compound, and the counter ions. This asymmetry is reflected both in the distances [Ag—C(42) = 2·486 (18), Ag—C(32) = 2·571 (15) Å] and in the angles [Ag—C(42)—C(32) = 77·4 (9), Ag—C(32)—C(42) = 70·6 (9)°]. Packing is determined by the Ag—C interactions and by hydrogen bonds involving the water molecules and the O atoms from pht anions of different chains.
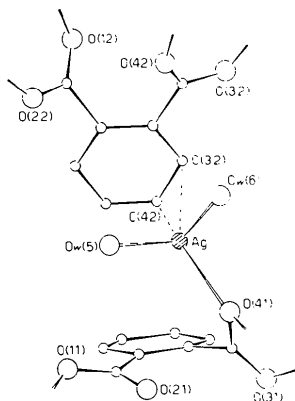

Fig. 2. Coordination around the Ag atom.

References

BIAGINI CINGI, M., GUASTINI, C., MUSATTI, A. & NARDELLI, M. (1970). Acta Cryst. B26, 1836–1843.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1977). Acta Cryst. B33, 659–664.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1978a). Acta Cryst. B34, 134–137.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1978b). Acta Cryst. B34, 406–411.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1978c). Acta Cryst. B34, 412–416.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1978d). Acta Cryst. B34, 774–778.

GRIFFITH, E. A. H. & AMMA, E. L. (1974). J. Am. Chem. Soc. 96, 743–749.

LITTLE, R. G., YAWNEY, D. B. & DOEDENS, R. J. (1972). J. Chem. Soc. Chem. Commun. pp. 228–229.

SHELDRICK, G. M. (1976). SHELX 76. Program for structure determination. Univ. of Cambridge.

Calcium Binding to α-Amino Acids: The Crystal Structure of Calcium Di-L-glutamate Tetrahydrate

BY HOWARD EINSPAHR AND CHARLES E. BUGG

Institute of Dental Research and Department of Biochemistry, University of Alabama in Birmingham, University Station, Birmingham, Alabama 35294, USA

Abstract

Crystals of calcium di-L-glutamate tetrahydrate Ca(C₅H₈NO₄)₂.4H₂O are tetragonal, space group P4₃2₁2, with a = 7·5624 (1), c = 29·0771 (9) Å, and four formula weights per unit cell. A trial structure was obtained by Patterson and Fourier techniques and was refined by full-matrix least-squares calculations using absorption-corrected, Cu Kα, diffractometer data. The later stages of refinement were based on an octant of data, and anomalous-dispersion effects were used to establish the proper enantiomorph. The final R index is 0·032 both for the octant of 1632 reflections and for the half-octant of 893 unique data. The Ca ion lies on a crystallographic twofold axis and is coordinated to two

α-carboxyl groups and two γ-carboxyl groups from glutamate ions, and to two water molecules. Each of the glutamate carboxyl groups contributes a single O atom to the Ca coordination polyhedron and serves as a unidentate ligand. The sixfold coordination polyhedron has distorted octahedral geometry.

Introduction

Ca ions are involved in a variety of biological processes, many of which are mediated by calcium–protein complexes. Crystallographic, spectroscopic, and chemical data all indicate that glutamate and aspartate residues are particularly common compo-

nents of the calcium-binding sites in proteins. We are currently investigating the crystal structures of calcium–glutamate and calcium–aspartate complexes in order to elaborate some of the geometrical factors that accompany Ca interactions with these amino acids. In previous papers, we reported the crystal structures of calcium L-glutamate trihydrate [CaGlu.3H$_2$O] (Einspahr & Bugg, 1974), and calcium L-glutamate chloride monohydrate [CaGluCl.H$_2$O] (Einspahr, Gartland & Bugg, 1977). We describe here the crystal structure of calcium di-L-glutamate tetrahydrate [Ca(Glu)$_2$.4H$_2$O].

Experimental

Calcium diglutamate tetrahydrate was purchased in powdered form from Grand Island Biological Co. Colorless, transparent crystals were prepared by slow cooling of warm, saturated, aqueous solutions of this material. The crystal shapes were all variants (by truncations of one type or another) of a square-bipyramidal morphology (octahedral modified by elongation along the fourfold axis). Preliminary oscillation, Weissenberg, and precession photographs indicated a tetragonal lattice and narrowed the choice of space group to one of the two enantiomers, $P4_12_12$ or $P4_32_12$ (systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l \neq 4n$).

Most of the specimens, regardless of shape, proved to be composed of more than one crystal. The crystal selected for data collection had the shape of one half of a bipyramid from which a small portion had been removed by truncation perpendicular to c, and approximated an irregular pyramid 0·1 mm in height with a pentagonal base with sides roughly 0·2 mm. This crystal was mounted on a Picker FACS-1 diffractometer with its c axis (corresponding to the twofold axis of the pentagonal base) slightly inclined to the φ axis of the goniostat. A scintillation counter, Ni-filtered Cu $K\alpha$ radiation, and a θ–2θ scanning procedure were used to collect intensity data for an octant of the reciprocal lattice out to $2\theta < 128°$, comprising 1623 reflections of the type hhl, hkl and khl, where $l \geq 0$ and $k > h \geq 0$. This octant includes a complete set of Friedel pairs for all acentric reflections, plus measurements of symmetry-equivalent pairs of reflections for the $0kl$ and $h0l$ zones. The half-octant of unique data (hkl, $h \geq k$) consists of 893 reflections. A scan speed of 1° min^{-1} was used, and the background was sampled for 40 s at each terminus of the scans. The scan spanned a 2θ range of 0·8° plus an increment to account for α_1–α_2 splitting.

The intensities of three reflections, which were monitored periodically during the data-collection procedure, gave no indication of systematic decay. Intensities were assigned variances, $\sigma^2(I)$, according to

Table 1. Crystal data

Calcium di-L-glutamate tetrahydrate
Ca(C$_5$H$_8$NO$_4$)$_2$.4H$_2$O
$P4_32_12$ FW 404·4
$a = 7·5624$ (1) Å $\rho_o{}^* = 1·608$ (3) Mg m^{-3}
$c = 29·0771$ (9) $\rho_c = 1·615$
$V = 1662·92$ Å^3 $Z = 4$

* The density was measured by flotation in a mixture of benzene and 1,1,2,2-tetrabromoethane.

counting statistics plus an additional term, $(0·03S)^2$, S being the scan count. Reflections with scan counts below background levels were assigned negative intensity values and were retained in subsequent calculations. Of the 893 reflections in the unique set, 851 had $I > \sigma(I)$. Intensities and variances were corrected for Lorentz and polarization effects. The program *ORABS* (Wehe, Busing & Levy, 1962) was used to make absorption corrections; transmission factors ranged from 0·70 to 0·81. The data were placed on absolute scale by means of a Wilson (1942) plot. Two files were prepared from the reduced data, one containing the octant and the other only the unique set.

Approximate cell parameters for use in data collection were calculated by a least-squares analysis of the angular settings for 12 high-angle reflections. Immediately after data collection, more precise cell parameters were obtained by least-squares analysis of the 2θ values of 29 Cu $K\alpha_1$ reflections ($\lambda = 1·54051$ Å) measured on the diffractometer at room temperature (297 ± 2 K). These latter values, which differ by no more than 2σ from those obtained prior to data collection, are listed together with other crystal data in Table 1.

Structure determination and refinement

The coordinates of the Ca ion were determined from a three-dimensional Patterson map. The Ca ion occupies a special position of twofold symmetry and, as a result, the Ca contributions to the intensities of reflections $h0l$ ($0kl$) for which $2h(2k) + l = 4n + 2$ are zero. Furthermore, on the basis of Ca contributions alone, the calculated phases for all other reflections are integer multiples of $\pi/4$. The remainder of the nonhydrogen-atom trial structure, comprised of one glutamate ion and two water molecules, was obtained with some difficulty from successive difference electron-density maps interpreted by trial and error. Nine of the twelve H atoms were located in a difference map calculated after three cycles of full-matrix least-squares refinement of nonhydrogen-atom positional and isotropic thermal parameters. The remaining three H atoms were located after an additional three cycles of refinement of a parameter set that was expanded to include positional and isotropic thermal parameters for H atoms,

and anisotropic thermal parameters for nonhydrogen atoms. Calculations were temporarily suspended after an additional three cycles of refinement of the completed model ($R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.043$). All calculations described above were made with the unique data set and without the use of imaginary components of anomalous-scattering factors. The model corresponds to the L-isomer ($P4_32_12$).

Refinement was resumed with the octant of data and with complex anomalous-scattering factors. Convergence of the $P4_32_12$ model was achieved in three cycles. This model included an isotropic secondary-extinction parameter [g of Zachariasen (1967) as formulated by Coppens & Hamilton (1970)]. The final value of the R index is 0.032 and the goodness-of-fit $\{[\sum w\Delta^2/(m - s)]^{1/2}$, where m is the number of observations and $s = 163$ is the number of parameters} is 1.29. Evaluated for the unique data set only, these values are 0.032 and 1.41, respectively. Refinement of the D-enantiomer, obtained by reflecting the asymmetric unit through the plane $z = 0$ and converting to space group $P4_12_12$, converged in four cycles with an R index of 0.064 and goodness-of-fit of 2.79, based upon

the octant of data. These results indicate that the correct choice of enantiomer is the L-isomer in space group $P4_32_12$.

All least-squares calculations were performed with a modified version of program *ORFLS* (Busing, Martin & Levy, 1962; Busing, 1971) that included a subroutine to accommodate refinement of parameters for atoms in special positions. The quantity minimized was $\sum w(F_o^2 - F_c^2/k^2)^2$, where k is the scale factor and the weights w are equal to $1/\sigma^2(F_o^2)$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

The final difference map (calculated with the unique data set) has no peaks or troughs of magnitude greater than 0.26 e Å^{-3}. In the final structure factor calculation, there are only six occurrences of $|\Delta/\sigma| > 4.0$. Of these the only truly aberrant value is that of the 004 reflection with $\Delta/\sigma = -9.2$. We could find no experimental explanation for this large term and, although there may be sufficient justification for excluding it from the refinement on size alone, this was not done. The final value of the extinction parameter is 0.025 (8). Table 2 lists the final values of the atomic positional parameters and their estimated standard deviations.*

Table 2. *Positional and isotropic thermal parameters*

(a) Nonhydrogen atoms. z parameters of all atoms and x and y parameters of Ca are multiplied by 10^5; all other parameters by 10^4. The y and z parameters of Ca have values determined by space-group symmetry.

	x	y	z
Ca	20382 (6)	20382	100000
O(1)	3033 (2)	3794 (2)	94031 (5)
O(2)	4424 (2)	6211 (2)	91560 (6)
O(3)	−86 (2)	11006 (2)	95058 (6)
O(4)	−2869 (2)	10790 (2)	92745 (6)
W(1)	4195 (3)	−27 (3)	97787 (7)
W(2)	744 (3)	2192 (3)	71208 (7)
N(1)	30 (3)	4540 (3)	89329 (8)
C(1)	3104 (3)	5256 (3)	91969 (7)
C(2)	1392 (3)	5972 (3)	89869 (8)
C(3)	719 (3)	7485 (3)	92850 (9)
C(4)	−987 (3)	8341 (3)	91262 (9)
C(5)	−1315 (3)	10176 (3)	93229 (7)

(b) Hydrogen atoms. z parameters are multiplied by 10^4; all others by 10^3. The isotropic thermal parameter is the coefficient in the expression $T = \exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$.

	x	y	z	U (Å^2)
H(1)	−62 (7)	428 (6)	9289 (15)	166 (21)
H(2)	−82 (4)	492 (4)	8740 (9)	40 (8)
H(3)	47 (4)	345 (5)	8824 (11)	68 (11)
H(4)	164 (3)	645 (3)	8690 (7)	23 (6)
H(5)	177 (4)	845 (4)	9328 (10)	77 (10)
H(6)	53 (3)	702 (3)	9628 (8)	36 (7)
H(7)	−98 (4)	865 (4)	8781 (9)	50 (8)
H(8)	−208 (4)	757 (3)	9222 (9)	49 (8)
H(9)	504 (5)	29 (5)	9672 (11)	67 (13)
H(10)	415 (4)	−106 (4)	9903 (11)	62 (10)
H(11)	190 (4)	192 (4)	7060 (9)	53 (9)
H(12)	9 (6)	121 (5)	7087 (12)	92 (14)

Results and discussion

Crystal packing

The crystal packing and hydrogen-bonding schemes are illustrated in Figs. 1, 2 and 3. Table 3 lists hydrogen-bond distances and angles. All H atoms that are attached to O or N atoms participate in hydrogen bonding. As shown in Fig. 1, the crystal structure consists of layers of glutamate ions alternating with layers of Ca ions and water molecules. These layers are stacked in the z direction. The layers of glutamate ions are stabilized by intralayer amino-to-carboxyl hydrogen bonds, and are joined together by H-bonds to water molecules and by Ca--O interactions.

Calcium–glutamate interactions

Fig. 2 shows the environment of the Ca ion, which is bound to carboxyl groups from four glutamate ions, and to two water molecules. The ligands coordinated to the Ca ion include atom O(1) from the α-carboxyl group of one glutamate ion, atom O(3) from the γ-carboxyl group of a second glutamate ion, and O atom W(1) of a water molecule. The coordination polyhedron is completed by symmetry-related O(1), O(3) and W(1) ligands, which are generated by the crystallo-

graphic twofold axis that passes through the Ca ion. The calcium–carboxyl interactions are of the unidentate type, and each carboxyl group contributes a single O atom to the coordination polyhedron. Carboxyl O atoms O(2) and O(4) do not interact with Ca ions, and there are no ligand bridges between symmetry-related Ca ions.

The six O atoms that are bound to the Ca ion assume a distorted-octahedral arrangement, with calcium–oxygen distances to O(3), O(1), and $W(1)$ of

2·292 (2), 2·311 (2), and 2·348 (2) Å, respectively. These distances are typical of those that are found for Ca--O contacts within sixfold coordination polyhedra. Other than those listed above, this crystal structure displays no calcium–oxygen distances that are shorter than 3·5 Å. No hydrogen bonds exist between atoms within the coordination polyhedron. The shortest O$\cdots$O distance within the polyhedron is 3·102 Å. The coordination polyhedra are separated by the glutamate–water medium. The minimum distance

Table 3. *Hydrogen-bond distances and angles*

D–H$\cdots A$	$D\cdots A$	H$\cdots A$	$\angle D$–H$\cdots A$	$\angle$H–$D\cdots A$
N(1)–H(1)$\cdots W(2)^h$	2·942 Å	1·91 Å	145°	22°
N(1)–H(2)$\cdots$O(4)^d	2·792	1·91	165	10
N(1)–H(3)$\cdots$O(2)^c	3·073	2·20	154	18
$W(1)^f$–H(9)$^f\cdots$O(4)	2·731	1·99	168	9
$W(1)$–H(10)$\cdots W(2)^c$	2·734	1·92	158	15
$W(2)^i$–H(11)$^i\cdots$O(4)	2·808	1·94	157	15
$W(2)^g$–H(12)$^g\cdots$O(2)	2·897	2·09	149	21

Symmetry code

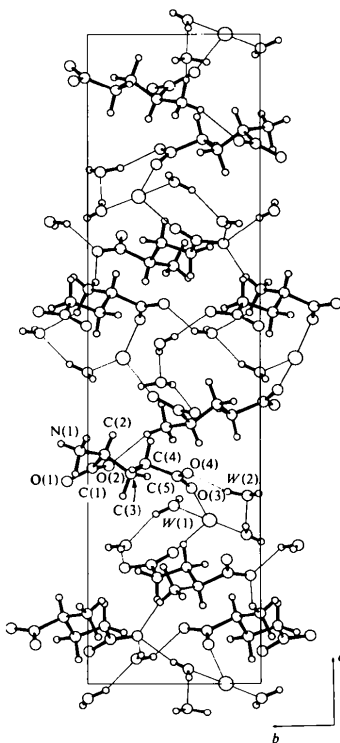|								
(a)	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{3}{4}-z$		(e)	x,	$y+1$,	z
(b)	$-\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{3}{4}-z$		(f)	$x-1$,	$y+1$,	z
(c)	$\frac{1}{2}-x$,	$y-\frac{1}{2}$,	$\frac{3}{4}-z$		(g)	$\frac{1}{2}+y$,	$\frac{1}{2}-x$,	$\frac{1}{4}+z$
(d)	$-\frac{1}{2}-x$,	$y-\frac{1}{2}$,	$\frac{3}{4}-z$		(h)	$y-\frac{1}{2}$,	$\frac{1}{2}-x$,	$\frac{1}{4}+z$

Fig. 1. A representation of the unit-cell contents as viewed from the $-a$ direction. Ca ions are shown as circles of larger diameter. Hydrogen bonds and Ca--O interactions are shown as thin lines. [This drawing, as well as those of Figs. 2–4, was prepared with the aid of program *ORTEP* (Johnson, 1965).]
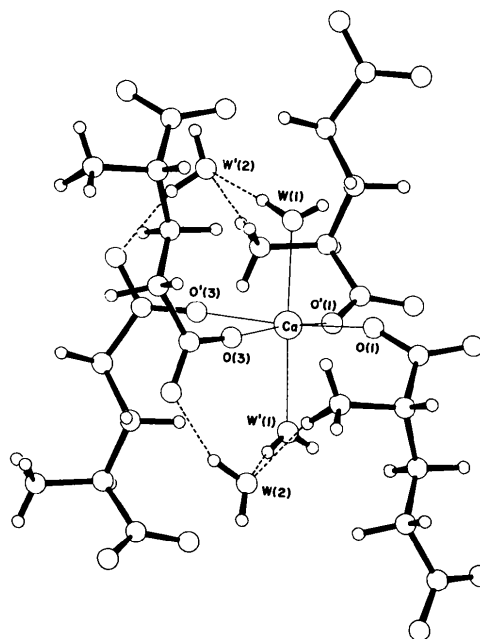

Fig. 2. A representation of the Ca environment. Positions of primed atoms are related to those of unprimed atoms by the operation y, x, $2-z$. The position of O(3) differs from that listed in Table 2 by the operation x, $y-1$, z. Hydrogen bonds are shown as dashed lines; Ca--O interactions as thin lines. Water molecule $W(2)$ is included to show its H-bond interactions with contributors to the Ca coordination shell. The twofold axis passes horizontally through the Ca ion.
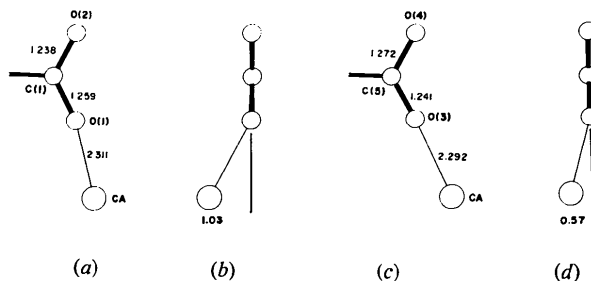

Fig. 3. The calcium–carboxyl geometries in Ca(Glu)$_2$.4H$_2$O. The α-carboxyl group is seen in (a) and (b); the γ-group in (c) and (d). Appropriate Ca--O and C–O distances (Å) are shown in (a) and (c); deviations (Å) of the calcium ion from the carboxyl planes are shown in (b) and (d). E.s.d.'s for these out-of-plane distances are of the order of 0·01 Å.

between Ca ions is 7·562 Å, the unit-cell translation in *a*.

The calcium–glutamate interactions observed in $Ca(Glu)_2.4H_2O$ are considerably different from those observed in $CaGlu.3H_2O$ and $CaGluCl.H_2O$. In the $CaGlu.3H_2O$ structure, the Ca ion is chelated by each of three symmetry-related glutamate anions. The α-amino groups of the glutamate moieties in that structure are not protonated, and one of the calcium-chelating sites is composed of the α-amino group, acting in concert with an O atom from the α-carboxyl group. Both the α- and the γ-carboxyl groups serve as bidentate ligands, each chelating a Ca ion by use of both carboxyl O atoms. The eightfold coordination polyhedron of $CaGlu.3H_2O$ is completed by two water molecules.

In the $CaGluCl.H_2O$ structure, the carboxyl groups do not chelate Ca ions, but participate instead in a number of unidentate interactions. The α-carboxyl group forms two unidentate contacts with Ca ions, and the γ-carboxyl group forms three. The sixfold coordination polyhedron of $CaGluCl.H_2O$ is completed by a water molecule. Despite the superficial similarities between the $Ca(Glu)_2.4H_2O$ and $CaGluCl.H_2O$ structures – including unidentate carboxyl–calcium interactions and sixfold coordination – the overall coordination patterns of the two show several significant differences. The carboxyl–calcium interactions in $Ca(Glu)_2.4H_2O$ are shown in more detail in Fig. 3. Whereas neither carboxyl group in the $Ca(Glu)_2.4H_2O$ structure interacts with more than one Ca ion, both the α- and the γ-carboxyl groups of the $CaGluCl.H_2O$ structure are involved in more than one unidentate interaction, and one of the O atoms of the γ-carboxyl group bridges two Ca atoms. The C—O--Ca angles in the $CaGluCl.H_2O$ structure cover a wide range of values whereas the two C—O--Ca angles in the $Ca(Glu)_2.4H_2O$ structure (151·2 and 164·9° for the α- and γ-groups, respectively) are more nearly linear. The average Ca--O contact distance involving carboxyl O atoms is about 0·04 Å shorter in the $Ca(Glu)_2.4H_2O$ structure than in the $CaGluCl.H_2O$ structure.

The glutamate ion

The glutamate ion and its immediate environment are shown in Fig. 4. Bond distances are included in the figure; covalent bond angles are listed in Table 4. The glutamate ion is bound to adjacent ions and to water molecules through two Ca--O interactions and eight hydrogen bonds. Each carboxyl group has one O atom that is only involved in a Ca interaction, and one that only accepts hydrogen bonds. Atom O(2) of the α-carboxyl group accepts two hydrogen bonds, and atom O(4) of the γ-carboxyl group accepts three. The geometry of the α-carboxyl group is somewhat unusual. For most carboxyl groups, the smaller of the two

C—C—O angles is opposite the shorter C—O bond; the geometry we find for the α-carboxyl group features the larger of the two C—C—O angles opposite the shorter C—O bond. This geometry is, however, consistent with that usually found in amino acids in that the larger C—C—O angle involves the O atom closer to the amino group (Marsh & Donohue, 1967).

Torsion angles within the glutamate ion are listed in Table 5. The conformation about the C(2)—C(3) bond is different from that found in the crystal structures of $CaGluCl.H_2O$ and $CaGlu.3H_2O$. In this structure, C(4) is *trans* to C(1), and is *gauche* to the amino group. In the other two crystal structures, C(4) is *gauche* to C(1) and is *trans* to the amino group. The variations in
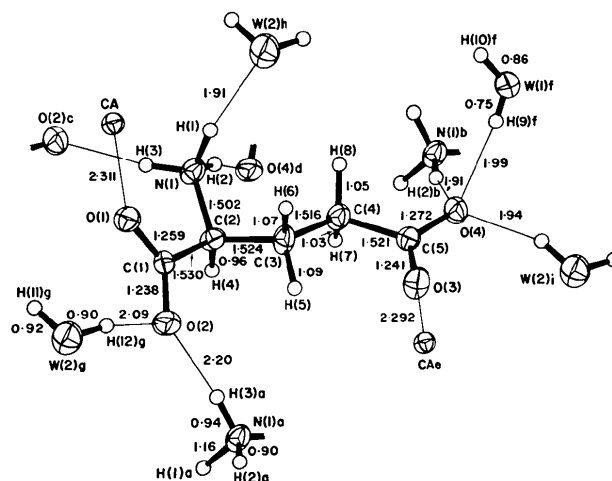

Fig. 4. The environment of the glutamate anion. Thermal ellipsoids are drawn at the 50% probability level. H atoms are drawn as spheres of radius 0·09 Å. E.s.d.'s for lengths (Å) of bonds between nonhydrogen atoms are 0·003–0·004 Å (0·002 Å if to a Ca ion); those involving an H atom are 0·05 Å. The code for symmetry-related atoms is given in Table 3.

Table 4. Bond angles (°)

E.s.d.'s of angles formed exclusively by nonhydrogen atoms are 0·2°, those involving H atoms are 2–3°.

O(1)—C(1)—O(2)	126·3	C(2)—C(3)—C(4)	115·6
O(1)—C(1)—C(2)	117·7	C(2)—C(3)—H(5)	109
O(2)—C(1)—C(2)	115·9	C(2)—C(3)—H(6)	109
C(1)—C(2)—C(3)	108·8	C(4)—C(3)—H(5)	112
C(1)—C(2)—N(1)	111·5	C(4)—C(3)—H(6)	108
N(1)—C(2)—C(3)	111·8	H(5)—C(3)—H(6)	102
C(1)—C(2)—H(4)	109	C(3)—C(4)—C(5)	114·5
N(1)—C(2)—H(4)	108	C(3)—C(4)—H(7)	113
C(3)—C(2)—H(4)	107	C(3)—C(4)—H(8)	111
C(2)—N(1)—H(1)	109	C(5)—C(4)—H(7)	99
C(2)—N(1)—H(2)	109	C(5)—C(4)—H(8)	106
C(2)—N(1)—H(3)	115	H(7)—C(4)—H(8)	113
H(1)—N(1)—H(2)	108	C(4)—C(5)—O(3)	120·0
H(1)—N(1)—H(3)	107	C(4)—C(5)—O(4)	116·3
H(2)—N(1)—H(3)	109	O(3)—C(5)—O(4)	123·7
H(9)—W(1)—H(10)	119	H(11)—W(2)—H(12)	108

Table 5. *Torsion angles* (°) *for the glutamate anion*

E.s.d.'s are 0·3°. Signs of the angles reflect the convention of Klyne & Prelog (1960).

O(1)–C(1)–C(2)–N(1)	−18·2
O(2)–C(1)–C(2)–N(1)	163·7
O(1)–C(1)–C(2)–C(3)	105·6
O(2)–C(1)–C(2)–C(3)	−72·6
C(1)–C(2)–C(3)–C(4)	−179·6
N(1)–C(2)–C(3)–C(4)	−56·0
C(2)–C(3)–C(4)–C(5)	−160·7
C(3)–C(4)–C(5)–O(3)	15·7
C(3)–C(4)–C(5)–O(4)	−166·4

glutamate conformation in these calcium glutamate salts are similar to those found in other glutamate crystal structures.

These studies of crystalline calcium–glutamate complexes suggest that the carboxyl groups of glutamate residues in proteins may serve as either bidentate or unidentate ligands in calcium binding sites. If the bidentate mode is employed, one should expect a higher Ca coordination number (*e.g.* 7 or 8) and somewhat larger Ca--O distances on average. On the other hand, if the unidentate mode is employed, lower Ca coordination numbers are possible and one should expect shorter Ca--O distances on average. A preliminary survey of calcium–carboxyl interactions in a variety of crystalline complexes has been made (Einspahr & Bugg, 1977). This survey suggests that the bidentate mode cannot be accommodated in sixfold calcium coordination polyhedra, although the unidentate mode often contributes to calcium-binding sites of coordination numbers seven and eight. In addition, the ratio of numbers of unidentate to bidentate examples in the survey is about four to one.

References

BUSING, W. R. (1971). *Acta Cryst.* A27, 683–684.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.
EINSPAHR, H. & BUGG, C. E. (1974). *Acta Cryst.* B30, 1037–1043.
EINSPAHR, H. & BUGG, C. E. (1977). *Calcium-Binding Proteins and Calcium Function, Proceedings of the International Symposium on Calcium-Binding Proteins and Calcium Function in Health and Disease,* Cornell Univ., Ithaca, New York, June 5–9, 1977, edited by R. H. WASSERMAN *et al.,* pp. 13–20. New York: Elsevier North-Holland.
EINSPAHR, H., GARTLAND, G. L. & BUGG, C. E. (1977). *Acta Cryst.* B33, 3385–3390.
International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2A, 2.2C and 2.3.1. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
KLYNE, W. & PRELOG, V. (1960). *Experientia,* 16, 521–523.
MARSH, R. E. & DONOHUE, J. (1967). *Adv. Protein Chem.* 22, 235–255.
WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS.* Report ORNL-TM-229. Oak Ridge National Laboratory, Tennessee.
WILSON, A. J. C. (1942). *Nature (London),* 150, 151–152.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* 23, 558–564.

The Crystal Structure of (+)₄₇₀-cis-Diamminebis(*R,R*-2,4-diaminopentane)cobalt(III) Trichloride Monohydrate

BY S. OHBA, H. MIYAMAE, S. SATO AND Y. SAITO

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan

Abstract

Crystals of $[Co(C_5H_{14}N_2)_2(NH_3)_2]Cl_3.H_2O$, $C_{10}H_{34}Cl_3CoN_6.H_2O$, are orthorhombic, space group $P2_12_12_1$, with $a = 11·575$ (1), $b = 17·023$ (1), $c = 10·679$ (1) Å and $Z = 4$. Block-diagonal least-squares refinement reduced the R value to 0·033 for 3784 independent reflexions collected by diffractometry. The complex cation has an approximate twofold symmetry. The six-membered chelate rings take the skew-boat conformation with both $C–CH_3$ bonds in equatorial positions. The absolute configuration of the complex