

Table 5. Lengths of dodecahedral edges in V(1) and V(2) complexes

V(1) complex			
<i>a</i>	S(1)–S(4)	2.89 (1) Å	(× 2)
<i>m</i>	S(1)–S(2')	2.74 (1)	(× 2)
<i>m</i>	S(3)–S(4')	2.77 (2)	(× 2)
<i>g</i>	S(2)–S(4)	3.14 (2)	(× 2)
<i>g</i>	S(1)–S(3)	3.14 (1)	(× 2)
<i>g</i>	S(1)–S(2)	3.20 (2)	(× 2)
<i>g</i>	S(3)–S(4)	3.16 (2)	(× 2)
<i>b</i>	S(3)–S(3')	3.58 (2)	
<i>b</i>	S(2)–S(2')	3.53 (1)	
<i>b</i>	S(2)–S(3')	3.56 (1)	(× 2)
V(2) complex			
<i>a</i>	S(5)–S(7)	3.09 (1) Å	(× 2)
<i>m</i>	S(7)–S(8')	2.71 (2)	(× 2)
<i>m</i>	S(5)–S(6)	3.09 (2)	(× 2)
<i>g</i>	S(5)–S(6')	2.74 (1)	(× 2)
<i>g</i>	S(7)–S(8)	3.07 (2)	(× 2)
<i>g</i>	S(5)–S(8)	3.10 (1)	(× 2)
<i>g</i>	S(6)–S(7')	3.13 (2)	(× 2)
<i>b</i>	S(6)–S(6')	3.19 (1)	
<i>b</i>	S(8)–S(8')	3.46 (2)	
<i>b</i>	S(6)–S(8)	3.97 (2)	(× 2)

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*Acta Cryst.* (1972). **B28**, 1302

## A Refinement of the Structure of Bis-(L-histidinato)zinc(II) Dihydrate\*

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(Received 24 June 1971)

The crystal structure of bis-(L-histidinato)zinc(II) dihydrate,  $Zn(C_6H_8N_3O_2)_2 \cdot 2H_2O$ , which was originally determined by Kretsinger, Cotton & Bryan [*Acta Cryst.* (1963), **16**, 651], has been further refined by full-matrix least-squares methods to a final *R* index of 0.071. Coordinates and individual anisotropic temperature parameters for Zn, C, N, and O were refined; hydrogen atoms were positioned on the basis of geometry. Contrary to the results of Kretsinger *et al.*, inclusion of the hydrogen atoms and anisotropic refinement have led to a significant improvement in the model.

### Introduction

The crystal structure of bis-(L-histidinato)zinc(II) dihydrate was determined by Kretsinger, Cotton & Bryan (1963) (KCB). They obtained Cu *Kα* intensity data from equi-inclination Weissenberg photographs and determined the structure by Patterson and Fourier methods. Refinement of the structure by least-squares methods was normal through isotropic refinement (*R*=0.108). However, the introduction of the hydrogen

atoms and anisotropic refinement of the heavy atoms caused an increase in *R* to 0.113 and significant changes in the dimensions of the histidine ligand. The most notable of these changes was in the C(3)–C(4) bond length (1.478 Å, isotropic without hydrogen atoms; 1.400 Å, anisotropic with hydrogen atoms). As previously noted by Donohue & Caron (1964), it is difficult to understand why the introduction of the hydrogen atoms and the allowance for anisotropy caused the large changes in the geometry and the increase in the *R* index.

Our recent interest in the geometry and dimensions of the histidine molecule (Kistenmacher & Marsh, 1971; Kistenmacher, Hunt & Marsh, 1971) led us to carry out further refinement of the structure of bis-(L-histidinato)zinc(II) dihydrate. Contrary to the experience of KCB, our refinement, including fixed hydrogen positions and individual anisotropic temper-

\* Contribution No. 4274 from the Arthur Amos Noyes Laboratory. This investigation was supported in part by Public Health Service Research Grant No. GM16966, from the National Institute of General Medical Sciences, National Institutes of Health, and in part by a National Science Foundation Post-doctoral Fellowship.

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ature parameters for all heavy atoms, proceeded nominally to a final  $R$  index of 0.071. The dimensions of the histidine ligand are normal, and at the termination of the refinement the C(3)–C(4) bond length was 1.469 Å.

### Refinement procedure

Bis-(L-histidinato)zinc(II) dihydrate crystallizes from aqueous solution in the tetragonal crystal system, space group  $P4_32_12$ ,\* with the following cell constants (KCB):  $a=b=7.53 \pm 0.02$ ,  $c=30.41 \pm 0.05$  Å. We used, as the basis of our refinement, the observed structure amplitudes of KCB (their Table 3). Weights were assigned by the method of Hughes (1941):  $1/w=1/F_o^2$  if  $F_o \geq 4F_{\min}$ ;  $1/w=1/(F_o \cdot 4F_{\min})$  if  $F_o < 4F_{\min}$ , where  $4F_{\min}=18$ . Structure amplitudes with zero intensity were assigned a weight of zero. All calculations were done under the *CRYM* system using an IBM 360/75 computer. The quantity minimized was  $\sum w(F_o^2 - S^2F_c^2)^2$  where  $1/S$  is the scale factor. Form factors for Zn, C, N, and O were taken from the compilation of Hanson, Herman, Lea & Skillman (1964). The hydrogen form

factors were those of Stewart, Davidson & Simpson (1965). The form factor for Zn was corrected for the real component of anomalous dispersion ( $\Delta f' = -1.7$ ; Cromer, 1965). No correction for the imaginary component was applied since full details of the data collection were not published by KCB.

Starting parameters were those of KCB [column (a), their Table 1] transformed to correspond to a single molecule in  $P4_32_12$ . Since KCB did not report thermal parameters, we initially assigned each of the atoms an isotropic temperature parameter of  $3.0 \text{ \AA}^2$ . Full-matrix isotropic refinement led to an  $R$  index,  $\sum ||F_o| - |F_c|| / \sum |F_o|$ , of 0.109, essentially the same value found by KCB. A difference Fourier map was then calculated to aid in positioning the hydrogen atoms and to assess the validity of introducing anisotropic thermal parameters. Calculated hydrogen positions based on the geometry of the histidine ligand were consistent with positive regions on the difference Fourier map. The hydrogen atoms of the water molecule were positioned on the basis of a hydrogen bonding scheme involving the carboxylate oxygen, O(2), as proposed by KCB. Inclusion of the contributions of the hydrogen atoms to the calculated structure factors lowered  $R$  to 0.105. The difference Fourier map also indicated significant anisotropic motion for several atoms; most notable

\* KCB gave the space group as  $P4_12_12$  with the ligands in the  $D$  configuration. We have reflected the structure through the  $ab$  plane, which requires the change to space group  $P4_32_12$ .

Table 1. Final nonhydrogen parameters ( $\times 10^4$ )

	$x$	$y$	$z$	$B_{11}\dagger$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
C(1)	5506 (11)*	1579 (12)	-496 (3)	101 (12)	134 (15)	9 (1)	-54 (31)	-8 (5)	-4 (6)
C(2)	5352 (11)	324 (12)	-110 (2)	94 (12)	136 (15)	9 (1)	30 (28)	-1 (5)	-10 (6)
C(3)	4622 (13)	-1493 (12)	-255 (3)	167 (17)	147 (17)	11 (1)	14 (33)	-4 (7)	8 (7)
C(4)	3027 (13)	-1384 (10)	-532 (3)	168 (18)	94 (14)	10 (1)	32 (32)	3 (6)	-8 (6)
C(5)	400 (13)	-590 (14)	-752 (3)	129 (16)	176 (20)	12 (1)	-41 (32)	-0 (7)	-10 (8)
C(6)	2725 (16)	-2223 (14)	-908 (4)	233 (24)	138 (17)	14 (1)	54 (41)	-5 (9)	-42 (8)
N(1)	4150 (10)	1107 (9)	233 (2)	141 (13)	127 (12)	6 (1)	-30 (23)	-7 (5)	-2 (5)
N(2)	1554 (10)	-333 (10)	-439 (2)	116 (12)	135 (13)	8 (1)	-33 (26)	8 (5)	-9 (5)
N(3)	1083 (13)	-1697 (14)	-1053 (3)	249 (21)	238 (21)	14 (1)	43 (43)	-35 (8)	-52 (8)
O(1)	4516 (12)	2855 (11)	-512 (2)	266 (18)	274 (20)	12 (1)	246 (37)	48 (7)	48 (7)
O(2)	6600 (11)	1215 (10)	-786 (2)	203 (14)	196 (15)	14 (1)	-54 (29)	57 (7)	-11 (6)
Zn	1701 (2)	1701	0	142 (2)	142	7 (0.1)	57 (6)	8 (1)	-8
O(3)	4437 (22)	-1474 (17)	921 (3)	956 (63)	512 (38)	20 (1)	-1069 (88)	-192 (16)	120 (13)

\* Numbers in parentheses are e.s.d.'s.

† Form of the anisotropic ellipsoid is:  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$ .

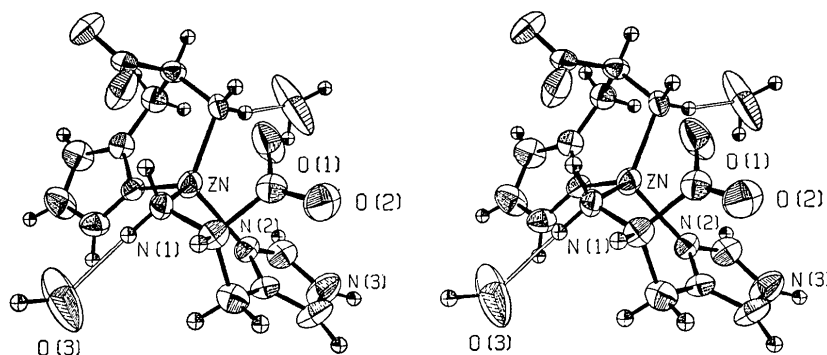


Fig. 1. A stereoview of the molecular conformation in bis-(L-histidinato)zinc(II) dihydrate.

among these is the water oxygen O(3). Five cycles of anisotropic refinement with periodic readjustment of the hydrogen positions led to a final *R* index of 0.071. No shift in the final cycle of least-squares refinement was greater than 0.2 times its standard deviation.

### Discussion of the results

Contrary to the results of KCB, we have found a significant improvement in the fit of the model by including the contributions of the hydrogen atoms and by going anisotropic. Our final *R* index of 0.071 is considerably lower than the value of 0.113 reported by KCB. The final heavy-atom parameters derived from the last cycle of least-squares refinement are given in Table 1. The assumed hydrogen parameters are given in Table 2. Our refinement has produced considerable change in the atomic parameters reported by KCB and, accordingly, in the intramolecular and intermolecular dimensions. The intramolecular distances obtained in our analysis are compared in Table 3 to

Table 2. Fixed hydrogen parameters ( $\times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(C2)	651	016	001	4.0
H1(C3)	552	-209	-042	4.0
H2(C3)	434	-215	000	4.0
H(C5)	-075	-007	-076	4.0
H(C6)	350	-304	-105	4.0
H1(N1)	403	027	047	4.0
H2(N1)	468	216	034	4.0
H(N3)	053	-205	-132	4.0
H1(O3)	670	-200	090	9.0
H2(O3)	500	-150	120	9.0

Table 3. Intramolecular distances

	KCB	K	HC
Zn—N(2)	2.041 Å	2.034 Å	2.000 Å
Zn—N(1)	2.049	2.026	2.049
C(1)—O(1)	1.199	1.217	1.243
C(1)—O(2)	1.252	1.237	1.260
C(1)—C(2)	1.530	1.509	1.519
C(2)—N(1)	1.500	1.503	1.473
C(2)—C(3)	1.519	1.540	1.539
C(3)—C(4)	1.478	1.469	1.486
C(4)—N(2)	1.378	1.392	1.417
C(4)—C(6)	1.378	1.326	1.369
N(2)—C(5)	1.308	1.302	1.329
C(5)—N(3)	1.324	1.342	1.324
C(6)—N(3)	1.408	1.372	1.374
$\sigma$	$\approx 0.02$	$\approx 0.02$	$\approx 0.02$

KCB: Kretsinger, Cotton & Bryan [1963, their Table 2, column (b)].

K: This study.

HC: Harding & Cole (1963).

Table 4. Intramolecular angles

O(1)—C(1)—O(2)	123.7°	N(2)—C(5)—N(3)	109.6°
O(1)—C(1)—C(2)	118.6	N(3)—C(6)—C(4)	107.2
O(2)—C(1)—C(2)	117.8	C(2)—N(1)—Zn	113.0
C(1)—C(2)—N(1)	109.9	C(4)—N(2)—C(5)	107.4
C(1)—C(2)—C(3)	111.2	C(4)—N(2)—Zn	121.2
N(1)—C(2)—C(3)	109.4	C(5)—N(2)—Zn	128.9
C(2)—C(3)—C(4)	114.0	C(5)—N(3)—C(6)	107.8
C(3)—C(4)—N(2)	124.6	N(1)—Zn—N(2)	96.5
C(3)—C(4)—C(6)	127.4	N(1')—Zn—N(1)	121.7
N(2)—C(4)—C(6)	108.0	N(1')—Zn—N(2)	116.3
		N(2')—Zn—N(2)	110.4

$\sigma \approx 1.0^\circ$

The primed atoms are related to the unprimed atoms by the twofold axis parallel to [110].

those of KCB (isotropic refinement without the hydrogen atoms, which KCB considered their best set of values) and those of bis-(DL-histidinato)zinc(II) pentahydrate (Harding & Cole, 1963). A compilation of the intramolecular angles obtained in this study of bis-(L-histidinato)zinc(II) dihydrate is given in Table 4.

The observed molecular conformation and thermal motions of the atoms are presented in the stereoview (Johnson, 1965) of Fig. 1. The water of crystallization shows high thermal motion approximately normal to the plane defined by its hydrogen bonding, in which direction there is little to restrict its motion. Hydrogen bonding in this structure has been discussed in detail by Freeman (1967), and our results have in no way altered the discussion of the hydrogen bonding.

The author would like to thank Dr Richard E. Marsh for many helpful suggestions and comments.

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