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The Crystal Structure of Di(Histidino)Zinc Pentahydrate

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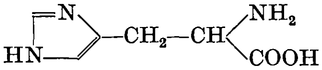
The crystal structure of di(histidino)zinc pentahydrate, $Zn(C_6H_8N_3O_2)_2.5H_2O$, has been determined by Fourier analysis and least-squares refinement using three-dimensional intensity data from Cu$K\alpha$ radiation. The crystals are monoclinic, with space group $C2/c$, and cell dimensions

$$a = 16{\cdot}41,\ b = 14{\cdot}755,\ c = 10{\cdot}99\ \text{Å},\ \beta = 129{\cdot}6°.$$

The primary co-ordination around the zinc atoms, which lie on two-fold axes, is a distorted tetrahedron, consisting of an amino nitrogen and an imidazole nitrogen (at 2·05 and 2·00 Å) from each of the two histidine groups. One oxygen atom from each histidine group is also very weakly associated (at 2·91 Å). The molecules of di(histidino)zinc and the water molecules take part in an elaborate system of hydrogen bonds holding the structure together.

Some evidence (Tanford & Epstein, 1954) suggested that in the association of zinc with insulin, histidine residues are involved; thus a knowledge of the structure of di(histidino)zinc seemed relevant to the studies of crystalline zinc insulin which are in progress in this laboratory. This, and a general interest in the coordination chemistry of both zinc and histidine



led us to undertake the structure determination. Some recent evidence (Marcker, 1960), however, suggests that it is not histidine, but the *N*-terminal phenylalanine of insulin which is co-ordinated to zinc.

The crystals whose structure determination we shall describe were prepared from DL-histidine and have the composition $Zn(C_6H_8N_3O_2)_2.5\,H_2O$. Kretsinger, Cotton & Bryan (1963) have studied crystals of $Zn(C_6H_8N_3O_2)_2.2\,H_2O$ prepared from L-histidine, and this structure determination is described in the following paper.

Crystal data

Crystals were obtained by slowly cooling an aqueous solution of zinc sulphate and DL-histidine (Weitzel *et al.*, 1957). Oscillation and Weissenberg photographs were taken with Cu $K\alpha$ radiation. For determination of the cell dimensions an oscillation camera with the film mounted according to Straumanis's method, and the extrapolation procedure described by Henry, Lipson & Wooster (1960), were used. The crystals are monoclinic, elongated along c.

$$a = 16{\cdot}41 \pm 0{\cdot}015,\ b = 14{\cdot}755 \pm 0{\cdot}015\ ,$$
$$c = 10{\cdot}99 \pm 0{\cdot}015\ \text{Å};\ \beta = 129{\cdot}6 \pm 0{\cdot}15°.$$

From systematic absences the space group is $C2/c$ or Cc; a statistical test (Wilson, 1949) on the $hk0$ intensity data indicated the centrosymmetric group $C2/c$, and throughout the subsequent structure determination this appeared to be satisfactory. The density, measured by flotation, is $1{\cdot}50_4$ g.cm^{-3}, so there are four molecules per unit cell (the calculated density is $1{\cdot}50_2$ g.cm^{-3}).

Structure determination

Multiple-film Wiessenberg photographs were taken of the layers $h0l$ to $h8l$ and $hk0$ to $hk4$, the intensities measured visually, and Lp corrections applied. Five-sixths of the reflections in the higher layers were measured as 'extended spots' and one-sixth as 'contracted spots'. Those reflections which could be measured in both extended and contracted forms on any one film were used to select an empirical spot-shape correction. The required correction, δ, as a fraction of the measured intensity is, to a good approximation, $(I_{\text{cont}}-I_{\text{ext}})/2I_{\text{mean}}$. In any layer it should be largest at $\xi \sim 0$ and decrease to zero at the edge of the film, *i.e.* at $\theta = 90°$ (θ is the Bragg angle, and ξ and ζ are reciprocal lattice co-ordinates). Various plots were made to find a linear relation between δ in any one layer, and some function of θ or ξ; three examples are given in Fig. 1. $\sqrt{(\sin\theta')}$ was chosen (where $\sin\theta' = \xi/2$), but $\sin\theta'$, $\sin\theta$, $\sqrt{(\sin\theta)}$ are not significantly less satisfactory since the errors in measurement of δ are considerable; $\cos\theta$, however, does seem to be much less satisfactory. Further, the slope of δ with respect to the chosen function of θ, should change smoothly with ζ, the layer height; here the slopes in all layers could be adequately represented by ζ multiplied by a single constant k. Thus the intensities were corrected in the following way:

$$I_{\text{ext}} \times (1 + k\zeta\sqrt{(\sin\theta')} + K)$$
$$I_{\text{cont}} \times (1 - k\zeta\sqrt{(\sin\theta')} + K)$$

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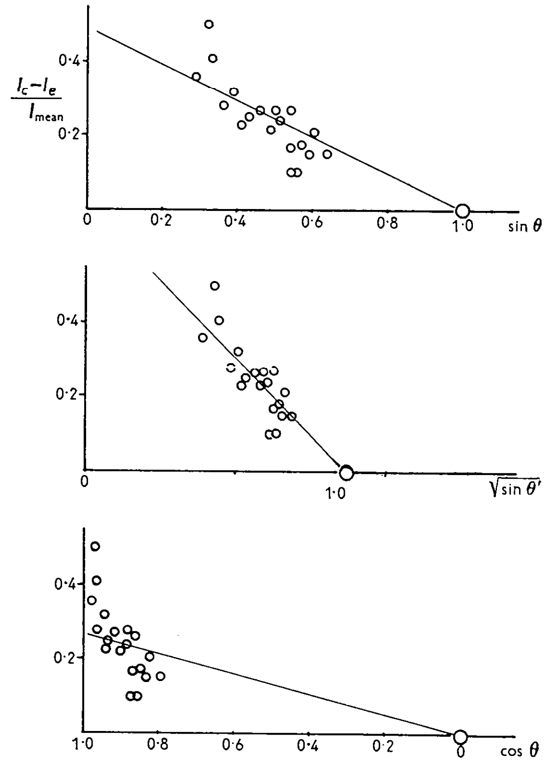

Fig. 1. Examples of plots, for the layer *hk*3, of $(I_{\text{cont}} - I_{\text{ext}})/I_{\text{mean}}$ which is equivalent to twice the required spot-shape correction (expressed as a fraction of I). The larger circles represent $\theta = 90°$ where the spot-shape correction should be zero.

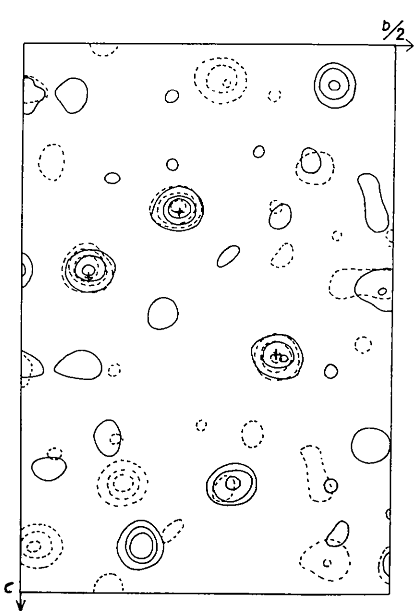

Fig. 2. Superposition of the sharpened three-dimensional Patterson series from the zinc atom at 0, 0·037, 0·25, as origin (full lines) and from the zinc atom at 0, −0·037, 0·75, as origin (dotted lines). The section at $x = 13/60$ is shown; the crosses mark the positions of C_3, N_3, and C_6' which all lie in or near this section.

k is one constant for all the data (=0·67 here),

K are normalising constants in each layer, to make the correction zero at $\theta = 90°$.

After this spot-shape correction, all the data were correlated and assembled. The intensities of 1370 reflections were measured, those of 557 were too small for observation, and about 300 were not recorded on any film, although they are within the Cu $K\alpha$ limit. An approximate scale and temperature factor were determined from a 'Wilson plot'.

Sharpened Patterson projections along the b and c axes gave tentative positions for the zinc atoms, which were confirmed by the three-dimensional Patterson synthesis, sharpened 'to point atoms at rest'. The zinc atoms are on two-fold axes at $0, y, \frac{1}{4}$, $0, -y, \frac{3}{4}$, etc., with $y = 0{\cdot}037$. By superposition of the Patterson sections from these two positions as origins, the positions of all atoms of the histidine residue (except hydrogen) were found (Fig. 2). From the smaller peaks three reasonable water-molecule oxygen positions were found, one being on a two-fold axis. The only other features in the superposition map were diffraction peaks around the zinc atom, and one small peak too near to other atomic positions to be a water molecule. Structure factors were calculated and gave $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 21\%$, for all observed reflections. Comparison of the positions with the co-ordinates subsequently found after refinement showed that C_2, which is nearly in the glide plane, had been misplaced by 0·15 Å; no other atom was more than 0·1 Å from its correct position, and the average displacement was 0·05 Å.

Refinement

Two $(F_o - F_c)$ series were calculated and appropriate changes made to the co-ordinates, scale, and temperature factors. R fell to 18%. The hydrogen atoms of the histidine group (at the expected positions) were included in the next and subsequent structure-factor calculations, and the co-ordinates and individual isotropic temperature factors of zinc, carbon, nitrogen, and oxygen atoms were refined by least squares. At the end of this refinement R was 12·7%.

To confirm the hydrogen positions already used, and to find others, another $(F_o - F_c)$ series was calculated in which no hydrogen contributions were included in F_c. Positive regions of electron density appeared in most places where hydrogen atoms of the histidine group were expected. For many of the hydrogen atoms of water molecules there are two alternative sites; such 'half' hydrogens were much less easy to find. It was evident that the largest features in the difference series were not due to hydrogen atoms but to anisotropic vibrations of the other atoms.

Three cycles of anisotropic least-squares refinement were then carried out, bringing R to 10·5% (for observed reflections only), and the co-ordinate shifts

Table 1(*a*). *Positional and thermal parameters, determined by anisotropic least-squares refinement*

The numbering of the atoms can be seen in Figs. 3 and 6

The temperature factor of an atom is

$$\exp -(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{23}kl+b_{31}hl+b_{12}hk)$$

	x	y	z	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
Zn	0	0·03718	0·2500	0·00288	0·00208	0·00925	0	0·00598	0
C_1	0·1733	0·0767	0·6328	0·00476	0·00220	0·01056	0·00155	0·01099	−0·00117
C_2	0·1908	−0·0097	0·5775	0·00442	0·00217	0·00826	−0·00236	0·00873	0·00001
C_3	0·2626	0·0094	0·5354	0·00313	0·00373	0·00895	−0·00171	0·00751	−0·00053
C_4	0·2286	0·0891	0·4302	0·00376	0·00318	0·00854	−0·00263	0·00932	−0·00092
C_5	0·1217	0·1842	0·2346	0·00634	0·00250	0·01074	−0·00096	0·01360	−0·00089
C_6	0·2887	0·1553	0·4341	0·00505	0·00411	0·01133	−0·00446	0·01137	−0·00329
N_1	0·0894	−0·0481	0·4403	0·00364	0·00243	0·01019	0·00213	0·00855	−0·00159
N_2	0·1217	0·1079	0·2989	0·00369	0·00259	0·00761	−0·00089	0·00837	−0·00010
N_3	0·2197	0·2135	0·3116	0·00871	0·00336	0·01559	−0·00332	0·01869	−0·00368
O_1	0·0821	0·1071	0·5572	0·00504	0·00299	0·01765	−0·00716	0·01252	−0·00156
O_2	0·2534	0·1141	0·7554	0·00713	0·00289	0·00913	−0·00403	0·01011	−0·00205
O_3	0·1557	0·2152	0·8665	0·01227	0·00465	0·02847	0·00134	0·02996	0·00166
O_4	0·0344	0·4097	0·0148	0·00597	0·01076	0·02138	−0·00685	0·00837	0·00491
O_5	0	0·3424	0·7500	0·00958	0·00519	0·01546	0	0·01513	0

Table 1(*b*). *Coordinates and temperature factors of hydrogen atoms used in structure factor calculations*

	x	y	z	B	On atom
H_1	0·234	−0·052	0·680	3·5 Å^{-2}	C_2
H_2	0·120	−0·108	0·425	3·5	N_1
H_3	0·028	−0·072	0·433	3·5	N_1
H_4	0·338	0·000	0·579	3·5	C_3
H_5	0·215	−0·045	0·400*	3·5	C_3
H_6	0·052	0·217	0·135	3·5	C_5
H_7	0·230	0·273	0·295	3·5	N_3
H_8	0·374	0·161	0·518	3·5	C_6
H_9	0·192	0·200	0·825	6·0	O_3
H_{10}	0·108	0·400	0·088	6·0	O_4
$\frac{1}{2}H_{11}$	0·220	0·247	0·962	6·0	O_3
$\frac{1}{2}H_{12}$	0·100	0·267	0·825	6·0	O_3
$\frac{1}{2}H_{13}$	0·050	0·300	0·762	6·0	O_5
$\frac{1}{2}H_{14}$	0·008	0·465	0·005	6·0	O_4
$\frac{1}{2}H_{15}$	0·025	0·384	−0·080	6·0	O_4
$\frac{1}{2}H_{16}$	0·020	0·380	0·839	6·0	O_5

* This coordinate was actually used in structure factor calculation, but should have been 0·4300.

indicated by a fourth cycle were all less than 0·0015 Å. These parameters are given in Table 1, and the observed and calculated structure factors in Table 2(*a*). When non-observed reflections are included R is 13·7% (Table 2(*b*)).

The atomic scattering factors used for carbon, nitrogen, and oxygen were those of Berghuis *et al.* (1955); O_1 and O_2, the carboxyl oxygen atoms were treated as $O^{\frac{1}{2}-}$. For hydrogen, McWeeny's (1951) scattering factor was used, and for zinc that of Thomas & Umeda (1957) with a correction for anomalous dispersion (Dauben & Templeton, 1955).

J. S. Rollett's 'Structure Factor and Least Squares' refinement program was used; reflections were given weights $|F_o|/960$ when $|F_o|<960$ (on the same scale as in Table 2), and $960/|F_o|$ otherwise. This and all the other calculations were done on the Ferranti 'Mercury' Computer at Oxford.

Standard deviations, calculated according to Ahmed and Cruickshank's formula (1953) (with Darlow's (1960) correction), are given in Table 3(*a*). In Table 3(*b*) the bond distances obtained at the end of the isotropic refinement are given for comparison with those obtained after the anisotropic refinement. There are small differences, but the largest (C_2–C_3) is 0·015 Å, and is smaller than the standard deviation of either. The same is true of bond angles. Thus three cycles of anisotropic least-squares refinement achieved an improvement in R, but no significant change in interatomic distances or angles, and only slightly smaller standard deviations in these distances and angles.

Description and discussion of the structure

The configuration of the molecule, and bond lengths and angles are shown in Fig. 3. The angles around the zinc atom are given in Table 4; bond lengths are also given in Table 3(*b*).

The primary co-ordination group around the zinc atom is a distorted tetrahedron, consisting of an amino nitrogen and an imidazole nitrogen from each of two

Table 2(*a*). *Observed and calculated structure factors*

The columns represent h, $50F_o$, $50F_c$. The lines preceded by an asterisk give the indices l and k for the group of reflections immediately below

* 0	0	
2	-1692	-1681
4	3950	3720
6	380	511
8	2575	2503
10	1415	1354
12	968	947
14	385	314
16	390	309
* 0	1	
1	5053	4962
3	-1547	-1377
5	179	467
7	955	1163
9	1521	1472
11	1633	1704
13	541	611
15	498	490
* 0	2	
0	5136	4164
2	2236	2215
4	2833	2891
6	667	794
8	998	1056
10	1116	1080
12	1161	1130
14	110	105
16	329	320
* 0	3	
1	1738	1827
3	3276	3196
5	3170	3206
7	1020	990
9	865	883
11	1413	1381
13	283	263
15	405	454
* 0	4	
0	-1107	-928
2	-245	-166
4	1137	1085
6	2285	2037
10	710	648
12	559	547
14	283	239
16	200	209
* 0	5	
1	1148	1082
3	830	813
5	2247	2056
7	1047	1075
11	347	310
15	316	343
* 0	6	
0	-1532	-1206
2	-290	-175
4	863	806
6	959	814
8	478	368
10	438	471
* 0	7	
1	-1742	-1435
3	1663	1522
5	-851	-876
7	400	170
9	-633	-677
11	276	106
13	-482	-526
* 0	8	
2	-1584	-1357
4	410	340
6	-837	-879
10	-347	-323
14	-167	-119
* 0	9	
3	-1676	-1699
7	-870	-745
11	-452	-345
13	-310	-314
* 0	10	
0	1141	1030
2	-2111	-2021
4	-957	-860
6	-1170	-1165
10	-775	-790
12	-429	-357
* 0	11	
1	-994	-1066
3	-1455	-1486
5	-901	-862
7	-600	-513
9	-587	-450
11	-478	-349
* 0	12	
0	-1059	-1053
2	-1219	-1222
4	-597	-520
6	-283	-246
8	-762	-736
10	-490	-447
12	-452	-459
* 0	13	
1	-1545	-1572
3	-1059	-1075
7	-623	-475
9	-1034	-931
11	-352	-222
* 0	14	
0	-912	-867
2	-1272	-1388
4	-335	-233
8	-964	-922
10	-429	-367
* 0	15	
1	-767	-723
3	-623	-650
7	-490	-351
9	-443	-423
* 0	16	
0	-667	-627
2	-461	-401
4	-518	-586
6	-478	-398
8	-237	-204
* 0	17	
3	-297	-305
5	-443	-500
* 0	18	
0	253	354
2	-210	-251
4	-179	-189
* 1	1	
1	1148	888
3	-1224	-1047
5	469	473
7	-710	-663
9	-1195	-1255
-1	-1426	-1442
-3	1801	1739
-5	-639	-511
-7	1040	903
-9	-808	-680
-11	469	408
-13	228	294
-15	-228	-269
* 1	2	
0	-1826	-1511
2	-1389	-1225
4	775	620
6	-874	-800
8	-976	-901
10	-696	-732
-2	-3015	-3375
-4	-1936	-1983
-6	-2501	-2439
-8	-1978	-1902
-10	-1332	-1345
-12	486	510
-14	-690	-722
* 1	3	
1	127	190
3	-1899	-1831
5	-2085	-1762
7	-2170	-1930
9	-1135	-1118
11	-443	-423
13	-276	-272
-1	-3307	-3143
-3	-190	-338
-5	-219	-22
-7	-1853	-1581
-9	-941	-868
-11	352	340
-13	-276	-300
-15	-303	-371
* 1	4	
0	604	412
2	-707	-740
4	-1859	-1712
6	-1094	-1159
8	-510	-539
10	-329	-239
12	-544	-476
14	-323	-338
-2	-3379	-3363
-4	-434	-679
-6	-2845	-2879
-8	-1817	-1904
-10	-947	-979
-12	-390	-371
-14	-461	-485
-16	-245	-198
* 1	5	
1	-3405	-2937
3	-4058	-3864
5	-3125	-2864
7	-865	-961
9	-803	-690
11	-702	-691
13	-456	-429
-1	-642	-776
-3	-1624	-1880
-5	-2658	-2862
-7	-1233	-1231
-9	-2027	-2204
-11	-597	-566
-13	-764	-811
-15	-283	-272
* 1	6	
0	-3058	-2637
2	-3533	-2839
4	-3124	-3850
6	-335	-504
8	-923	-894
10	-443	-425
12	-610	-626
14	-465	-535
-2	1348	914
-4	-1862	-2742
-6	-735	-885
-8	-2053	-1958
-10	-1333	-1137
-12	-777	-775
-14	-245	-131
-16	-245	-266
* 1	7	
1	-2590	-2550
3	-2838	-2751
5	-1324	-1309
9	790	117
11	-639	-597
13	-374	-449
-1	-849	-1040
-3	-502	-791
-5	-1210	-1633
-7	-2093	-2139
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-11	-1139	-1206
-13	-529	-441
-15	-310	-245
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4	-1668	-1774
6	-2402	-2416
10	-730	-717
12	-533	-615
-2	-395	-469
-4	-1612	-1658
-6	-1016	-1089
-8	-1909	-1938
-10	-526	-472
-12	-897	-1000
* 1	9	
1	-1547	-1575
3	-1010	-1016
5	-1103	-1065
7	-926	-775
11	-562	-557
13	-283	-361
-1	-724	-820
-3	-1264	-1591
-5	-1436	-1571
-7	-1293	-1360
-9	-537	-583
-11	-959	-1063
-13	-297	-232
-15	-190	-175
* 1	10	
0	-526	-630
2	-1530	-1436
6	-1510	-1331
10	-518	-525
12	-253	-162
-2	-727	-814
-4	-1267	-1339
-6	-899	-985
-10	-813	-909
-12	-245	-230
-14	-167	-130
* 1	11	
1	-1207	-1276
5	-461	-408
7	-836	-851
9	-502	-561
11	-283	-275
-1	-998	-952
-3	-710	-826
-5	-1426	-1543
-9	-764	-872
-13	-190	-129
* 1	12	
0	-610	-594
4	968	917
6	-555	-571
8	-533	-552
-2	-874	-945
-6	-461	-524
* 1	13	
3	533	496
5	261	227
7	-555	-675
-1	-815	-767
-11	167	224
* 1	14	
2	420	383
-4	-420	-586
-6	310	574
* 1	15	
1	803	778
7	283	288
-1	310	178
-7	772	956
-9	316	100
* 1	16	
0	374	251
2	374	381
6	415	480
-2	429	527
-6	573	675
* 1	17	
1	245	212
3	219	193
5	329	366
-1	261	235
-3	210	229
-5	369	443
-7	290	302
* 1	18	
0	385	365
2	179	134
-4	490	540
* 2	0	
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2	-681	-731
4	-1433	-1692
6	-2635	-2596
8	-2516	-2400
12	-544	-614
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-4	-1383	-1514
-6	-2105	-2227
-8	-3645	-3932
-10	-2110	-2367
-14	-1006	-1057
-16	-699	-822
-18	-583	-618
* 2	1	
1	-2841	-2453
3	-1797	-1799
5	-1744	-1753
7	-2615	-2412
9	-716	-730
13	-335	-321
-1	-2635	-2638
-3	-2960	-2644
-5	-3303	-3572
-7	-1848	-2049
-9	-2461	-2468
-11	-593	-596
-15	-713	-761
-17	-400	-425
* 2	2	
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2	-5413	-3321
4	-374	-159
6	-2351	-2079
8	-1262	-1560
10	-390	-332
12	-490	-505
-2	-1439	-1445
-4	-3252	-3703
-6	-2478	-2457
-8	-741	-726
-10	-1564	-1716
-12	-702	-640
-14	-990	-956
-16	-424	-424
-18	-141	-374
* 2	3	
1	-3689	-3383
3	-1782	-1642
5	-1548	-1360
7	-1330	-1273
9	-555	-567
11	-600	-562
13	-390	-492
-1	1927	1532
-3	-4561	-6372
-5	-2834	-2844
-7	-1010	-1175
-9	-676	-685
-11	-861	-769
-13	-1497	-1445
-15	-341	-323
-17	-335	-426
* 2	4	
0	-400	-537
2	-1981	-1745
4	-482	-696
6	-861	-818
10	-724	-771
-2	-4070	-4186
-4	-730	-882
-6	-1958	-1985
-8	648	511
-10	-830	-804
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−5	303	336
−7	−297	−251
−21	−155	−184
• 9	2	
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2	−323	−476
−2	−839	−977
−6	−721	−806
−10	−844	−896
−12	−685	−746
−14	−400	−397
−16	−374	−305
• 9	3	
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−7	−400	−278
−9	−390	−361
−11	−580	−561
−13	−951	−969
−19	−469	−458
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−4	−710	−735
−8	−478	−421
−10	−678	−712
−12	−964	−897
−14	−1105	−1074
−18	−341	−233
−20	−329	−421
• 9	5	
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−3	−1249	−1115
−5	−420	−295
−7	−767	−704
−9	−486	−322
−11	−1137	−947
−13	−936	−835
−15	−897	−809
−17	−510	−404
• 9	6	
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−2	−741	−572
−4	−832	−817
−6	−380	−234
−8	−1010	−1052
−12	−707	−617
−14	−822	−740
−16	−1014	−938
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−9	−693	−744
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−15	−953	−861
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• 9	8	
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−4	−569	−451
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−8	−456	−467
−12	−447	−331
−14	−953	−893
−16	−482	−404
−18	−490	−507
• 10	0	
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−6	−424	−319
−8	−919	−867
−12	−2054	−1809
−14	−478	−280
−16	−945	−796
−20	−465	−366
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−3	−533	−662
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−7	−777	−838
−11	−1179	−1258
−13	−754	−790
−15	−290	−116
−17	−533	−428
−21	−555	−563
• 10	2	
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−4	−438	−529
−10	−915	−912
−12	−1105	−1063
−16	−363	−167
−18	−593	−596
• 10	3	
−1	−465	−519
−3	−290	−289
−5	−390	−363
−7	−510	−578
−9	−461	−452
−11	−1217	−1265
−15	−410	−377
−17	−341	−247
−19	−544	−588
• 10	4	
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−4	347	443
−6	−696	−711
−8	−639	−694
−10	−369	−370
−14	−415	−291
−18	−541	−661
• 10	5	
−7	−1249	−1306
−15	−465	−526
−17	−237	−205
• 10	6	
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−6	−713	−799
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−14	−429	−434
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−13	329	451
−17	447	437
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−18	443	546
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−5	510	537
−7	424	378
−13	681	660
−17	363	293
−19	447	426
• 11	4	
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−8	438	282
−12	347	341
−14	276	200
−16	245	27
−18	482	617
−20	261	299
• 11	5	
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−7	555	537
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−11	390	354
−13	434	395
−17	559	547
−19	502	545
• 11	6	
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−12	707	626
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−18	461	351
• 11	7	
−7	636	717
−9	617	421
−15	670	560
−17	478	454
• 11	8	
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−8	410	432
−10	651	734
−16	693	650
−18	200	82
• 12	0	
−4	562	787
−8	438	497
−12	363	208
−14	851	950
−16	604	460
−20	245	174
• 12	1	
−5	555	776
−9	434	491
−13	510	525
−15	705	658
−17	329	109
• 12	2	
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−10	593	723
−14	537	501
−16	390	267
• 12	3	
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−9	452	552
−13	469	410
−15	253	216
−17	347	367
−19	253	195
• 12	4	
−10	380	457
−16	506	595
• 12	5	
−7	283	266
−9	261	137
−17	410	549
• 12	6	
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−16	−245	−164
• 13	1	
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• 13	2	
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−14	−400	−557
• 13	3	
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• 13	4	
−10	−705	−728
−14	−290	−218
• 13	5	
−9	−245	−213
−11	−424	−491
−17	−245	−309
• 13	6	
−10	−228	−194
−12	−429	−241
−14	−179	−49
−16	−179	−263
• 13	7	
−11	−141	−102
−13	−167	−29
• 14	0	
−12	−219	−324
−14	−268	−347
• 14	1	
−13	−200	−234
−15	−276	−482
• 14	2	
−14	−179	−177

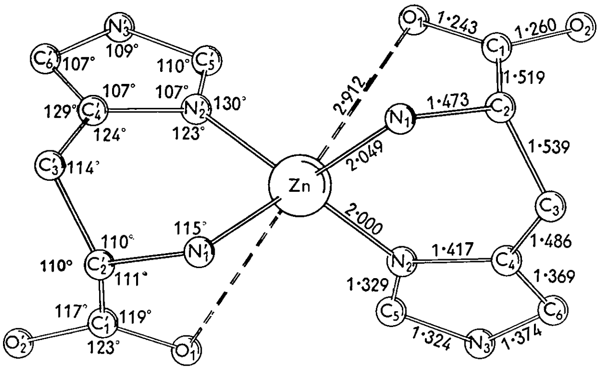

Fig. 3. Bond lengths and angles in one molecule of di(histidino)-zinc, viewed along the two-fold axis. The bond angles around the zinc atom are given in Table 4.

histidine groups. But there is also one oxygen atom from each histidine group 2·91 Å from the zinc atom, which suggests a weak association. The two histidine groups are related by a two-fold axis through the zinc atom; thus the crystal contains molecules of di(D-histidino)zinc and of di(L-histidino)zinc related to each other by centres of symmetry.

With oxygen- or nitrogen-containing ligands zinc is frequently found in regular, or nearly regular, octahedral co-ordination, for example in zinc oxinate (Merritt, Cady & Mundy, 1954). But the co-ordination group found here in di(histidino)zinc closely resembles that in zinc salicylate dihydrate (Klug, Alexander & Sumner, 1958), where the zinc atom has four near neighbours (oxygen atoms at 2·03 and 2·06 Å) and two more oxygen atoms are further away (at 2·52 Å).

The arrangement of each histidine group with respect to the zinc atom is very nearly the same in these molecules as it is in the molecules described by Kretsinger, Cotton & Bryan (KC&B); the arrangement of four nitrogen atoms around zinc is also similar in the

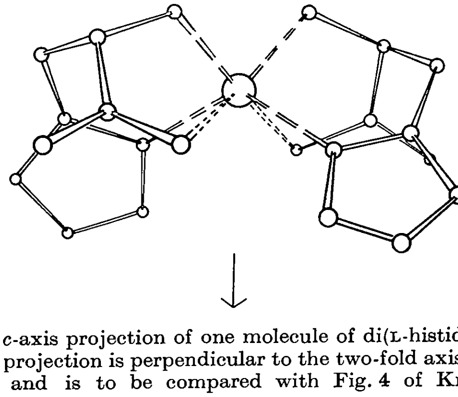

Fig. 4. *c*-axis projection of one molecule of di(L-histidino)zinc. This projection is perpendicular to the two-fold axis through zinc and is to be compared with Fig. 4 of Kretsinger, Cotton & Bryan.

Table 2(*b*). *Structure factors for non-observed reflections are given in the same form as in Table 2(a) except that F_o is replaced by the square root of half the minimum observable intensity multiplied by the appropriate L_p factor*

• 0	5	
9	237	29
13	-219	-296
• 0	6	
12	-237	-88
14	179	232
• 0	7	
15	110	272
• 0	8	
8	-237	-160
12	-219	-103
• 0	9	
1	200	4
5	-219	-311
9	-245	-277
• 0	10	
8	-245	-104
• 0	11	
13	-110	-498
• 0	13	
5	-245	0
• 0	14	
6	228	119
• 0	15	
5	-219	-31
• 0	17	
1	-190	-62
7	-110	-162
• 0	19	
1	89	72
• 1	1	
11	245	256
13	-210	-81
15	-110	-13
-17	-110	-221
• 1	2	
12	228	264
14	-167	-187
-16	-167	-141
• 1	3	
15	-89	-235
-17	-89	-364
• 1	7	
7	-245	-736
• 1	8	
8	-245	-24
• 1	9	
9	237	158
• 1	10	
4	-228	-138
8	-237	-273
-8	245	156
• 1	11	
3	237	203
-7	245	160
-11	-219	-40
• 1	12	
2	237	25
10	-167	-195
-4	245	119
-8	-237	-96
-10	-219	-302
-12	167	117
• 1	13	
1	245	13
9	-179	-90
11	-63	-130
-3	245	74
-5	-245	-67
-7	237	207
-9	-219	-157
• 1	14	
0	-245	-166
4	228	38
6	210	3
8	179	25
10	-89	-52
-2	245	119
-8	210	113
-10	-167	-14
-12	-63	-19
• 1	15	
3	-219	-285
5	200	224
9	89	123
-3	228	287
-5	-219	-220
-11	63	82
• 1	16	
4	-190	-113
-4	-210	-184
-8	155	256
• 1	18	
4	89	630
-2	155	104
-6	89	332
• 1	19	
-1	63	292
• 2	0	
10	-245	-84
14	-110	-107
-12	-237	-98
• 2	1	
11	228	150
-13	-245	-28
• 2	2	
14	-110	-209
• 2	4	
8	-237	-21
-12	-237	-16
-16	190	121
• 2	5	
11	-210	-278
-7	-179	-108
-17	-127	-164
• 2	6	
8	245	198
12	-179	-72
-6	-179	-214
-12	-245	-190
-16	167	259
• 2	7	
13	-89	-195
-3	167	52
-9	-219	-62
-11	245	131
-13	-237	-327
• 2	8	
4	-219	-14
8	237	270
12	141	3
-12	237	250
-14	210	312
• 2	9	
3	219	273
5	237	56
7	245	213
-7	219	32
• 2	10	
8	228	182
-10	-245	-269
• 2	11	
1	-228	-90
7	228	112
-9	245	62
-15	89	417
• 2	12	
-10	228	21
• 2	14	
2	237	166
-10	190	148
• 2	15	
1	228	168
• 2	16	
2	190	295
6	110	320
-4	210	225
• 2	17	
1	167	73
5	89	118
-3	179	56
-7	141	27
-9	63	61
• 2	18	
0	141	127
• 3	1	
7	-228	-57
9	237	205
11	200	4
13	-89	-4
-7	-141	-6
-15	237	127
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7	237	118
9	237	145
-15	228	213
• 3	4	
8	237	177
-16	210	62
• 3	6	
6	237	132
-18	63	266
• 3	7	
-11	237	151
• 3	9	
11	89	144
• 3	10	
6	228	162
10	-127	-47
-8	237	224
-16	-110	-63
• 3	11	
5	-228	-44
9	141	173
-5	228	14
-13	200	166
• 3	12	
0	237	309
4	-228	-207
8	155	175
-6	-237	-323
-12	-200	-294
-14	141	171
• 3	13	
1	237	244
3	-228	-53
5	-200	-19
7	155	31
-9	228	223
-11	200	18
-13	-155	-77
• 3	14	
2	219	4
4	200	197
6	155	27
-2	237	148
-4	-237	-53
-6	228	88
-8	219	130
-12	155	114
• 3	15	
3	-190	-76
5	155	116
-5	219	223
-7	210	210
-11	-141	-182
• 3	16	
4	141	291
-4	-200	-6
-6	190	146
-8	-167	-34
• 3	17	
3	-110	-27
-3	-167	-117
• 4	0	
6	228	96
• 4	5	
1	179	92
5	228	109
7	228	5
9	200	61
11	110	126
-13	228	99
-15	228	68
-17	-190	-5
• 4	6	
2	200	236
6	-237	-175
8	210	314
10	155	90
-2	-167	-139
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-16	200	205
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3	210	140
9	-167	-48
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4	-219	-198
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10	-110	-58
-12	200	62
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• 5	4	
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2	-210	-186
6	-200	-277
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8	-141	-248
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• 6	3	
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7	-179	-33
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7	-155	-147
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• 9	8	
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-11	141	101
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-18	-127	-306
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-18	-89	-17
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-15	110	225
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-10	110	35
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-17	63	264
• 13	2	
-8	63	178
-10	-63	-142
-16	63	146
-18	63	3
• 13	3	
-7	-63	-19
-9	63	131
-13	-63	-62
-15	-63	-337
-17	63	299
• 13	4	
-8	63	368
-12	-63	-175
-16	63	61
• 13	5	
-13	-63	-256
-15	63	27

Table 3(*a*). *Standard Deviations*

	Anisotropic refinement	Isotropic refinement
Bonds between zinc and nitrogen or oxygen	0·012 Å	0·014 Å
Bonds between carbon, nitrogen and oxygen	0·020 Å	0·023 Å
Bond angles	1·3°	1·5°

Table 3(*b*). *Bond distances within the di(histidino)zinc molecule*

	Anisotropic refinement	Isotropic refinement
Zn–N_2	2·000 Å	1·994 Å
Zn–N_1	2·049	2·046
Zn–O_1	2·912	2·900
C_1–O_1	1·243	1·241
C_1–O_2	1·260	1·263
C_1–C_2	1·519	1·518
C_2–N_1	1·473	1·474
C_2–C_3	1·539	1·554
C_3–C_4	1·486	1·495
C_4–N_2	1·417	1·412
C_4–C_6	1·369	1·361
N_2–C_5	1·329	1·337
C_5–N_3	1·324	1·313
C_6–N_3	1·374	1·375

two molecules, but the relation of one histidine group to the other is not. This can be seen by comparing Fig. 4 here with Fig. 4 in their paper. The KC&B molecule can be obtained (approximately) by rotating one histidine group in our molecule through 180° so that N_1 and N_2 replace each other.

The conformation of the histidine group can be compared with that in histidine hydrochloride (Donohue, Lavine & Rollett, 1956). The chief difference results from a rotation around the bond C_3–C_4, of the imidazole ring relative to the rest of the molecule (Fig. 5). This rotation allows both N_1 and N_2 to be co-ordinated to the zinc atom.

C_3 and the atoms of the imidazole ring are coplanar within the limits of accuracy of the structure

Table 4. *Bond angles around the zinc atom*

N_2–Zn–N_2'	117·1°	N_2–Zn–O_1	81·9°
N_1–Zn–N_1'	104·2	N_1–Zn–O_1	62·2
N_2–Zn–N_1	96·0	N_2–Zn–O_1'	76·8
N_2–Zn–N_1'	122·5	N_1–Zn–O_1'	154·5
		O_1–Zn–O_1'	138·5

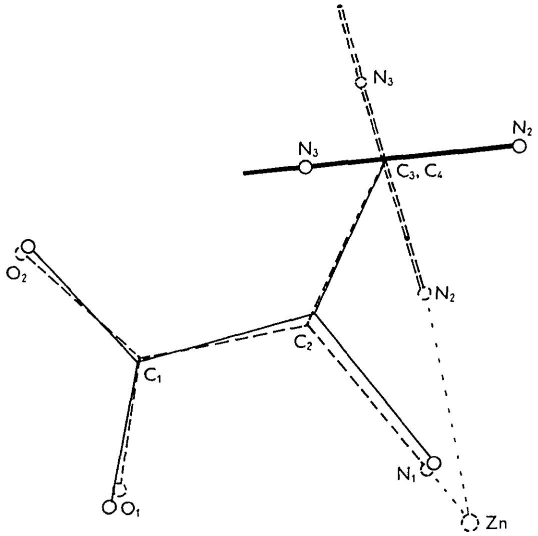

Fig. 5. Projection along the bond C_3–C_4 of the histidine group in histidine hydrochloride (full lines) and in di(histidino)zinc (dotted lines). Double lines represent the plane of the imidazole ring.

determination; the largest calculated displacement from the mean plane is 0·013 Å. This plane is

$$9{\cdot}700x - 8{\cdot}023y - 9{\cdot}186z + 2{\cdot}442 = 0\,.$$

The zinc atom, however, is 0·15 Å from the plane. The atoms of the carboxyl group and C_2 and N_1 are nearly coplanar, the largest displacements from their plane being 0·027 Å (N_1) and −0·033 Å (C_2).

Zinc, and the atoms nearest it (C_2, C_3, C_4, N_1, and N_2) have the smallest and most isotropic vibrations (mean B values 2–3 Å^2). Towards either extremity of the histidine group—N_3 or O_1 and O_2—the vibrations are larger and more anisotropic; for N_3, the 'B' value in the b axis direction is 2·9 Å^2 but the values perpendicular to this are in the region of 4 to 6 Å^2.

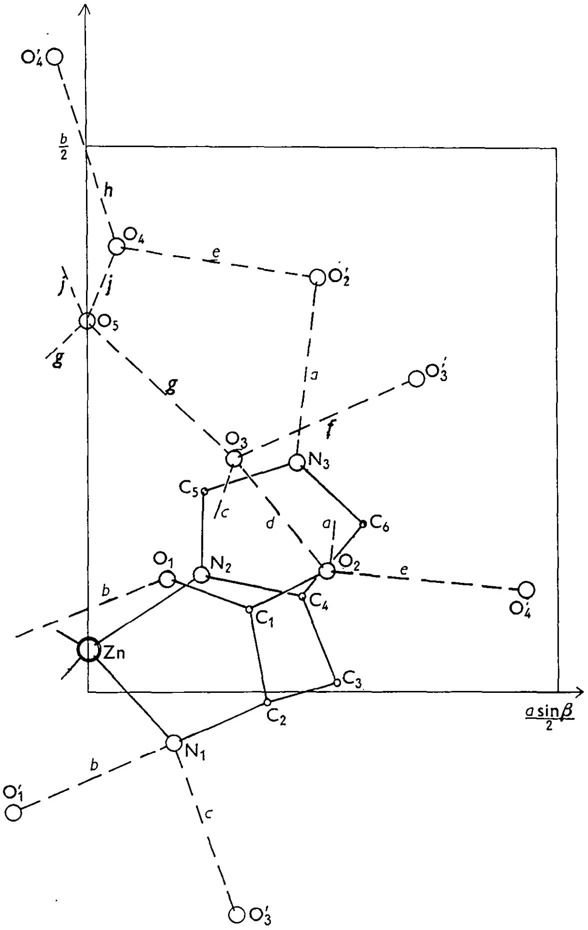

Fig. 6. c-axis projection showing the hydrogen bonds around one histidine group and the three water molecules. The hydrogen bonds (dotted lines) are lettered, and their lengths are given in Table 5.

One water molecule oxygen atom (O_5) is on a two-fold axis; the others (O_3 and O_4) are in general positions. Details of the intricate system of hydrogen bonds are given in Table 5 and Fig. 6. Two hydrogen bonds, a and b, provide direct links between molecules in the crystal lattice, and there are many other links through water molecules. O_3 and O_5 take part in four

Table 5. *Hydrogen bonds*

(1)	(2)	(3)	(4)
a	2·762	N_3–O_2 at $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$	N_3–H_7 .... O_2
b	2·963	N_1–O_1 at $-x, -y, 1-z$	N_1–H_3 .... O_1
c	3·008	N_1–O_3 at $x, -y, -\frac{1}{2}+z$	N_1–H_2 .... O_3
d	2·964	O_2–O_3	O_2 .... H_9–O_3
e	2·724	O_2–O_4 at $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$	O_2 .... H_{10}–O_4
f	2·768	O_3–O_3 at $\frac{1}{2}-x, \frac{1}{2}-y, 2-z$	O_3 .. $\frac{1}{2}H_{11}$ .. $\frac{1}{2}H_{11}$ .. O_3
g	2·742	O_3–O_5	O_3 .. $\frac{1}{2}H_{12}$ .. $\frac{1}{2}H_{13}$ .. O_5
h	2·831	O_4–O_4 at $-x, 1-y, -z$	O_4 .. $\frac{1}{2}H_{14}$ .. $\frac{1}{2}H_{14}$ .. O_4
j	2·771	O_4–O_5 at $x, y, -1+z$	O_4 .. $\frac{1}{2}H_{15}$ .. $\frac{1}{2}H_{16}$ .. O_5

(1) These are the letters used to label the hydrogen bonds in Fig. 6.

(2) Length of the hydrogen bond (Å).

(3) If the hydrogen bond does not join a pair of atoms with the coordinates listed in Table 1 the appropriate equivalent position of the second atom is given.

(4) This allocation of hydrogen atoms and 'half hydrogen atoms' is essential if the space-group is truly centrosymmetric.

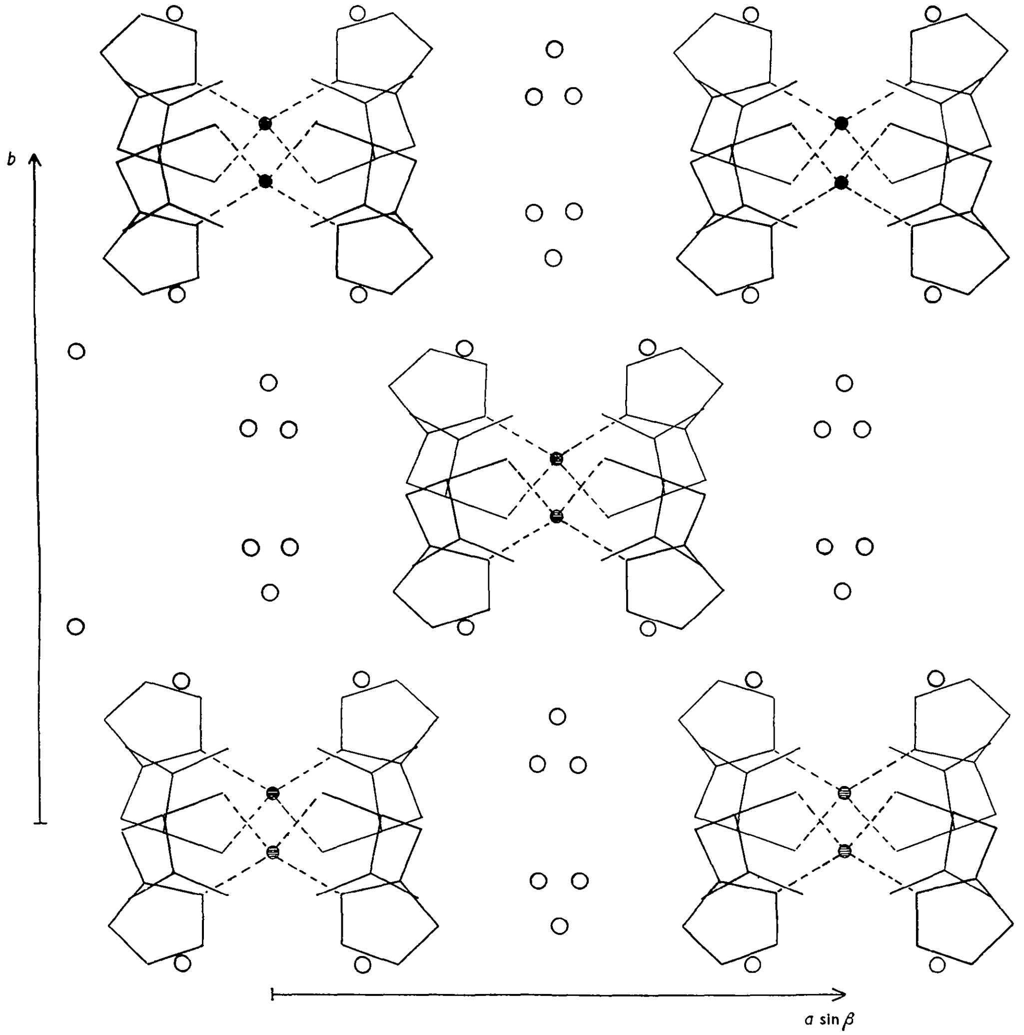

Fig. 7. The packing of di(histidino)zinc molecules and water molecules (open circles) as seen in projection along the c-axis

hydrogen bonds each, while O_4 takes part in only three; O_4 has a significantly larger temperature factor than O_3 and O_5. Fig. 7 shows the resultant packing of the molecules.

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