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The Crystal and Molecular Structure of Di-(L-Histidino)-Zinc (II) Dihydrate

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Di-(L-histidino)-zinc(II) dihydrate crystallizes in the tetragonal system with space group $P4_12_12$, $a=b=7{\cdot}53$, $c=30{\cdot}41$ Å. The molecular structure of the complex has been determined by three-dimensional Fourier methods and refined by full-matrix least-squares analysis making use of isotropic thermal parameters for the light atoms. The complex consists of two molecules of L-histidine chelated to a zinc atom through the amino group and an imidazole nitrogen atom. The two acid residues are related by a two-fold axis of symmetry passing through the Zn atom. The primary coordination around the zinc is approximately tetrahedral, Zn–N = 2·04, 2·05 Å, and a carboxyl oxygen atom of each histidine approaches to within 2·79 Å of the zinc to form a secondary coordination grouping.

Bond lengths and angles within the histidine residues have been determined (σC–C = 0·025 Å) and are within acceptable limits.

The structure in the crystal involves an intricate three-dimensional network of hydrogen bonds in which the water molecules take part. The few van der Waals contacts between the molecules are of standard lengths.

Introduction

The exceptional ability of histidine to bind metal ions has long been recognized and it has been suggested (Leberman & Rabin, 1959; Edsall *et al.*, 1954) that this is due to the formation of six-membered chelate rings with the metal attached to an imidazole nitrogen atom and the α-amino group. However, there has been no direct evidence for this. It has been reported (Weitzel *et al.*, 1957) that the zinc complex $Zn(C_6H_8N_3O_2)_2.2H_2O$ is stable and readily obtainable in crystalline form. We have accordingly examined the crystal and molecular structure of this substance by three-dimensional X-ray methods.

Experimental

The crystals used, kindly supplied by Dr Margaret Goodgame, were obtained by slow evaporation of an aqueous solution of the complex and contained only L-histidine. Replicate analyses for C, H, and N confirmed the stoichiometry.

Crystal data

The unit-cell dimensions were determined from Weissenberg photographs calibrated against the diffraction pattern from aluminum wire. The space group identification was made from 30° precession photographs taken with Cu $K\alpha$ radiation. The crystals belong to the tetragonal system with:

$$a=b=7{\cdot}53\pm0{\cdot}02,\quad c=30{\cdot}41\pm0{\cdot}05\ \text{Å}\,.$$

The space group is $P4_12_12(P4_32_12)$. The X-ray density, calculated on the basis of four molecules of the complex per unit cell, is 1·57 g.cm^{-3}; that found by flotation is 1·57 g.cm^{-3}.

Intensity data

Very small equi-dimensional crystals were used in the collection of intensity data so as to reduce absorption errors in any instance below 10% of the observed intensity. Equi-inclination Weissenberg and rotation photographs were used to record the diffraction pattern. Some 1100 out of a possible total of 1290 independent reflections accessible to Cu $K\alpha$ radiation were recorded and measured visually. These embraced the indices $0 \le h(k) \le 9$, $0 \le l \le 39$. The internal consistency in measuring reflections common to more than one film is such as to indicate that errors in measurement do not exceed 12%. The absorption coefficient for Cu $K\alpha$ radiation is 23·8 cm^{-1}. No corrections were made for this effect, nor for primary or secondary extinction. Lorentz and polarization corrections were applied in the usual way and the corrected intensities reduced to relative structure amplitudes. These were set upon an approximation to the absolute scale by Wilson's (1942) method.

Structure determination

The four zinc atoms in the unit cell occupy the space group special positions, $x, x, 0$; $x, x, \frac{1}{2}$; $\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{4}$; $\frac{1}{2}+x, \frac{1}{2}-x, \frac{3}{4}$. A preliminary value of 0·169 was found for x from the Patterson synthesis $P(u, 0, w)$. The contributions of the zinc atoms to all structure factors were then calculated and a three-dimensional Fourier synthesis, phased upon the zinc contributions, was evaluated at intervals of $x/30$, $y/30$, $z/120$. From this a trial structure was obtained for the zinc histidine molecule, though it was not possible to distinguish the electron-density corresponding to the water molecule from the many spurious peaks present. The postulated structure accounted satisfactorily for all but a few peaks in the three-dimensional Patterson function and its essential correctness was confirmed by the appearance of the electron-density distribution in a second three-dimensional Fourier synthesis phased on the trial parameters. The water molecules were found from this synthesis, which was free from false peaks, and their positions shown to account for the remaining maxima in the Patterson function. The value of the conventional R, excluding unobserved reflections, was then 0·23.

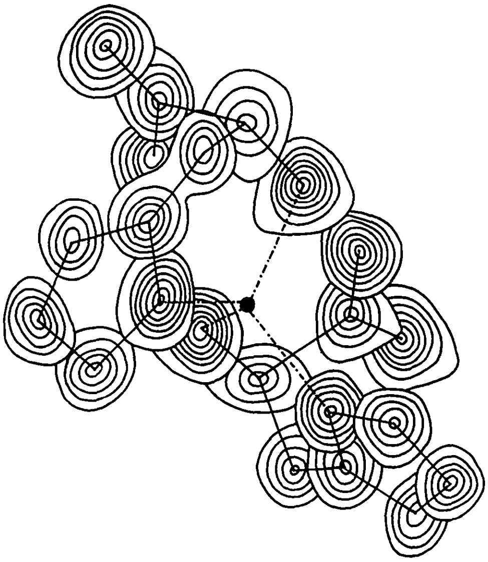

Fig. 1. Electron-density sections for a molecule of di-(L-histidino)-zinc (II). Contours are at equal intervals, each increment representing approximately 1 e.Å^{-3}.

A view of the electron-density distribution for one molecule of the complex is shown in Fig. 1 where the sections are drawn perpendicular to the a axis.

Refinement of the structure

The refinement of the structural parameters was carried out by least-squares methods on an IBM 7090 electronic data processing machine. The ORXLS program, written by Busing & Levy for the IBM 704 machine, was used in the early stages but was superseded by a FORTRAN version of the same. The scattering functions chosen were those of Berghuis *et al.* (1955), that for zinc corresponding to the neutral atom.

Table 1. *Fractional coordinates at various stages in the refinement*

Atom		*a*	*b*	*c*	*d*
C(1)	x/a	0·3433	0·3436	0·3431	0·3404
	y/b	0·0512	0·0509	0·0517	0·0509
	z/c	0·29900	0·29963	0·29981	0·29999
C(2)	x/a	0·4715	0·4710	0·4696	0·4698
	y/b	0·0403	0·0330	0·0354	0·0351
	z/c	0·26129	0·26070	0·26104	0·26111
C(3)	x/a	0·0361	0·0334	0·0371	0·0394
	y/b	0·3483	0·3487	0·3494	0·3485
	z/c	0·22360	0·22411	0·22250	0·22249
C(4)	x/a	0·2000	0·1958	0·1948	0·1934
	y/b	0·3609	0·3618	0·3626	0·3624
	z/c	0·19678	0·19702	0·19671	0·19689
C(5)	x/a	0·4629	0·4589	0·4540	0·4556
	y/b	0·4290	0·4361	0·4385	0·4370
	z/c	0·17453	0·17472	0·17487	0·17481
C(6)	x/a	0·2222	0·2228	0·2238	0·2274
	y/b	0·2750	0·2742	0·2760	0·2793
	z/c	0·15768	0·15780	0·15850	0·15911
N(1)	x/a	0·1136	0·1115	0·1116	0·1111
	y/b	0·4151	0·4174	0·4186	0·4199
	z/c	0·02500	0·02384	0·02335	0·02318
N(2)	x/a	0·3377	0·3418	0·3427	0·3436
	y/b	0·4653	0·4666	0·4672	0·4673
	z/c	0·20565	0·20563	0·20545	0·20547
N(3)	x/a	0·3882	0·3917	0·3899	0·3912
	y/b	0·3350	0·3317	0·3330	0·3333
	z/c	0·14412	0·14390	0·14476	0·14506
O(1)	x/a	0·4551	0·4544	0·4549	0·4537
	y/b	0·2803	0·2829	0·2810	0·2845
	z/c	0·05128	0·05144	0·05165	0·05138
O(2)	x/a	0·3781	0·3793	0·3789	0·3782
	y/b	0·1611	0·1617	0·1623	0·1602
	z/c	0·32895	0·32901	0·32883	0·32856
O(H_2O)	x/a	0·0643	0·0620	0·0648	—
	y/b	0·3575	0·3549	0·3548	—
	z/c	0·34375	0·34294	0·34354	—
Zn	x/a	0·1693	0·1694	0·1694	0·1694
	y/b	0·1693	0·1694	0·1694	0·1694
	z/c	0·00000	0·00000	0·00000	0·00000

After four cycles of refinement, with individual isotropic thermal parameters, a three-dimensional difference synthesis was calculated in an attempt to locate the hydrogen atoms of the structure and to detect any appreciable anisotropy in the thermal motion of the atoms. No convincing electron-density maxima were found which might have been assigned to hydrogen atoms, although in most cases the electron-density at the expected sites was positive, nor was there any indication of strong anisotropic thermal distortion of the shapes of the atoms. Indeed, the residual density around the zinc atom was clearly distributed spherically. Accordingly, no allowance was made for these two effects in cycles 5, 6 and 7. The refinement seemed to be complete after cycle 7 with the atomic parameters oscillating ($\bar{\Delta}(r) = \pm 0{\cdot}002$ Å) about the mean positions listed in Table 1(a).

The ORXLS program calculates the standard

Table 2. *Bond lengths and angles in the histidine molecule*

Bond	*a* False minimum	*b* Isotropic	*c* Isotropic with H atoms	*d* Anisotropic with H atoms	*e* H. & C.	*f* D., L. & R.
C1–C2	1·503	1·530	1·520	1·537	1·519	1·522
C2–C3	1·545	1·519	1·551	1·553	1·539	1·526
C3–C4	1·481	1·478	1·427	1·400	1·486	1·528
C4–C6	1·365	1·378	1·350	1·332	1·369	1·365
C6–N3	1·392	1·408	1·387	1·368	1·374	1·360
N3–C(5)	1·291	1·324	1·306	1·290	1·324	1·352
C(5)–N(2)	1·361	1·308	1·271	1·278	1·329	1·327
N(2)–C(4)	1·330	1·378	1·390	1·404	1·417	1·379
C(1)–O(1)	1·180	1·199	1·187	1·193	1·243	1·252
C(1)–O(2)	1·259	1·252	1·243	1·231	1·260	1·274
C(2)–N(1)	1·590	1·500	1·498	1·487	1·473	1·517
	σC–C=0·025, C–N=0·023, C–O=0·021 Å				σC–C=0·020	σC–C=0·013 Å

Angle	*a*	*b*	*c*	*d*	*e*	*f*
O(1)–C(1)–O(2)	122	122·8	123·3	125·0	123	126·1
C(2)–C(1)–O(1)	121	118·4	119·3	118·6	119	120·1
C(2)–C(1)–O(2)	117	118·7	117·3	116·6	117	113·7
C(1)–C(2)–C(3)	111	110·7	110·2	109·4	110	115·0
C(1)–C(2)–N(1)	108	109·5	108·7	108·9	111	108·4
C(3)–C(2)–N(1)	110	113·0	111·0	111·9	110	111·2
C(2)–C(3)–C(4)	115	112·5	114·2	114·6	114	112·8
C(3)–C(4)–N(2)	125	126·3	127·0	128·0	124	122·4
C(3)–C(4)–C(6)	123	124·9	125·0	127·3	129	131·7
C(4)–C(6)–N(3)	102	104·2	104·8	107·6	110	108·4
C(6)–N(3)–C(5)	111	108·4	108·0	107·5	109	108·2
N(3)–C(5)–N(2)	108	110·8	111·9	111·6	110	108·1
C(5)–N(2)–C(4)	106	107·5	107·0	107·2	107	109·8
N(2)–C(4)–C(6)	111	108·7	108·0	105·6	107	105·8
	σ=2°				σ=1·3°	σ=0·9°

error in a parameter by means of the following expression

$$\sigma(p_i) = \sqrt{b_{ii}}\,.\,[\Sigma(w\Delta)^2 - \Sigma\Delta p_i v_i]^{\frac{1}{2}}$$

where w is the least-squares weighting factor,

b_{ii} represents the diagonal elements of the inverse matrix,

$$\Delta = ||F_o| - |F_c||$$

and

$$v_i = \Sigma(\sqrt{w}\,.\,D_i)(\sqrt{w}\,.\,\Delta)$$

where D_i is the appropriate derivative.

The average $\sigma(r)$ in a light atom position, calculated in this way, was 0·017 Å. The average oscillation in any positional parameter at the conclusion of cycle 7 was thus about one eighth of the estimated standard error in the parameter. The value of R, in the conventional terms and excluding unobserved reflections, was 0·133.

A calculation of bond lengths and angles in the molecule, based on the coordinates of Table 1(*a*) showed that the C–N bond in the α-amino group had a length of 1·59 Å; moreover individual deviations of up to 0·09 Å were found from the least-squares mean plane of the histidine ring and C(3). It was felt that these defects were rather larger than might reasonably be expected and so a further three cycles of refinement were undertaken with the inclusion of contributions from the hydrogen atoms in the calculated structure factors. This produced shifts in the atomic positions, in some cases by as much as 0·06 Å, but no noticeable improvement in either the molecular geometry or the discrepancy. A critical examination of the agreement between F_o and F_c for individual structure factors revealed the presence of a systematic error in scaling in a group of about one hundred and fifty high order reflections, consistent with failure to compensate completely for variation in spot size. This error was corrected and the refinement recommenced. Four cycles were run, starting from the values listed in Table 1(*a*) and still neglecting the contributions of the hydrogen atoms. The parameters obtained are given in Table 1(*b*). The oscillations about these mean values were again very small (~ 0·002 Å). The values of the bond lengths and angles resulting from these parameters are listed in Table 2(*b*). Although in terms of the calculated standard deviations there is no significant difference between these coordinates and those obtained previously it is interesting to note that the anomalous C–N distance has now a much more acceptable length.

The value of R for the observed reflections was 0·108 (0·129 including unobserved reflections).

Four further cycles were run with reasonable fixed contributions (B=5·0) postulated for the hydrogen

Table 3. *List of structure factors calculated from the coordinates of Table* 1(*b*), *compared with the observed structure amplitudes*

H	K	L	Fo	Fc
0	0	4	142.3	143.1
0	0	8	14.2	14.2
0	0	12	83.5	82.5
0	0	16	21.7	24.7
0	0	20	80.6	79.8
0	0	24	47.4	45.4
0	0	28	10.1	7.0
0	0	32	.0	.3
0	0	36	27.4	21.6
5	0	1	14.5	14.4
5	0	2	20.5	15.0
5	0	3	42.7	44.1
5	0	4	20.7	19.3
5	0	5	29.6	34.3
5	0	6	39.4	44.5
5	0	7	10.1	16.0
5	0	8	10.5	8.6
5	0	9	45.1	43.8
5	0	10	36.1	31.2
5	0	11	12.6	9.2
5	0	12	32.6	33.5
5	0	13	21.1	23.4
5	0	14	20.9	18.6
5	0	15	30.1	32.8
5	0	16	.0	2.5
5	0	17	20.7	23.2
5	0	18	15.9	18.6
5	0	19	14.8	19.8
5	0	20	.0	4.5
5	0	21	38.3	40.0
5	0	22	21.1	18.3
5	0	23	13.9	15.2
5	0	24	9.5	6.0
5	0	25	26.4	24.0
5	0	26	12.0	15.1
5	0	27	19.7	15.8
5	0	28	7.9	5.8
5	0	29	10.2	7.1
5	0	30	13.7	12.2
6	0	0	52.4	52.8
6	0	1	13.4	18.6
6	0	2	.0	5.0
6	0	3	.0	5.9
6	0	4	45.0	46.6
6	0	5	13.1	12.4
6	0	6	23.1	4.1
6	0	7	13.1	10.2
6	0	8	32.4	31.3
6	0	9	28.7	25.5
6	0	10	12.6	10.2
6	0	11	7.1	3.9
6	0	12	23.7	24.6
6	0	13	14.6	16.6
6	0	14	8.6	8.6
6	0	15	12.6	13.0
6	0	16	29.7	35.3
6	0	17	13.5	8.4
6	0	18	11.4	3.9
6	0	19	.0	.4
6	0	20	31.2	33.9
6	0	21	.0	4.2
6	0	22	13.2	8.5
6	0	23	.0	2.5
6	0	24	29.4	23.9
6	0	25	.0	1.6
6	0	26	.0	.3
6	0	27	4.5	9.3
6	0	28	22.4	15.3
7	0	1	14.0	15.4
7	0	2	35.6	37.5
7	0	3	14.0	14.8
7	0	4	.0	3.6
7	0	5	25.3	27.6
7	0	6	10.8	11.0
7	0	7	16.8	12.7
7	0	8	10.8	9.0
7	0	9	12.7	12.7
7	0	10	.0	3.7
7	0	11	17.2	18.0
7	0	12	.0	2.9
7	0	13	13.1	10.5
7	0	14	.0	3.0
7	0	15	22.9	25.1
7	0	16	.0	4.1
7	0	17	12.3	14.3
7	0	18	19.0	15.6
7	0	19	21.1	20.5
7	0	20	[illegible]	4.8
7	0	21	9.2	9.4
7	0	22	9.7	12.7
7	0	23	23.4	19.0
8	0	0	22.1	19.0
8	0	1	17.4	19.3
8	0	2	.0	2.7
8	0	3	20.4	21.1
8	0	4	13.6	14.5
8	0	5	9.0	9.6
8	0	6	9.0	6.8
8	0	7	9.2	8.2
8	0	8	8.0	7.1
8	0	9	10.3	14.1
8	0	10	11.5	6.0
8	0	11	10.0	9.1
8	0	12	9.7	8.9
8	0	13	22.1	20.5
8	0	14	12.0	9.0
8	0	15	10.0	11.0
8	0	16	11.9	13.7
8	0	17	12.3	13.7
8	0	18	.0	2.4
8	0	19	10.0	8.0
8	0	20	10.3	11.2
8	0	21	10.0	14.4
9	0	1	.0	4.7
9	0	2	10.3	15.9
9	0	3	7.8	6.8
9	0	4	6.2	6.6
9	0	5	.0	.0
9	0	6	11.5	13.7
9	0	8	7.8	8.1
9	0	10	7.3	10.4
0	1	1	128.5	127.3
0	1	2	73.5	78.7
0	1	3	81.0	84.2
0	1	4	86.5	87.9
0	1	5	92.2	95.7
0	1	6	5.8	2.5
0	1	7	47.3	50.1
0	1	8	56.0	59.6
0	1	9	48.2	44.4
0	1	10	56.5	58.3
0	1	11	23.8	16.8
0	1	12	43.0	44.4
0	1	13	33.7	39.6
0	1	14	37.5	35.3
0	1	15	53.9	57.3
0	1	16	10.4	6.9
0	1	17	30.5	27.2
0	1	18	28.7	26.3
0	1	19	53.6	50.2
0	1	20	10.8	8.9
0	1	21	45.2	44.5
0	1	22	18.9	20.1
0	1	23	26.5	25.1
0	1	24	18.0	19.8
0	1	25	18.0	18.1
0	1	26	33.3	33.9
0	1	27	25.0	22.2
0	1	28	23.4	22.4
0	1	29	5.8	5.1
0	1	30	17.3	13.6
0	1	31	14.5	12.9
0	1	32	.0	1.2
0	1	33	12.3	10.7
0	1	34	.0	.4
0	1	35	15.2	10.5
0	1	36	.0	1.9
0	1	37	15.2	10.2
0	1	38	8.3	6.1
0	2	0	6.4	6.2
0	2	1	11.8	14.4
0	2	2	12.6	7.7
0	2	3	120.2	118.5
0	2	4	25.1	15.1
0	2	5	20.9	25.0
0	2	6	22.7	25.0
0	2	7	76.7	76.7
0	2	8	31.5	27.6
0	2	9	11.5	23.5
0	2	10	29.7	17.0
0	2	11	89.6	82.9
0	2	12	40.4	36.3
0	2	13	45.6	39.7
0	2	14	25.6	23.1
0	2	15	59.4	59.3
0	2	16	31.0	25.3
0	2	17	44.9	41.7
0	2	18	6.8	1.6
0	2	19	19.8	25.0
0	2	20	40.2	43.5
0	2	21	18.8	19.6
0	2	22	22.7	12.0
0	2	23	30.0	25.5
0	2	24	20.9	22.0
0	2	25	39.0	43.7
0	2	26	.0	3.3
0	2	27	25.8	23.9
0	2	28	15.0	10.4
0	2	29	16.6	16.0
0	2	30	3.9	4.7
0	2	31	10.6	7.2
0	2	32	21.7	20.1
0	2	33	8.3	7.7
0	2	34	.0	5.1
0	2	35	5.4	1.5
0	2	36	13.8	11.6
0	2	37	16.2	12.1
0	3	1	21.6	15.9
0	3	2	141.0	133.6
0	3	3	8.8	3.4
0	3	4	6.2	6.4
0	3	5	11.3	8.0
0	3	6	72.1	76.5
0	3	7	18.1	19.5
0	3	8	62.6	61.2
0	3	9	46.7	46.4
0	3	10	68.7	76.0
0	3	11	27.6	23.8
0	3	12	24.9	15.8
0	3	13	25.2	25.2
0	3	14	21.0	19.1
0	3	15	8.6	7.4
0	3	16	19.3	14.0
0	3	17	21.4	26.5
0	3	18	48.2	54.5
0	3	19	29.3	24.7
0	3	20	.0	5.0
0	3	21	12.4	15.5
0	3	22	41.6	39.7
0	3	23	.0	5.4
0	3	24	11.3	10.9
0	3	25	18.8	18.3
0	3	26	20.2	18.3
0	3	27	.0	3.2
0	3	28	8.8	6.7
0	3	29	.0	4.0
0	3	30	19.3	19.2
0	3	31	.0	1.0
0	3	32	9.8	8.2
0	3	33	.0	.5
0	3	34	23.1	18.1
0	4	0	57.5	58.4
0	4	1	45.5	45.6
0	4	2	.0	.6
0	4	3	37.6	36.6
0	4	4	13.8	15.4
0	4	5	52.8	53.8
0	4	6	16.7	12.9
0	4	7	34.7	33.6
0	4	8	31.6	23.3
0	4	9	19.8	16.2
0	4	10	.0	6.4
0	4	11	24.9	25.5
0	4	12	14.8	21.3
0	4	13	33.3	33.4
0	4	14	8.3	2.3
0	4	15	27.4	22.9
0	4	16	6.2	8.3
0	4	17	30.1	20.6
0	4	18	9.0	10.3
0	4	19	16.6	14.0
0	4	20	10.4	2.7
0	4	21	14.1	17.2
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0	4	24	4.4	6.2
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0	4	27	16.6	18.5
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5	1	25	7.9	9.4
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2	2	21	.0	7.2
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9	3	1	8.3	4.6
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9	3	3	.0	1.9
9	3	4	13.4	13.9
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9	3	6	5.8	6.5
1	4	0	60.7	62.1
1	4	1	41.4	39.9
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1	4	4	47.3	55.6
1	4	5	17.3	17.9
1	4	6	21.5	18.0
1	4	7	35.8	36.1
1	4	8	31.3	33.9
1	4	9	35.2	36.3
1	4	10	30.5	27.2
1	4	11	24.0	20.5
1	4	12	49.4	47.8
1	4	13	18.9	17.6
1	4	14	13.9	10.5
1	4	15	31.5	29.8
1	4	16	44.9	44.3
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1	4	18	24.9	21.7
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1	4	21	9.8	13.0
1	4	22	14.6	13.0
1	4	23	17.0	13.6
1	4	24	23.7	26.0
1	4	25	7.5	5.7
1	4	26	10.4	9.5
1	4	27	14.2	11.3
1	4	28	22.9	19.4
1	4	29	5.0	7.6
1	4	30	7.2	6.4
1	4	31	8.9	8.5
1	4	32	12.3	10.7
1	4	33	7.8	9.1
1	4	34	.0	.9
1	4	35	8.0	7.9
2	4	0	.0	1.1
2	4	1	35.1	29.7
2	4	2	62.9	66.7
2	4	3	37.6	41.6
2	4	4	16.5	16.8
2	4	5	34.3	30.7
2	4	6	34.1	36.8
2	4	7	27.5	27.8
2	4	8	44.0	50.2
2	4	9	38.4	32.5
2	4	10	26.2	28.7
2	4	11	29.0	30.9
2	4	12	22.1	22.9
2	4	13	26.4	23.0
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2	4	16	32.6	31.9
2	4	17	9.8	10.9
2	4	18	22.3	20.3
2	4	19	20.6	16.7
2	4	20	6.9	[illegible]
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2	4	22	20.0	20.0
2	4	23	9.7	9.4
2	4	24	5.4	6.6
2	4	25	18.5	13.2
2	4	26	19.9	19.3
2	4	27	7.1	8.3
2	4	28	9.4	[illegible]
2	4	29	8.6	[illegible]
2	4	30	11.4	10.8
2	4	31	.0	6.3
2	4	32	3.0	3.4
2	4	33	12.4	[illegible]
2	4	34	9.4	10.5
3	4	0	15.5	13.0
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4	4	6	43.9	44.9
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4	4	8	21.5	15.0
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4	4	25	16.8	13.3
4	4	26	16.1	16.0
4	4	27	.0	2.3
4	4	28	.0	1.8
4	4	29	3.9	[illegible]
4	4	30	13.6	13.6
4	4	31	13.8	12.6
5	4	0	36.7	36.5
5	4	1	15.3	11.1
5	4	2	.0	8.0
5	4	3	23.1	21.6
5	4	4	39.3	36.4
5	4	5	11.9	11.0
5	4	6	18.2	17.3
5	4	7	19.5	18.0
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5	4	9	15.3	14.6
5	4	10	7.2	10.2
5	4	11	13.0	10.0
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5	4	26	.0	3.8
5	4	27	9.0	10.6
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6	4	0	8.8	9.6
6	4	1	21.4	21.2
6	4	2	.0	1.7
6	4	3	13.2	14.2
6	4	4	14.6	14.7
6	4	5	20.7	17.4
6	4	6	10.2	10.0
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6	4	14	.0	6.2
6	4	15	17.3	18.1
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6	4	17	4.9	5.3
6	4	18	.0	4.7
6	4	19	12.0	10.5
6	4	20	8.3	9.5
6	4	21	12.0	12.7
6	4	22	.0	1.7
6	4	23	.0	7.3
6	4	24	7.5	9.9
6	4	25	11.5	13.7
7	4	0	11.0	9.6
7	4	1	7.0	7.7
7	4	2	9.0	7.1
7	4	3	7.0	6.8
7	4	4	11.8	11.0
7	4	5	8.8	9.9
7	4	6	.0	3.5
7	4	7	9.0	11.6
7	4	8	20.8	22.0
7	4	9	10.0	9.9
7	4	10	8.6	6.2
7	4	11	10.2	8.5
7	4	12	24.0	22.6
7	4	13	14.0	13.4
7	4	14	.0	3.1
7	4	15	4.4	4.7
7	4	16	14.2	15.8
7	4	17	.0	7.7
7	4	18	.0	1.8
7	4	19	.0	1.6
7	4	20	8.6	10.2
8	4	1	6.0	6.2
8	4	2	7.8	7.1
8	4	3	6.9	5.2
8	4	4	9.7	9.4
8	4	5	6.1	6.2
8	4	6	.0	6.5
8	4	7	7.8	7.8
8	4	8	5.5	5.5
8	4	9	6.3	6.0
8	4	10	8.3	7.8
8	4	11	6.6	6.2
8	4	12	.0	1.4
8	4	13	9.7	[illegible]
8	4	14	10.5	10.0

atoms of the histidine molecule. The resulting coordinates are given in Table 1(*c*), the corresponding bond lengths and angles in Table 2(*c*). Again, there are no significant differences between these values and those obtained previously, but the atom C(3) moves by 0·055 Å. The value of *R* rose slightly to 0·113.

Two cycles of refinement were calculated with anisotropic temperature factors for the atoms (except hydrogen) but the deviations from spherical symmetry in the shapes of the atoms were not significant in terms of the calculated standard deviations. The coordinates obtained are listed in Table 1(*d*), the corresponding molecular geometry in Table 2(*d*).

Because of the slight increase in *R* when hydrogen atoms are included in the refinement and the apparent spherical symmetry of the atoms, we consider the coordinates of Table 1(*b*) to represent the best solution to the structure and the description of the molecule and its packing in the crystal which follows is based upon these parameters. The major difference between this molecule and that resulting from the values in Table 1(*c*) or 1(*d*) is in the length of the bond C(3)–C(4). Inclusion of hydrogen atoms in the refinement reduces this distance to 1·400 Å (although this length is not significantly different from 1·477 Å) which seems unduly short in view of the results of Harding & Cole (1963). Donohue, Lavine & Rollett (1955) give a value of 1·53 Å for the corresponding bond in histidine hydrochloride but they did not take hydrogen atoms into account in their refinement.

A list of structure factors calculated from the values in Table 1(*b*) is given in Table 3.

Description of the structure

The atomic coordinates resulting from the least-squares refinement with isotropic temperature factors and excluding the contributions of hydrogen atoms have been used in the calculation of the molecular geometry. A view of the molecular arrangement and packing within the crystal is shown in Fig. 2.

A molecule of the complex is made up of two histidine residues, both bonded to the zinc atom through their α-amino groups and N(2) of the imidazole ring. A two-fold axis of symmetry passing through the zinc atom relates the two organic components.

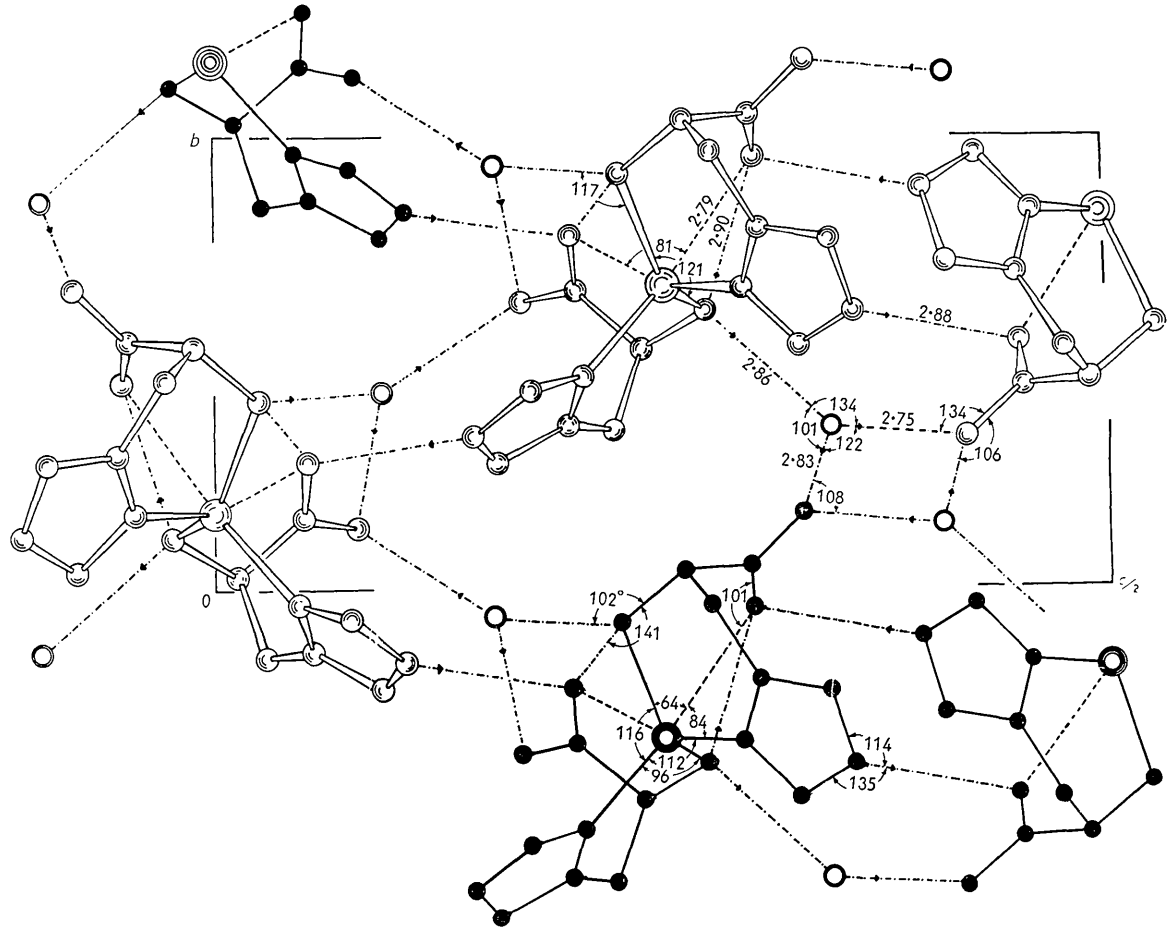

Fig. 2. View of the molecular arrangement in the crystal showing the hydrogen bonding between molecules.

The distribution of Zn–N bonds is roughly tetrahedral but this primary coordination is disturbed by the close approach of the oxygen atom O(1) to within 2·79 Å of the zinc atom on the face defined by N(1), N(2) and N(1′). This close approach may be attributed, at least in part, to attraction between the positive zinc ion and the carboxylate ions, since the charge distribution is, formally, $Zn^{2+}–(C_3H_3N_2)CH_2CH(NH_2)COO^-)_2$. It also appears that the weak hydrogen bond, N(1)–H ··· O(1′), shown in Fig. 2, helps to maintain the oxygen atoms at such a short distance from the Zn atom. The lengths of the Zn–N bonds are effectively equal and may be compared to the sum of the covalent radii for these atoms, 2·03 Å.

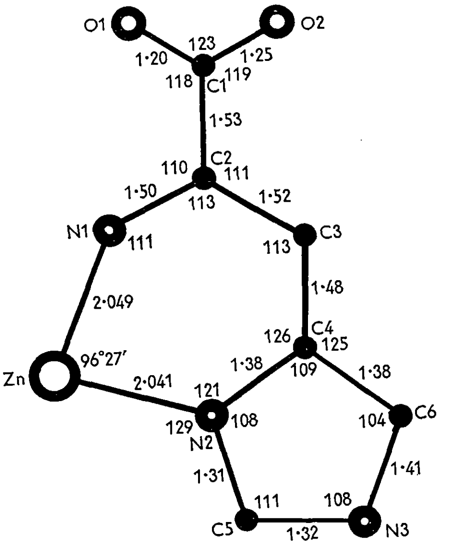

Fig. 3. Bond lengths and angles in the molecule of di-(L-histidino)-zinc (II).

Values of the bond lengths and angles within the histidine residue are shown in Fig. 3 and are listed in Table 2(*b*) together with their estimated standard deviations calculated in the manner outlined above. For comparison, the values found by Harding & Cole (1963) in the molecule of di-(DL-histidino)-zinc (II) pentahydrate and by Donohue, Lavine & Rollett (1956) for histidine hydrochloride monohydrate are also listed in the table.

The atoms of the imidazole ring and C(3) are coplanar, the equation of their mean plane being given (Blow, 1960) by:

$$0·7707X - 0·4010Y - 0·4952Z + 3·2957 = 0 .$$

The average deviation of an atom from this plane is 0·016 Å, or about one standard deviation in position, and the maximum is 0·036 Å. The zinc atom is 0·57 Å from this plane. The mean plane of the atoms of the carboxyl group, C(2) and N(1) is defined by the equation:

$$-0·5365X + 0·7197Y - 0·4407Z - 0·2947 = 0$$

and the average deviation from this plane is 0·055 Å, or more than three standard deviations. By contrast, the equation of the plane of the atoms of the carboxyl group and C(2) alone is given by:

$$-0·5334X + 0·6839Y - 0·4977Z - 0·5133 = 0$$

and the average deviation is 0·006 Å. N(1) lies 0·256 Å from this plane. We conclude, therefore, that in contrast to the situation in the molecule of di-(DL-histidino)-zinc (II), the 'peptide' grouping in this case is not planar. Donohue, Lavine & Rollett (1955) describe a similar effect in histidine hydrochloride, but the magnitude of the deviation is given as only 0·029 Å.

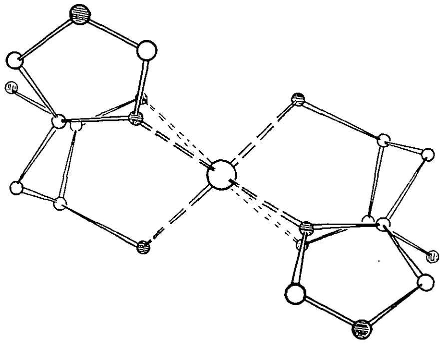

Fig. 4. Representation of the molecule of di-(L-histidino)-zinc (II) viewed down the two-fold axis passing through the Zn atom. This should be compared with Fig. 4 of Harding & Cole, p. 647.

The relationship between the configuration of the histidine groups in the present instance and in the case of the molecule of di-(L-histidino)-zinc (II) as found by Harding & Cole may be seen by referring to our Fig. 4 and their Fig. 4. The configuration of the individual histidine molecules is almost the same in each case. In our case the angle between the plane of the carboxyl group and C(2) and the plane defined by C(2), C(3) and C(4) is 60·5° whilst the angle between the plane of the imidazole ring and the atoms of the carboxyl group is 139·5°. The way in which histidine residues are related to one another differs in each case, corresponding to the difference in orientation of the two-fold axis in the two structures. The difference corresponds, very roughly, to a rotation of one histidine residue through 180° with the interchange in position of N(1) and N(2). This illustrates the way in which the configuration of such a molecule is determined by environmental pressures.

There is a marked inequality in the structure of histidine hydrochloride between the angles C(3)–C(4)–C(6) and C(3)–C(4)–N(2) (132° and 122° respectively) presumably caused by steric repulsion between N(1) and C(6). In our structure the two angles are not significantly different presumably because rotation about the bond C(3)–C(4) replaces the bulkier carbon atom by N(2). It would seem, if the difference in angles in the structure proposed by Donohue, Lavine

& Rollett is really significant, that a considerable strain in a bond angle may be tolerated if a more satisfactory packing or hydrogen bond pattern may be so achieved. The individual molecules in the crystal are held together by a three-dimensional network of hydrogen bonds in a manner which might well serve as a model to demonstrate the importance and effectiveness of such bond formation in determining the molecular packing within a crystal. The thoroughness and simplicity of the scheme may be seen from Fig. 3.

The two hydrogen atoms of the amino group both take part in bond formation, in the one case to form an intra-molecular linkage N(1)–H · · · O(1′), in the other the bond N(1)–H · · · O(H_2O). In turn, the two hydrogens of the water molecule participate in the bonds O(H_2O)–H · · · O(2), $x, y-1, z$, and O(H_2O)–H · · · O(2), $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{4}-z$ The lengths of these bonds, 2·83 and 2·75 Å, indicate that they are fairly weak interactions, and this is confirmed by the significantly higher value of B found for the water oxygen atoms than for the other light atoms.

The remaining hydrogen atom available for bond formation, that attached to N(3) bonds to O(1) of a neighbouring molecule, as shown. In turn, the atom N(3) of that molecule is involved in an analogous bond to the O(1) of the molecule one translation along a from the first, and so on, forming a spiralling system of interactions.

The sole van der Waals contacts between molecules occur at C(6) and N(3) where molecules approach to within 3·76 Å of each other.

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The Crystal Structure of Acrylic Acid

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The structure of crystalline acrylic acid ($C_3H_4O_2$) has been determined at −135 °C by X-ray diffraction methods. The crystals were found to be orthorhombic, space group $Ibam$–D_{2h}^{26} with 8 molecules per unit cell. The cell constants are

$$a=9{\cdot}966\pm0{\cdot}007,\ b=11{\cdot}744\pm0{\cdot}013,\ c=6{\cdot}306\pm0{\cdot}016\ \text{Å}\,.$$

The structure was refined by least-squares techniques. The molecules are planar hydrogen bonded dimers lying on crystallographic mirror planes.

Introduction

The structure of acrylic acid, ($CH_2=CH-COOH$), has been examined as part of a series of investigations of the structures of low molecular weight carboxylic acids. Acrylic acid is the simplest unsaturated aliphatic acid. Its melting point (12 °C) is some 30° higher than that of propionic acid (−22 °C) and very close to that of acetic acid (16·5 °C). This fact suggested that the hydrogen bonding system is of the infinite chain type as in acetic acid (Jones & Templeton, 1958) and not dimeric as in propionic acid (Strieter, Templeton, Scheerman & Sass, 1962). This investigation shows, however, that acrylic acid crystallizes in hydrogen bonded dimers across a symmetry center, the observed high melting point not being a consequence of the hydrogen bonding.