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An X-ray and Neutron Diffraction Study of Aqua(L-glutamato)cadmium(II) Hydrate

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The structure of aqua(L-glutamato)cadmium(II) monohydrate has been determined from both X-ray and neutron diffraction data. The purpose of the neutron structure analysis was to demonstrate that the neutron anomalous scattering of ^{113}Cd was large enough to make possible the direct solution of the structure. The structure was solved *via* the 'sine-Patterson' function. The crystals are orthorhombic with $a = 11\cdot61(1)$, $b = 10\cdot79(1)$, $c = 7\cdot286(7)$ Å, $Z = 4$ and space group $P2_12_12_1$. The residuals after least-squares refinement are 0·038 for 1562 observed X-ray structure amplitudes and 0·086 for 601 observed neutron structure amplitudes respectively. The H atom parameters were determined and refined in the neutron structure analysis. There are no significant differences between corresponding parameters derived from the X-ray and neutron structure analyses. Each Cd atom is coordinated by one glutamate ligand *via* the N(amino) and one O(carboxyl) atom, by a second glutamate *via* the other O(carboxyl) of the terminal carboxyl group, by a third glutamate *via* both O(carboxyl) atoms of the side-chain carboxyl group, and by a water molecule. The donor atoms have a distorted octahedral configuration about the metal.

Introduction

One of the results of the availability of synchrotron X-radiation with a wide range of accessible wavelengths has been an increasing interest in methods of structure analysis which take advantage of the anomalous scattering properties of one or more atomic species in a crystal. In principle such methods are not confined to X-ray diffraction, and neutron anomalous scattering can be used to solve structures directly from neutron diffraction data. Structure analyses have been reported for $Cd(NO_3)_2.4D_2O$ and Cd(tartrate).$5H_2O$ using ^{113}Cd (MacDonald & Sikka, 1969; Sikka & Rajagopal, 1975), and for $Sm(BrO_3)_3.9H_2O$ and NaSm(EDTA).$8H_2O$ using ^{149}Sm (Sikka, 1969*b*; Koetzle & Hamilton, 1975). We undertook the present work in order to show that the neutron anomalous scattering of ^{113}Cd is sufficiently large to make possible the direct structure analysis of a non-centrosymmetric and chiral Cd complex. The desired result was achieved by means of the 'sine-Patterson' function (Okaya, Saito & Pepinsky, 1955). The isotope ^{113}Cd, which is present in naturally occurring Cd to the extent of 12·3%, is a particularly attractive candidate for this technique because it is one of the four nuclides that exhibit significant anomalous dispersion for both neutrons and X-rays.

We here report neutron and X-ray diffraction studies of the structure of aqua(L-glutamato)cadmium(II) hydrate, Cd(L-Glu)(H_2O).H_2O. The analysis is part of a series designed to provide precise structural data for cadmium–protein interactions [see Flook, Freeman, Moore & Scudder (1973); Flook, Freeman, Huq & Rosalky (1973); Freeman, Huq & Stevens (1976)]. In addition to the present complex we have crystallized a second cadmium glutamate derivative with the same stoichiometry but a different structure, Cd(L-Glu)(H_2O).Cd(L-Glu)$(H_2O)_2$.H_2O (Flook, Freeman, Moore & Scudder, 1973). Details of the structure of this second complex will be reported later.

Experimental

Colourless prismatic crystals of Cd(L-Glu)H_2O.H_2O were grown from an aqueous solution of $CdCl_2.2\frac{1}{2}H_2O$ (0·25*M*) and L-glutamic acid (0·25*M*) at *p*H7 (adjusted by adding NaOH).

Crystal data

$C_5H_7NO_4Cd.2H_2O$, F.W. 293·6. Orthorhombic, $a = 11\cdot61(1)$, $b = 10\cdot79(1)$, $c = 7\cdot286(7)$ Å, $U = 913(3)$ Å^3, $D_m = 2\cdot20$ g cm^{-3}, $D_x = 2\cdot14$ g cm^{-3} (by flotation in $CHCl_3/CHBr_3$), $Z = 4$, μ(Cu $K\alpha$) = 199·4 cm^{-1}, μ(neutrons) = 15·34 cm^{-1}. λ(Cu $K\alpha_1$) = 1·5405, λ(Cu $K\alpha_2$) = 1·5443, λ(neutrons) = 0·981 Å. Space group $P2_12_12_1$ (No. 19) from systematic absences.

X-ray data

All X-ray measurements were made on a computer-controlled Buerger–Supper equi-inclination diffractometer (Freeman, Guss, Nockolds, Page & Webster, 1970). The unit-cell data were determined from precise measurements of several axial reflexions with high θ values. Intensities were recorded in the range $15° < 2\theta < 140°$ with Ni-filtered Cu $K\alpha$ radiation. The layers $0kl$ to $11kl$ and $hk0$ to $hk7$ were recorded from crystal

specimens whose dimensions were, respectively, 0·10 × 0·12 × 0·25 and 0·13 × 0·12 × 0·25 mm parallel to **a**, **b** and **c**. Only one octant of data was measured for the crystal mounted parallel to **a**. The second crystal was used to measure a full quadrant of data, *i.e.* a complete set of Bijvoet pairs. All the measurements and subsequent calculations were made with reference to a right-handed system of coordinates. The parameters used for the scan-speed and scan-range calculations, as defined in the cited reference, were: $\Delta\lambda = 0{\cdot}007$ Å, $X = 0{\cdot}6°$, $\varphi_M = 1{\cdot}3°$, $P = 0{\cdot}001$, $\delta\mu = 0{\cdot}05°$, $\varphi'_{max} = 0{\cdot}33°\ s^{-1}$, $\varphi'_{min} = 0{\cdot}05°\ s^{-1}$, and $R_e = 0{\cdot}02$. The intensity I of a reflexion with integrated peak count P (recorded in time t) and background counts B_1 and B_2 (each recorded in time $t/2$) was given by $I = P - (B_1 + B_2)$ with variance $\sigma^2(I) = P + B_1 + B_2$. Reflexions for which $I < 2\sigma(I)$ were considered to be unobservably weak. Corrections were made for Lorentz–polarization and absorption effects. The grid used for the absorption calculations (Coppens, Leiserowitz & Rabinovich, 1965) was 8 × 8 × 6 parallel to **a**, **b** and **c** respectively. The procedures described by Freeman & Guss (1972) were followed to bring the two data sets to a common scale and to derive standard deviations $\sigma(F)$ of the structure amplitude $|F|$. However, the contribution of the systematic errors to $\sigma(F)$ was calculated as a function of $\sin\theta/\lambda$ as well as $|F|$. The final data set comprised 1614 reflexions (including 43 below the threshold value).

Neutron data

The neutron source was the HIFAR reactor at the Australian Atomic Energy Commission Research Establishment, Lucas Heights. A computer-controlled four-circle diffractometer was used in the $\theta/2\theta$-scan mode. The crystal specimen had approximate dimensions 3·0 × 1·7 × 1·2 mm. The wavelength of the neutron radiation was 0·981 Å. The flux at the specimen was 8×10^5 neutrons $cm^{-2}\ s^{-1}$. The method used to record the intensity data, and the programs by which the measurements were converted to structure amplitudes, have been described elsewhere (Elcombe, Cox, Pryor & Moore, 1971). Pairs of hkl and $\bar{h}\bar{k}\bar{l}$ reflexions were recorded in the range $0 \le 2\theta \le 50°$. Additional data were recorded in the range $50° \le 2\theta \le 70°$, but in this range the Bijvoet equivalent $\bar{h}\bar{k}\bar{l}$ was measured only when a reflexion hkl had an intensity above the observable threshold $[I > \sigma(I)]$. All measurements and subsequent calculations were made with respect to a right-handed system of coordinates.

The neutron absorption coefficient of the crystal was determined by taping the crystal over a pin-hole in a Cd disc and measuring the attenuation of the neutron beam passing through the pin-hole. Given the thickness of the crystal, it was found that the absorption coefficient was 15·3(3) cm^{-1}. Absorption corrections were applied as for the X-ray data, with a 5 × 5 × 5 grid. Standard deviations were calculated with allowance for uncertainties in the absorption corrections as well as in the measurements (Elcombe *et al.*, 1971). 1255 reflexions (360 Bijvoet pairs and 535 hkl reflexions) were recorded. The 360 Bijvoet pairs were used to solve the structure (see below). There were 302 Bijvoet pairs for which the two reflexions did not have significantly different intensities. In these cases the two intensities were averaged and given an appropriate standard deviation. The refinement was carried out with 953 reflexions (58 surviving Bijvoet pairs and 837 hkl reflexions, including 352 below the observable threshold).

Structure analysis

Except as noted below, the structure was solved from the neutron diffraction data alone. Values of $|F_H|^2 - |F_{\bar{H}}|^2$ were computed for the 360 recorded Bijvoet pairs. These values were used as coefficients for the sine-Patterson function (Okaya, Saito & Pepinsky, 1955):

$$P_s(\mathbf{u}) = \sum_H{}' (|F_H|^2 - |F_{\bar{H}}|^2) \sin 2\pi\mathbf{H}.\mathbf{u}.$$

In this expression Σ' indicates that the summation is for $H \ge 0$. Deconvolution of $P_s(\mathbf{u})$ was achieved by means of the Buerger (1964) sum function. In this procedure a prior knowledge of the position of the anomalous scatterer is implied. The position of the anomalous scatterer can in principle be found by the 'two wavelength' methods of Ramaseshan (1966) and Sikka (1969*a*), but when the anomalous scatterer is ^{113}Cd both these methods require the use of a neutron wavelength of about 0·7 Å. In this wavelength range the neutron flux available to us was too low for the purposes of the

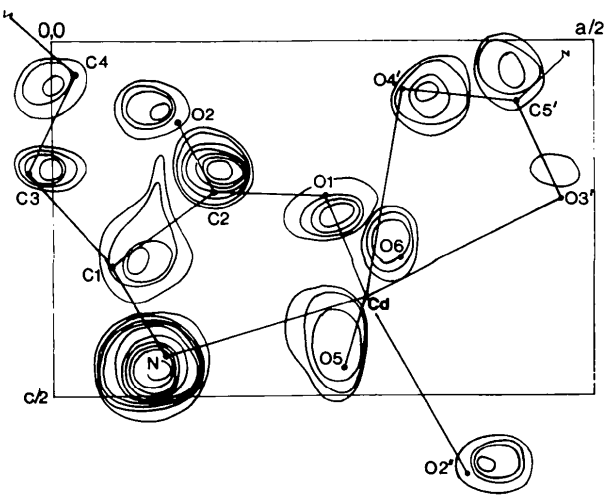


Fig. 1. *b*-Axis projection of the three-dimensional sum-function map and final atomic positions of Cd(L-Glu)(H_2O).H_2O.

experiment. The position of the Cd atom was accordingly determined by standard methods from the X-ray data that had already been recorded. The sum function map had 97 peaks (including negative peaks) above background noise level. The peaks corresponding to all the non-hydrogen atoms with the exception of one molecule of water of crystallization were identified by applying reasonable criteria of chemical connectivity (Fig. 1). The procedure was similar to that commonly used in interpreting an electron-density map at an early stage in an X-ray crystal structure analysis. A neutron ($F_o - F_c$) synthesis revealed the positions of the miss-

Table 1. *Atomic fractional positional parameters and anisotropic or isotropic vibrational parameters* ($\times 10^3$) *for aqua(*L*-glutamato)cadmium*(II) *hydrate*

The atomic coordinates are referred to a right-handed system of axes. Numbers in parentheses are estimated standard deviations in the units of the least significant digit of the preceding number. The anisotropic temperature factors are given by:

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

(*a*) X-ray structure analysis

	10^4x	10^4y	10^4z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	2909 (0)	1836 (0)	3609 (1)	35·5 (6)	47·2 (5)	38·7 (5)	−3·8 (5)	5·1 (3)	1·6 (3)
N	1060 (4)	1296 (5)	4412 (7)	46 (5)	55 (5)	36 (5)	−5 (4)	9 (4)	−6 (5)
O(1)	2531 (4)	−19 (5)	2213 (7)	40 (4)	71 (5)	73 (5)	0 (4)	10 (3)	−25 (4)
O(2)	1145 (4)	−1271 (4)	1174 (7)	72 (4)	64 (4)	56 (5)	−5 (4)	12 (4)	−18 (4)
O(3)	−308 (4)	2880 (5)	−2243 (7)	49 (4)	111 (7)	67 (5)	−5 (4)	−9 (4)	40 (5)
O(4)	−1752 (4)	2130 (5)	−651 (7)	36 (4)	111 (7)	59 (5)	5 (4)	−4 (3)	31 (5)
O(5)	2688 (6)	3816 (5)	4552 (7)	172 (10)	50 (5)	75 (6)	10 (5)	41 (6)	4 (4)
O(6)	1804 (4)	3930 (5)	8014 (6)	57 (5)	78 (5)	60 (5)	−14 (4)	−3 (3)	5 (4)
C(1)	567 (5)	326 (6)	3195 (8)	37 (5)	46 (6)	35 (6)	0 (5)	−3 (4)	7 (5)
C(2)	1498 (5)	−369 (6)	2147 (9)	49 (7)	35 (6)	35 (5)	3 (5)	1 (4)	8 (5)
C(3)	−311 (6)	857 (6)	1870 (9)	38 (5)	66 (7)	55 (8)	3 (5)	−3 (6)	10 (6)
C(4)	184 (5)	1751 (8)	454 (9)	41 (5)	80 (7)	57 (6)	4 (5)	−4 (6)	29 (7)
C(5)	−692 (6)	2275 (6)	−874 (9)	59 (7)	55 (6)	53 (8)	9 (5)	−7 (6)	2 (6)

	10^4x	10^4y	10^4z		10^4x	10^4y	10^4z
H(1)	587	2014	4345	H(7)	813	1277	−307
H(2)	1066	993	5636	H(8)	2387	3855	5730
H(3)	154	−286	4102	H(9)	2859	4580	4028
H(4)	−699	117	1167	H(10)	1080	3571	7925
H(5)	−938	1332	2636	H(11)	2284	3578	8889
H(6)	568	2493	1157				

(*b*) Neutron structure analysis

	10^4x	10^4y	10^4z	U_{iso} or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	2907 (13)	1827 (15)	3620 (22)	22 (4)	—	—	—	—	—
N	1067 (6)	1305 (7)	4410 (10)	52 (8)	54 (7)	33 (8)	5 (6)	15 (6)	−9 (8)
O(1)	2529 (10)	−40 (12)	2238 (17)	29 (3)	—	—	—	—	—
O(2)	1145 (10)	−1247 (12)	1176 (15)	28 (3)	—	—	—	—	—
O(3)	−306 (10)	2870 (12)	−2254 (18)	35 (3)	—	—	—	—	—
O(4)	−1750 (11)	2121 (12)	−652 (19)	37 (3)	—	—	—	—	—
O(5)	2687 (13)	3832 (12)	4531 (21)	187 (22)	41 (13)	67 (15)	15 (15)	73 (17)	29 (15)
O(6)	1796 (11)	3925 (14)	8014 (18)	57 (14)	98 (15)	48 (12)	−20 (14)	−2 (11)	14 (15)
C(1)	568 (8)	323 (9)	3214 (13)	53 (10)	44 (11)	32 (11)	−1 (9)	−12 (8)	13 (10)
C(2)	1502 (8)	−367 (9)	2126 (13)	48 (10)	41 (9)	36 (9)	−3 (8)	9 (8)	22 (10)
C(3)	−318 (8)	865 (10)	1867 (16)	29 (11)	60 (11)	63 (12)	−1 (9)	−22 (9)	25 (10)
C(4)	191 (8)	1748 (11)	420 (16)	44 (11)	81 (14)	56 (12)	4 (10)	−3 (10)	39 (11)
C(5)	−686 (8)	2287 (10)	−870 (15)	53 (11)	57 (12)	54 (12)	−1 (8)	−5 (9)	21 (10)

	10^3x	10^3y	10^3z	U_{iso}		10^3x	10^3y	10^3z	U_{iso}
H(1)	49 (2)	200 (2)	454 (4)	49 (5)	H(7)	87 (2)	125 (3)	−38 (4)	65 (8)
H(2)	125 (2)	95 (3)	559 (4)	58 (6)	H(8)	239 (2)	396 (2)	581 (4)	49 (6)
H(3)	11 (2)	−38 (2)	403 (3)	32 (5)	H(9)	290 (2)	457 (3)	396 (4)	48 (6)
H(4)	−68 (2)	5 (3)	110 (4)	62 (8)	H(10)	107 (2)	350 (2)	801 (3)	42 (5)
H(5)	−97 (2)	138 (3)	265 (4)	54 (6)	H(11)	226 (2)	344 (2)	880 (3)	44 (6)
H(6)	59 (2)	247 (3)	112 (4)	61 (8)					

ing water molecule and all the H atoms. The glutamate residue had the required L-configuration at the chiral Cα atom.

Refinement

Separate full-matrix least-squares refinements were carried out with the X-ray and neutron diffraction data. The program *ORFLS* (Busing, Martin & Levy, 1962) was modified to permit the inclusion of anomalous dispersion effects. The function minimized was $\Sigma\, w(|F_o| - s|F_c|)^2$ where $w = \sigma^{-2}(F_o)$. Unobservably weak reflexions were not included in the calculation of derivatives.

In the X-ray refinement, the variables refined were the positional and anisotropic thermal parameters of the non-hydrogen atoms. The H atoms were included in the structure factor calculations with fixed isotropic temperature factors ($B = 4{\cdot}5$ Å^2) and in positions which were recalculated after each refinement cycle [d(C–H) = 1·05, d(N–H) = 0·95, d(O–H) = 0·93 Å]. It was assumed that the H atoms of the glutamate molecule were bonded to tetrahedral C and N atoms, and that the H atoms of the water molecules lay along the hydrogen bonds formed by them. The atomic scattering factors of Cd^{2+}, O, N and C were taken from Cromer & Waber (1965), the scattering factor of H from Stewart, Davidson & Simpson (1965), and the anomalous dispersion correction for Cd^{2+} from Cromer (1965). Nine reflexions thought to be suffering from extinction were not included in the final refinement cycles. The refinement converged with residuals $R = \Sigma\, ||F_o| - s|F_c||/\Sigma|F_o| = 0{\cdot}034$ and $R_w = [\Sigma\, w(|F_o| - s|F_c|)^2/\Sigma\, wF_o^2]^{1/2} = 0{\cdot}033$, respectively, for the complete data. An $(F_o - F_c)$ synthesis based on the final parameters showed no excursions greater than 0·4 e Å^{-3} except near the Cd atom where excursions of 1·0 e Å^{-3} occurred.

In the neutron refinement only the N and C atoms of the glutamate molecule (the 'heaviest' atoms) and the two water O atoms were refined anisotropically. A neutron scattering length of $(0{\cdot}38 + 0{\cdot}12i) \times 10^{-12}$ cm was used for Cd^{2+} (Peterson & Smith, 1962), and the values published by the Neutron Diffraction Commission (1969) were used for O, N, C and H. The refinement converged with $R = 0{\cdot}086$ and $R_w = 0{\cdot}080$ for the 601 independent reflexions with intensities above the observable threshold, and $R = 0{\cdot}143$ and $R_w = 0{\cdot}112$ for the full set of 953 independent reflexions. The atomic parameters from the X-ray and neutron structure analyses are given in Table 1.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32107 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

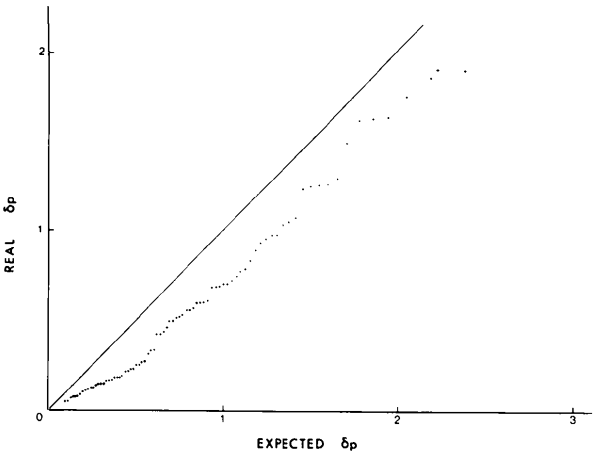


Fig. 2. Half-normal probability plot of the parameters derived from the X-ray and neutron structure analyses of Cd(L-Glu)-(H_2O).H_2O. The straight line with slope 1·0 represents ideal correspondence between the two sets of parameters.

Comparison of parameters derived from X-ray and neutron structure analyses

The χ^2 test (Hamilton, 1969) indicates that the results of the two independent structure analyses are not different at the 95% significance level. The values of M for the positional parameters, the anisotropic thermal parameters, and all common parameters are 39, 48 and 87 respectively; the values of $\chi^2_{M,5}$ for the same groups of parameters are 54·6, 65·2 and 109·7 respectively; and sums of the squares of the weighted differences between corresponding pairs of parameters in the three groups are 22·6, 27·8 and 50·4 respectively. The sum of the squares of the weighted differences is clearly smaller than $\chi^2_{M,5}$ for each group of parameters.

A half-normal probability plot (Abrahams & Keve, 1971) is shown in Fig. 2. The calculated points lie close to a straight line, confirming that there are no systematic differences between the two sets of results. The fact that the line has a slope of 0·85 indicates that one or both sets of standard deviations have been overestimated.

Results

The dimensions derived from the two structure analyses are compared in Table 2. The greater precision of the values derived from the X-ray experiment is a consequence of the larger number of structure amplitudes used in that analysis. The dimensions derived from the X-ray structure analysis will be used in the following description of the structure, except where the discussion of the hydrogen bonding makes it necessary to refer to the positions of the H atoms.

Table 2. *Dimensions of* Cd(L-Glu)(H_2O).H_2O *from X-ray and neutron structure analyses*

In this and the following tables, superscripts indicate transformations with respect to the coordinates listed in Table 1.

Superscript				Superscript			
None	x	y	z	vi	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$
′	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$	vii	x	y	$1+z$
″	$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$	viii	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
‴	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$	ix	x	y	$-1+z$
iv	$\frac{1}{2}-x$	$-y$	$-\frac{1}{2}+z$	x	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
v	$\frac{1}{2}-x$	$1-y$	$-\frac{1}{2}+z$	xi	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$

(*a*) Bond lengths

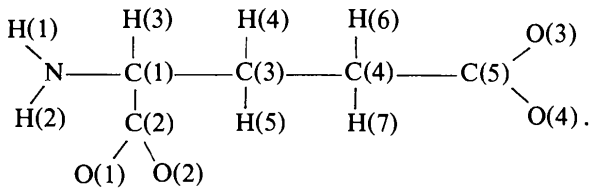
	X-ray	Neutron		Neutron
Cd–O(1)	2·288 (5) Å	2·29 (2) Å	N–H(1)	1·01 (3) Å
Cd–O(2″)	2·252 (5)	2·25 (2)	N–H(2)	0·97 (4)
Cd–O(3′)	2·317 (5)	2·32 (2)	C(1)–H(3)	1·10 (2)
Cd–O(4′)	2·458 (5)	2·47 (2)	C(3)–H(4)	1·12 (3)
Cd–O(5)	2·258 (5)	2·28 (2)	C(3)–H(5)	1·09 (3)
Cd–N	2·299 (5)	2·28 (2)	C(4)–H(6)	1·04 (4)
N–C(1)	1·486 (8)	1·49 (1)	C(4)–H(7)	1·11 (3)
C(1)–C(2)	1·521 (8)	1·54 (1)	O(5)–H(8)	1·01 (3)
C(2)–O(1)	1·257 (7)	1·25 (2)	O(5)–H(9)	0·93 (4)
C(2)–O(2)	1·271 (8)	1·25 (2)	O(6)–H(10)	0·95 (3)
C(1)–C(3)	1·516 (8)	1·54 (1)	O(6)–H(11)	0·94 (4)
C(3)–C(4)	1·525 (9)	1·54 (1)		
C(4)–C(5)	1·513 (9)	1·50 (1)		
C(5)–O(3)	1·273 (8)	1·27 (2)		
C(5)–O(4)	1·251 (8)	1·26 (2)		

(*b*) Bond angles

	X-ray	Neutron		Neutron
O(1)–Cd–O(2″)	103·0 (2)°	102·3 (7)°	Cd–N–H(1)	118 (1)°
O(1)–Cd–O(3′)	95·5 (2)	96·1 (7)	Cd–N–H(2)	97 (2)
O(1)–Cd–O(4′)	92·2 (2)	92·8 (7)	C(1)–N–H(1)	109 (1)
O(1)–Cd–O(5)	160·3 (2)	160·1 (9)	C(1)–N–H(2)	109 (2)
O(1)–Cd–N	73·3 (2)	73·4 (6)	H(1)–N–H(2)	111 (2)
O(2″)–Cd–O(3′)	87·5 (2)	87·5 (7)	N–C(1)–H(3)	111 (1)
O(2″)–Cd–O(4′)	140·5 (2)	140·5 (8)	C(2)–C(1)–H(3)	107 (1)
O(2″)–Cd–O(5)	93·4 (2)	94·5 (8)	C(3)–C(1)–H(3)	107 (1)
O(2″)–Cd–N	100·1 (2)	100·4 (7)	C(1)–C(3)–H(4)	106 (2)
O(3′)–Cd–O(4′)	54·6 (2)	54·4 (5)	C(1)–C(3)–H(5)	109 (2)
O(3′)–Cd–O(5)	96·1 (2)	95·3 (7)	C(4)–C(3)–H(4)	107 (2)
O(3′)–Cd–N	167·6 (2)	167·9 (9)	C(4)–C(3)–H(5)	108 (2)
O(4′)–Cd–O(5)	81·7 (2)	80·6 (7)	H(4)–C(3)–H(5)	113 (2)
O(4′)–Cd–N	119·2 (2)	119·0 (7)	C(3)–C(4)–H(6)	107 (2)
O(5)–Cd–N	93·2 (2)	93·2 (7)	C(3)–C(4)–H(7)	110 (2)
Cd–N–C(1)	112·7 (4)	113·1 (7)	C(5)–C(4)–H(6)	108 (2)
N–C(1)–C(2)	111·9 (5)	111·9 (7)	C(5)–C(4)–H(7)	109 (2)
C(1)–C(2)–O(1)	120·7 (6)	120 (1)	H(6)–C(4)–H(7)	108 (2)
C(1)–C(2)–O(2)	115·3 (5)	114·9 (9)	Cd–O(5)–H(8)	116 (2)
O(1)–C(2)–O(2)	123·9 (6)	125 (1)	Cd–O(5)–H(9)	130 (2)
Cd–O(1)–C(2)	117·5 (4)	117·4 (9)	H(8)–O(5)–H(9)	113 (2)
N–C(1)–C(3)	111·9 (5)	111·3 (8)	H(10)–O(6)–H(11)	104 (2)
C(2)–C(1)–C(3)	110·1 (5)	109·1 (8)		
C(1)–C(3)–C(4)	114·6 (5)	114·5 (8)		
C(3)–C(4)–C(5)	114·6 (5)	114·0 (8)		
C(4)–C(5)–O(3)	117·3 (6)	117·0 (9)		
C(4)–C(5)–O(4)	122·1 (6)	122 (1)		
O(3)–C(5)–O(4)	120·7 (6)	121 (1)		
Cd–O(3′)–C(5′)	95·3 (4)	95·7 (9)		
Cd–O(4′)–C(5′)	89·3 (4)	89·0 (9)		
Cd–O(2″)–C(2″)	120·8 (4)	120·6 (9)		

Description of the structure

The atoms of the glutamate ligand, NH_2—CH-(—$CH_2CH_2COO^-$)—COO^-, have been labelled as follows:



The coordinated and free H_2O molecules are H(8)—O(5)—H(9) and H(10)—O(6)—H(11) respectively. Each glutamate ligand forms a total of five bonds with three Cd atoms (Fig. 3). One Cd atom is chelated *via* the amino N atom and a carboxylate O atom, O(1), to form a typical five-membered amino acid chelate ring. A second Cd atom is bonded to the 'free' carboxylate O(2). A third Cd atom is coordinated by both O(3) and O(4) of the side-chain carboxylate group, resulting in the formation of a four-membered chelate ring.

Conversely, each Cd atom forms a total of five bonds with three glutamate molecules. A sixth bond is formed with O(5) of a water molecule, resulting in a distorted octahedral coordination geometry. The donor atoms N, O(1), O(3′) and O(5) are approximately coplanar, the maximum deviation from the plane of best fit being 0·09 Å (Table 3, plane I). The Cd atom is displaced 0·22 Å from this plane towards O(2″). The bonds Cd—O(2″) and Cd—O(4′) lie at angles of 7 and

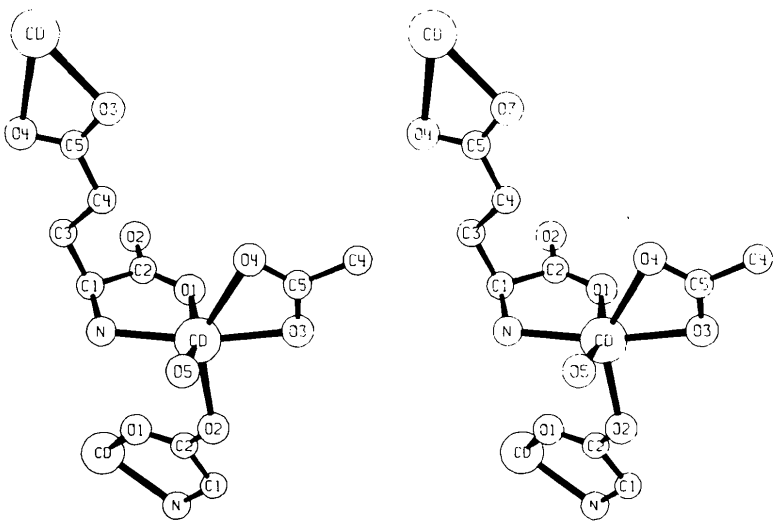


Fig. 3. Stereoscopic diagram of bonding in Cd(L-Glu)(H_2O).H_2O.

Table 3. *Planes fitted by least squares to groups of atoms in* Cd(L-Glu)(H_2O).H_2O *(X-ray parameters)*

(*a*) Coefficients of the planes. Each plane is defined by $pX + qY + rZ + s = 0$, where $X = ax$, $Y = by$, $Z = cz$.

Plane	p	q	r	s (Å)
I	−0·3892	0·3624	−0·8469	2·604
II	−0·1446	0·6096	−0·7794	1·699
III	0·0380	−0·8444	−0·5343	1·763

(*b*) Deviations from planes (Å). Deviations shown in parentheses refer to atoms which were not included in the calculation of the plane of best fit.

Plane							
I	N	O(1)	O(3′)	O(5)	Cd	O(2″)	O(4′)
	−0·090	0·088	−0·071	0·073	(−0·218)	(−2·450)	1·857
II	C(1)	C(2)	O(1)	O(2)	Cd	Cd^{iv}	
	0·004	−0·014	0·005	0·005	(0·369)	(0·931)	
III	C(4)	C(5)	O(3)	O(4)	Cd$'''$		
	0·000	0·000	0·000	0·000	(0·194)		

30°, respectively, from the normal to the same plane of best fit. Both carboxylate groups are planar within experimental error (Table 3, planes II and III). The two Cd atoms bound to the amino acid carboxyl group C(1)C(2)O(1)O(2) are in a *syn–anti* configuration. They deviate significantly (0·37, 0·93 Å) from the carboxylate plane. The Cd atom chelated by the side-chain carboxyl group lies only 0·19 Å from the plane of that group. With the exception of the C—O bond lengths in the carboxyl groups [which are particularly sensitive to small differences in metal—O(carboxyl) interactions], the dimensions of the glutamate ligand in this complex agree closely with those found in L-glutamic acid hydrochloride (Sequeira, Rajagopal & Chidambaram, 1972), β-glutamic acid (Lehmann, Koetzle & Hamilton, 1972), Cu(L-Glu)(H_2O).H_2O (Gramaccioli & Marsh, 1966), and Zn(L-Glu)(H_2O).H_2O (Gramaccioli, 1966).

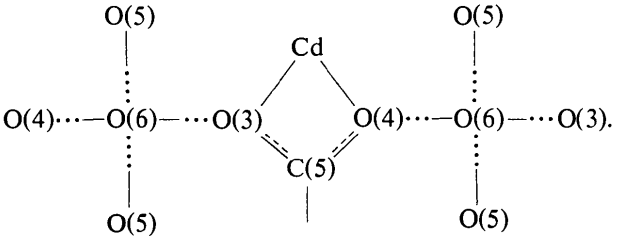
Comparison with analogous Cu *and* Zn *complexes*

The present complex is isostructural but not isomorphous with Cu(L-Glu)(H_2O).H_2O (Gramaccioli & Marsh, 1966) and Zn(L-Glu)(H_2O).H_2O (Gramaccioli, 1966). The metal–ligand bond lengths in the three complexes are listed in Table 4. All three complexes have distorted octahedral coordination geometries, but the extent of distortion decreases in the order Cu > Zn > Cd. When Cu is replaced by Zn, the equatorial bonds become on the average 0·09 Å longer and the axial bond M—O(2″) becomes 0·27 Å shorter. The second axial interaction M—O(4′) is weak in both complexes. When Zn is replaced by Cd, the M—O(4′) bond length decreases by 0·12 Å and the other five bond lengths increase by an average of 0·21 Å. The fact that the four M—O(carboxyl) bond lengths are more nearly equal in the Cd complex than in the Cu and Zn complexes is reflected in the greater symmetry of the carboxyl groups in the Cd complex. The differences between the two C⋯O bond lengths in the side-chain carboxyl group are 0·054, 0·042 and 0·022 Å in the Cu, Zn and Cd complexes respectively. The corresponding differences in the amino acid carboxyl groups are 0·042, 0·023, and 0·014 Å respectively.

The conformations of five-membered amino acid chelate rings are conveniently described in terms of two dihedral angles, w_1 and w_2, between specified pairs of planes (Freeman, Healy & Scudder, 1977). In the present complex, w_1 is defined as the angle between the planes of atoms Cd, O(1), C(2) and Cd, C(2), C(1); w_2 is then the angle between the planes of Cd, C(2), C(1) and Cd, C(1), N. The particular values of w_1 and w_2 (Table 5) correspond to an 'envelope' configuration of the chelate ring. The chelate ring of the Cd complex is slightly more puckered (as measured by the sum of $|w_1|$ and $|w_2|$) than the rings in the analogous Zn and Cu complexes (Table 5). The small negative value of w_2 implies in each case that the orientation of the side chain C(1)—C(3) bond with respect to the chelate ring is more axial than equatorial: the angles between C(1)—C(3) and the reference plane containing M, C(1), C(2) are 60·5, 55·7 and 60·2° in the Cd, Zn and Cu glutamate complexes respectively. The torsion angles χ_1, χ_2 and χ_3 about the side chain C(1)—C(3), C(3)—C(4) and C(4)—C(5) bonds in the three complexes are also included in Table 5. To a first approximation the side chains are planar. The C(3)—C(4) bonds are staggered with respect to N and C(2), and the bonds C(1)—C(3) and C(4)—C(5) are *trans* with respect to C(3)—C(4).

Hydrogen bonding

The hydrogen bonds are listed in Table 6 and shown diagrammatically in Fig. 4. There are intermolecular hydrogen bonds N—H···O(1″) and O(1)···H—N^{iv} between the N(amino) atoms and chelating O(carboxyl) atoms. The coordinated water molecule O(5) forms hydrogen bonds to two lattice water molecules, O(6) and O(6^{v}). The lattice water molecule O(6) is hydrogen bonded to side-chain O(carboxyl) atoms O(3^{vii}) and O(4^{viii}) in two complexes as well as to the coordinated water molecules O(5) and O(5^{vi}) in two other complexes. The following motif extends throughout the structure:



The H atom positions found by neutron structure analysis indicate that all the hydrogen bonds involving

Table 4. *Metal–ligand bond lengths in* M(L-Glu)(H_2O).H_2O, M = Cu, Zn, Cd

	Cu	Zn	Cd
M—N	1·998 (8) Å	2·103 (8) Å	2·299 (5) Å
M—O(1)	1·967	2·106	2·288
M—O(2″)	2·299	2·030	2·252
M—O(3′)	1·981	2·036	2·317
M—O(4′)	2·588	2·576	2·458
M—O(5)	1·991	2·070	2·258

Table 5. *Dihedral angles, w, for chelate-ring conformations, and torsion angles, χ, for side-chain conformations, in* M(L-Glu)(H_2O).H_2O, M = Cu, Zn, Cd

	Cu	Zn	Cd
w_1	−9·5°	−8·1°	−7·5°
w_2	−15·1	−9·5	−18·4
χ_1	67·8	67·1	66·1
χ_2	177·1	176·6	179·7
χ_3	6·7	7·8	10·0

Table 6. *Hydrogen bonds in* Cd(L-Glu)(H_2O).H_2O (*neutron parameters*)

(*a*) Interatomic distances*

Bond X–H···Y	Equivalent bond	$d(X\cdots Y)$	$d(H\cdots Y)$	$\angle(X$–H···$Y)$
N–H(2)···O(1″)	O(1)···H(2^{iv})–N^{iv}	2·96 Å	2·10 Å	147°
O(5)–H(8)···O(6)		2·74	1·74	170
O(5)–H(9)···O(6′)	O(6)···H(9^{vi})–O(5^{vi})	2·73	1·80	174
O(6)–H(10)···O(3^{vii})	O(3)···H(10^{ix})–O(6^{ix})	2·70	1·75	172
O(6)–H(11)···O(4^{viii})	O(4)···H(11^{x})–O(6^{x})	2·80	1·87	165

(*b*) Bond angles at hydrogen-bonded atoms†

Cd–O(1)···H(2^{iv})	122°	Cd–O(4)···O(6^{x})	134°	O(4^{viii})···O(6)···O(5)	113°
Cd–O(1)···N^{iv}	127	C(5)–O(4)···H(11^{x})	138	O(4^{viii})···O(6)···O(5^{vi})	87
C(2)–O(1)···H(2^{iv})	119	C(5)–O(4)···O(6^{x})	137	O(5)···O(6)···O(5^{vi})	109
C(2)–O(1)···N^{iv}	111	Cd–O(5)···O(6)	110	H(8)···O(6)···H(9^{vi})	105
Cd–O(3)···H(10^{ix})	144	Cd–O(5)···O(6′)	134	H(8)···O(6)–H(10)	111
Cd–O(3)···O(6^{ix})	141	O(5)···O(5)···O(6′)	115	H(8)···O(6)–H(11)	110
C(5)–O(3)···H(10^{ix})	115	O(3^{vii})···O(6)···O(4^{viii})	115	H(9^{vi})···O(6)–H(10)	127
C(5)–O(3)···O(6^{ix})	118	O(3^{vii})···O(6)···O(5)	105	H(9^{vi})···O(6)–H(11)	99
Cd–O(4)···H(11^{x})	133	O(3^{vii})···O(6)···O(5^{vi})	127	Cd–N···O(1″)	77
				C(1)–N···O(1″)	107

* Estimated standard deviations are: $d(X\cdots Y)$, 0·03; $d(H\cdots Y)$, 0·05 Å; $\angle(X$–H···$Y)$, 4°. The $d(X$–H) are included in Table 2(*a*).

† Estimated standard deviations are: $\angle(Z$–$X\cdots$H), 2; $\angle(Z$–$X\cdots Y)$, 1°. Some angles involving H atoms are listed in Table 2(*b*).

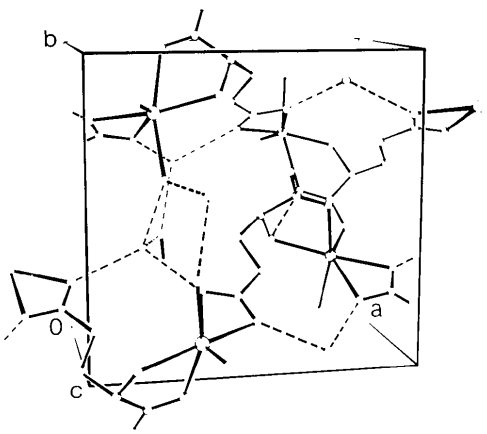


Fig. 4. Molecular packing in the unit cell of Cd(L-Glu)(H_2O).H_2O.

water molecules are approximately linear. The N–H···O angle in the N(amino)···O(carboxyl) hydrogen bond is 147°.

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Crystallographic Studies of Dehydrohalogenation in Solid *meso*-Dibromobutane Derivatives. I. The Crystal and Molecular Structures of Dimethyl (*RSRS*)- *and* (*RRSS*)-α,α'-Dimethyl-β,β'-dibromoadipate

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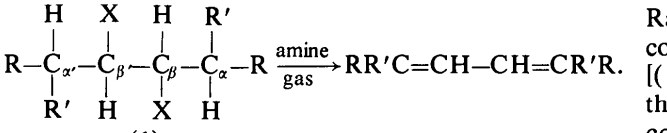
The structures of dimethyl (*RSRS*)- *and* (*RRSS*)-α,α'-dimethyl-β,β'-dibromoadipate were determined from diffractometer data by Patterson and heavy-atom techniques. Both crystals are monoclinic, space group $P2_1/c$, with $a = 9{\cdot}2632$, $b = 5{\cdot}4810$, $c = 13{\cdot}1657$ Å, $\beta = 92{\cdot}442°$, $Z = 2$; $a = 8{\cdot}865$, $b = 8{\cdot}872$, $c = 8{\cdot}339$ Å, $\beta = 96{\cdot}46°$, $Z = 2$ respectively. The structures were refined to $R = 0{\cdot}057$, $0{\cdot}049$. The two compounds react in the solid state with gaseous ammonia or amines and yield, by double dehydrobromination, the corresponding diester of 1,3-*trans,trans*-butadiene and 1,3-*cis,cis*-butadiene respectively. In both cases the reaction is strictly topochemical in the sense that the configurations of the products correlate directly with the conformations of the starting molecules in the crystal.

Introduction

The double dehydrohalogenation of solid *meso*-dihalogenobutanes by gaseous ammonia or amines has been performed by Friedman, Lahav & Schmidt (1969, 1974) in a series of compounds yielding quantitatively the corresponding 1,3-butadienes.



(1)

The configurations of the dienic products were established by chemical methods.

The stereo course of the reaction has been investigated in terms of the correlation between the molecular conformations of the starting compounds and the configurations of the products. We have already reported (Kaufman, Rabinovich & Schmidt, 1974) the structure of the dimethyl ester of *meso*-β,β'-dichloroadipic acid [(1): X = Cl; R = $COOCH_3$; R′ = H] and have shown that the reaction is controlled by the conformation of the molecule in the reacting crystal.

In a recent communication (Friedman, Gati, Lahav, Rabinovich & Shakked, 1975) we dealt with the stereo course of the reaction of solid dihalogenoadiponitriles [(1): X = Cl, Br; R = CN; R′ = H, CH_3] and shown that when R′ = H the reaction is not topochemically controlled. The apparent lack of control was attributed to a mechanism involving pre-reaction equilibrium of rotamers in the solid. The full X-ray structure analyses of some of the dihalogenoadiponitriles will be reported in part II of the present series.

In part I we present the detailed analyses of the two *meso*-diastereoisomers of another dimethyl adipate, dimethyl α,α'-dimethyl-β,β'-dibromoadipate [(1): X =

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