}57$ (1), $b=8{\cdot}83$ (1), $c=16{\cdot}17$ (2) Å, $\beta=99{\cdot}0$ (1)°, $Z=4$ and the space group is $P2_1/c$. The positional and anisotropic thermal parameters have been refined by least-squares methods. The final residual R is 0·049 for 2618 independent reflexions (479 unobservably weak), and the positional parameters of the light atoms have a mean e.s.d. of 0·004 Å. The complex is octahedral and the configuration around the metal ion is *cis*-O(carboxyl), *cis*-N(amino), *cis*-N(imidazole). The mean metal–ligand bond lengths are Ni–O(carboxyl) = 2·09, Ni–N(amino) = 2·10, and Ni–N(imidazole) = 2·07 Å.

Introduction

The structure of bis(glycinato)bis(imidazole)nickel(II), $Ni(Gly)_2(ImH)_2$, is inherently interesting as an example of a mixed-ligand complex, and more specifically as a model for the type of interaction that may occur between a metal ion and donor groups widely separated along a protein chain.

Among the mixed-ligand complexes whose preparations and spectra have been reported are copper(II) complexes of imidazole and glycylglycine (Driver & Walker, 1968), and cadmium(II) and nickel(II) complexes of peptides, amino acids and imidazole (Rao & Li, 1966). X-ray crystal structure analyses of glycylglycinatobis(imidazole)copper(II) perchlorate, glycylglycinatoaquoimidazolecopper(II) sesquihydrate and diglycylglycinatoaquoimidazolecopper(II) monohydrate have been made (Bell, Freeman, Wood, Driver & Walker, 1969). The only previous structure analysis of a mixed-ligand complex containing amino-acid ligands is that of L-histidinato-L-threoninatoaquocopper(II) hydrate (Freeman, Guss, Healy, Martin, Nockolds & Sarkar, 1969).

Experimental

Crystal data

$Ni(Gly)_2(ImH)_2$, prepared by the method of Rao & Li (1966), forms large blue-purple crystals. The unit cell is monoclinic with $a=10{\cdot}57$ (1), $b=8{\cdot}83$ (1), $c=16{\cdot}17$ (2) Å, $\beta=99{\cdot}0$ (1)°, $U=1491$ (3) Å^3, $D_m=1{\cdot}54$ (2) g.cm^{-3} (by flotation in a mixture of chloroform and 1,2-dibromoethane), $D_x=1{\cdot}528$ g.cm^{-3} for $C_{10}H_{16}NiN_6O_4$, $Z=4$ with F.W. 342·8, and μ(Cu $K\alpha$) = 20·8 cm^{-1}. The space group is $P2_1/c$ (No. 14) from systematic absences ($0k0$ absent for $k=2n+1$, $h0l$ absent for $l=2n+1$).

The reciprocal cell constants a^*, b^* and c^* were calculated from precise measurements of high-angle reflexions from two crystal specimens, using an equi-inclination diffractometer with Cu $K\alpha$ radiation [λ(Cu $K\alpha_1$) = 1·5405, λ(Cu $K\alpha_2$) = 1·5443 Å]. Adequate accuracy (confirmed by comparing the calculated and experimental directions of other reflexions) was obtained by measuring the Bragg angle θ of one reflection along each reciprocal axis. The angle β^* was fitted to the differences between the φ (crystal rotation) angles of all the $h00$ and $00l$ reflexions. The probable errors in the resulting unit-cell dimensions were derived directly from estimates of the errors in θ and φ.

X-ray data collection

The data were collected using one crystal of dimensions 0·13 × 0·08 × 0·25 mm, mounted successively about the [0,1,0] and [0,0,1] directions. The intensity measurements were made with a fully automatic Supper diffractometer (Freeman, Guss, Nockolds, Page & Webster, 1970), and the control parameters for the scan-range and scan-speed calculations as defined in the cited reference were: $\Delta\lambda=0{\cdot}007$ Å, $X=0{\cdot}6°$, $\varphi_m=1{\cdot}2°$, $P=0{\cdot}001$, $\delta\mu=0{\cdot}05°$, $\varphi'_{max}=0{\cdot}25$ deg. sec^{-1}, $\varphi'_{min}=0{\cdot}04$ deg. sec^{-1}, and $R_e=2\%$.

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