among the shortest of their kind found in either copper tetrammine compound while the remaining two are at separations over 3·7 Å Such large separations are even greater than the typical bifurcated hydrogen bonds found in several hydrates (separations summarized by Morosin, 1967) and, hence, do not appear to be involved in the hydrogen bonding network. There are three near-neighbor oxygen atoms for N(3) which are at typical interatomic separations; however, there is an additional near-neighbor oxygen atom at 3·44 Å. When the spatial arrangement of the near-neighbor oxygen atoms is considered, this latter oxygen atom can be eliminated from the possibility of being involved in the hydrogen bonding network. As was the case for CTASUL, the observed hydrogen positions lie off the lines connecting these atoms as can be seen from the angles listed in Table 10(*d*).

The anisotropic thermal parameters in these copper tetrammine compounds are compatible with the strong bonding which occurs along particular directions. For example, the magnitude of the nitrogen thermal parameters perpendicular to the square plane formed by the copper and nitrogen atoms is significantly larger than those parallel to this plane. Similarly, oxygen atoms constrained by chemical bonds to the sulfur, selenium or copper atoms have thermal parameters which are smaller parallel to, rather than perpendicular to, the bond directions.

The thermal and magnetic properties of CTASEL are being investigated and will be reported elsewhere.

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The Crystal Structure of Bis-L-histidinecopper(II) Dinitrate Dihydrate

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The crystal structure of bis-L-histidinecopper(II) dinitrate dihydrate has been determined and refined using three-dimensional X-ray data. The crystals were prepared by crystallization from a solution of pH = 3·7 containing copper(II) ions and histidine molecules in the ratio 1:2 and $NaNO_3$ in large excess. The crystals are triclinic and belong to space group $P\bar{1}$. The unit cell contains one formula unit and has the dimensions $a = 5{\cdot}458_2$, $b = 7{\cdot}153_3$, $c = 13{\cdot}844_4$ Å, $\alpha = 98{\cdot}61_7°$, $\beta = 87{\cdot}07_0°$ and $\gamma = 109{\cdot}83_0°$. The intensity data were treated by Fourier methods and by least-squares refinement. The anisotropic refinement converged to $R = 7{\cdot}6\%$ using 1813 independent reflexions. Two histidine molecules coordinate to a central copper atom, each through the amino nitrogen and a carboxylate oxygen. The imidazole groups are not coordinated to the copper atom and turn away from it. The coordination about copper is square planar with the four donor atoms situated 1·93–2·00 Å from the copper. There are two water molecules, one above and one below this plane, at distances of 2·46 and 2·78 Å. The nitrate ions are situated between the imidazole rings. The structure is linked together by an extensive hydrogen bond network.

Introduction

Crystal structure investigations of biochemically interesting metal complexes have been started in conjunction with the Department of Biochemistry at this University. In this paper the results of the structure determination of bis-L-histidinecopper(II) dinitrate dihydrate are presented.

In metal activated enzymes, histidyl residues are known to be important metal binding sites. Owing to

this fact, it appears particularly important to study the nature of copper(II) histidine complexes as possible simple model compounds for metal–protein interaction.

The interaction between histidine and metal ions has been extensively studied in solution, abnormal behavior of copper and histidine being reported in all cases (*e.g.* Albert, 1952).

Preparation and analysis of the crystals

The crystals were prepared according to a method described by Valladas-Dubois (1961). A concentrated solution of $CuSO_4$ was mixed with a concentrated solution of L-histidine so as to give a Cu(II):histidine molar ratio of 1:2. A large excess of solid $NaNO_3$ was dissolved in the resulting solution whereupon clusters of blue-violet needle-shaped crystals of $[(C_6H_9O_2N_3)_2Cu](NO_3)_2(H_2O)_2$ were slowly deposited.

The *p*H of the solution was 3·7 at the crystallization point.

An analysis of the crystals yielded 27·0% C, 20·8% N, 4·13% H (calc: 27·0% C, 21·0% N, 4·15% H).

Unit cell and space group

The crystals of bis-L-histidinecopper(II) dinitrate dihydrate are triclinic with the following unit-cell parameters:

$C_{12}H_{22}O_{12}N_8Cu$ M.W. 533·90

$a = 5{\cdot}4582 \pm 0{\cdot}0010$, $b = 7{\cdot}1533 \pm 0{\cdot}0013$, $c = 13{\cdot}8444 \pm 0{\cdot}0011$ Å,

$\alpha = 98{\cdot}617 \pm 0{\cdot}016$, $\beta = 87{\cdot}070 \pm 0{\cdot}025$, $\gamma = 109{\cdot}830 \pm 0{\cdot}006°$

$U = 502{\cdot}8$ Å^3, $D_m = 1{\cdot}77$ g.cm^{-3}, $D_{calc} = 1{\cdot}763$ g.cm^{-3}

$F(000) = 275$, $Z = 1$.

The cell dimensions were determined from powder photographs taken with a Guinier camera, using KCl as an internal standard (Cu $K\alpha_1$ radiation, $\lambda = 1{\cdot}54050$Å, $a_{KCl} = 6{\cdot}2919_4$Å at 20 °C) (Hambling, 1953). 106 reflexions were indexed using the Algol program Xalg Powder (Lindqvist & Wengelin, 1967), and the cell constants were refined with the same program.

The observed and calculated values of $\sin^2\theta$ and the corresponding intensities for the first 47 reflexions are listed in Table 1.

A sample of the crystals was decomposed by 0·5 M hydrochloric acid and the specific rotation was measured and found to be $+11{\cdot}0°$, which is close to the specific rotation of pure L-histidine in 0·5 M hydrochloric acid, $+11{\cdot}1°$ (Landolt-Börnstein). The complex thus contains two L-histidine molecules coordinated to copper and the correct space group must then be the non-centrosymmetric no. 1 – $P1$. This is confirmed by a clearly positive piezoelectric effect measured by

Table 1. *Powder photograph of* $[(C_6H_9O_2N_3)_2Cu](NO_3)_2(H_2O)_2$

Cu $K\alpha_1$ radiation. $\lambda_{Cu\ K\alpha_1} = 1{\cdot}54050$ Å.

h k l	$10^5 \cdot \sin^2\theta$ obs.	$10^5 \cdot \sin^2\theta$ calc.	*I* obs.	*I* calc.	*h k l*	$10^5 \cdot \sin^2\theta$ obs.	$10^5 \cdot \sin^2\theta$ calc.	*I* obs.	*I* calc.
0 0 1	313	317	*vs*	603	2–1 1	8142	8141	*s*	3
0 0 2	1260	1267	*s*	135	1 1 3	8142	8151		97
0 1 0	1331	1337	*w*	32	1–1–4	8218	8225	*vw*	7
0–1 1	1461	1470	*w*	47	0–1 5	8318	8336	*vw*	12
0 1 1	1830	1837	*vs*	144	2–1–1	8495	8510	*vw*	16
0–1 2	2223	2236	*w*	14	2–1 2	8919	8906	*m*	7
1 0 0	2223	2250		14	0–2–4	8919	8946		53
1–1 0	2413	2422	*m*	43	1 1–4	9073	9086	*vw*	20
1 0 1	2558	2567	*vvs*	323	2 0 1	9289	9317	*m*	11
1 0–1	2558	2568		32	2 0–1	9289	9319		15
0 0 3	2833	2850	*s*	207	2–2 0	9675	9689	*m*	31
1–1–1	2909	2923	*m*	56	1 2–1	9872	9877	*w*	13
0 1 2	2959	2970	*s*	159	1 0 5	10150	10164	*m*	11
1 0 2	3506	3516	*vs*	59	1 0–5	10150	10169		19
1 0–2	3506	3518		191	0 1 5	10150	10171		22
1–1–2	4045	4057	*m*	29	2 0 2	10252	10266	*vw*	2
1 1 0	4742	4752	*vs*	125	2 0–2	10252	10270		6
0 0 4	5053	5066	*vw*	10	2–2–1	10351	10374	*vw*	5
1 1 1	5238	5252	*vs*	157	1 1 4	10546	10550	*m*	43
0–2 1	5288	5297	*s*	86	1–3 0	10770	10787	*w*	10
0 2 0	5333	5347	*m*	39	1–3 2	10961	10952	*vvw*	2
1 1–2	5644	5653	*vw*	3	1–1–5	11252	11259	*w*	18
0–1 4	5644	5669		7	2–1–3	11411	11412	*m*	11
1–2 2	5786	5800	*vvs*	274	2–2 3	11411	11435		20
1–2–1	5933	5952	*s*	91	0–2 5	11411	11428		14
1 1 2	6378	6385	*vs*	135	1–3–1	11643	11655	*w*	10
1–2 3	7001	7015	*m*	60	1 1–5	11727	11753	*w*	34
1 1–3	7042	7053	*w*	35	2–2–2	11727	11692		14
0–2 3	7113	7096	*w*	20	2 0 3	11836	11848	*vw*	13
1 0 4	7304	7315	*s*	14	2 0–3	11836	11855		12
1 0–4	7304	7319		60	1 2 2	11921	11926	*w*	19

two independent methods, on one hand according to the principle of Giebe & Scheibe (1925), on the other using an apparatus with a mechanical vibrator.

An intensity distribution analysis (Howells, Phillips & Rogers, 1950) of the $0kl$ reflexions also indicated non-centrosymmetry (see Fig. 1).

Determination of F_{obs}

Complete three-dimensional data were recorded with Cu $K\alpha$ radiation using multiple film Weissenberg techniques with rotation about the a and c axes. Rotation about the needle-axis (corresponding to the crystallographic a axis) was used to register the layers $0kl$–$4kl$. A crystal cut to a suitable size was rotated about the c axis and the layers $hk0$–$hk9$ were recorded.

For both crystal settings the crystal was rotated through 360° and consequently two sets of films were recorded for each layer. The intensities of the two sets obtained were scaled together using approximately 25 common reflexions.

1594 and 1215 reflexions were recorded about the a and c axes, respectively, leading to a total of 1813 independent reflexions. A further 244 reflexions fell within the θ range recorded, but were too weak to be observable. Within the copper reflexion sphere there are 2535 reflexions, 478 being situated outside the range of observation.

The intensities were estimated visually by comparison with a scale prepared by making timed exposures using a strong reflexion of medium extension from the crystals used. The estimated relative intensities varied from 1 to 4000.

The intensities were corrected for Lorentz and polarization effects. No absorption corrections were, however, applied owing to the low linear absorption coefficient ($\mu_{Cu\ K\alpha}=23{\cdot}5\ cm^{-1}$) and the small dimensions of the crystals used.

Structure determination and refinement

Since there is only one copper atom in the unit cell, it was arbitrarily assigned the position $P1:1(a)$ with $x=0$, $y=0$ and $z=0$.

A three-dimensional electron density summation based on this copper position and the $0kl$–$4kl$ Weissenberg data, scaled together using the Weissenberg photograph $hk0$, was calculated. The approximate positions of two histidine molecules, two nitrate ions and two single atoms in the vicinity of the copper atom, assumed to be the water oxygens, could be deduced from the electron density peaks. Each pair was at this stage situated symmetrically about the copper atom with the latter as inversion centre. The histidine molecule with configuration in agreement with the known absolute configuration of L-histidine (Langenbech, 1925) was then chosen. The character of the atoms in the imidazole ring, except the carbon bound to the methylene group, could not be distinguished and they were labelled nitrogen. An electron density calculation based on this histidine molecule and the copper atom was calculated, but still no significant deviation from centrosymmetry in the copper-histidine complex could be detected. In the next electron density calculation one nitrate ion and one water oxygen were added to the atoms previously included. The asymmetric carbon of the other histidine molecule now changed position considerably and its configuration passed over to the L-form. A structure factor calculation based on the atomic positions thus obtained, with assigned isotropic temperature factors of 2 for copper and 4 for all the other atoms, gave an R value of 22·0%. Three cycles of isotropic least-squares refinement of these parameters gave $R=14{\cdot}4\%$.

Two of the four atoms labelled nitrogen in each ring had rather high temperature factors. In both rings the atoms with high temperature factors alternated with atoms of low ones, just as nitrogen and carbon alternate in imidazole. Thus the atoms with high temperature factors were now labelled carbon. In the subsequent cycles of refinement the temperature factors which were formerly high became normal and the R value dropped to 14·1%, thus confirming that the correct symbol had been assigned to every atom.

A structure factor calculation was based on the unscaled $hk0$–$hk9$ data and the approximate atomic parameters. From the F_o/F_c ratios for the different layers of the c axis, layer scale factors could be calculated. The parameters obtained from a axis data were refined isotropically with the new data. The R value converged after three cycles to 13·3%, with only small differences in the atomic positions.

The two sets of structure factors were combined, equal weight being given to observations from the a and c axes. The mean values of the parameters obtained were also used. After three further cycles of isotropic least-squares refinement, the R value converged to 14·1%.

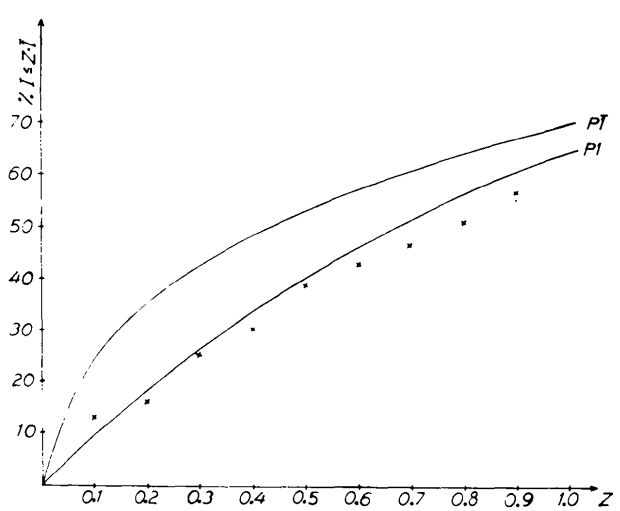

Fig. 1. Intensity distribution analysis of the $0kl$ reflexions.

15 cycles of block-diagonal least-squares refinement with anisotropic thermal parameters brought the refinement to convergence, the R value now being 8·3% and all shifts being less than one-third of the corresponding standard deviations.

A difference ($F_o - F_c$) synthesis at this stage showed no peaks or depressions in the neighbourhood of the copper, oxygen, nitrogen or carbon atoms. On the other hand there were some small maxima that could be attributed to hydrogen atoms. The coordinates of these maxima were checked geometrically against the known positions of the carbon, oxygen and nitrogen atoms, the occurrence of short O–O and N–O distances indicating hydrogen bonds. It was, in this way, possible to find the positions of all the hydrogen atoms except that bound to C(1), one of those bound to O(12) and one of those bound to C(3). It was, however, very easy to assign parameter values to these hydrogen atoms from the tetrahedral arrangement of bonds around C and O and the distances C–H = 1·09 Å and O–H = 0·99 Å (*International Tables*, 1962).

The hydrogen atom positions alone were then refined by three-dimensional isotropic least-squares refinement. With regard to the standard deviations, all hydrogen atoms except one bound to N(6) and another bound to O(12) remained close to the positions found. The refinement was then continued by varying all the positional and thermal parameters (isotropic for the hydrogen atoms). Nothing essentially new appeared.

The hydrogen atom positions were then deduced from the considerations of geometrical arguments, from the difference ($F_o - F_c$) calculations, and from the least-squares refinement. A list of the parameters obtained is given in Table 2. A final least-squares refinement was calculated keeping these hydrogen atom positions fixed, and only the positional and anisotropic thermal parameters of the other atoms were refined.

Table 2. *Hydrogen atom positions*

	x	y	z
H(1)	0·83	0·97	0·17
H(2)	0·68	0·79	0·10
H(3)	0·31	0·20	0·89
H(4)	0·16	0·03	0·81
H(5)	0·56	0·78	0·49
H(6)	0·44	0·22	0·51
H(7)	0·96	0·88	0·39
H(8)	0·03	0·10	0·57
H(9)	0·23	0·48	0·41
H(10)	0·76	0·50	0·61
H(11)	0·23	0·86	0·17
H(12)	0·21	0·40	0·89
H(13)	0·46	0·42	0·23
H(14)	0·46	0·21	0·07
H(15)	0·49	0·76	0·92
H(16)	0·51	0·58	0·75
H(17)	0·33	0·39	0·09
H(18)	0·66	0·61	0·89
H(19)	0·93	0·45	0·77
H(20)	0·84	0·17	0·76
H(21)	0·80	0·49	0·16
H(22)	0·05	0·54	0·22

The weight applied to each F_o-value was $w = [1 + (|F_o| - a)^2/b^2]^{-1}$ with $a = 7500$ and $b = 5500$ (Abrahamsson, Aleby, Larsson, Nilsson, Selin & Westerdahl, 1965).

After 10 cycles of block-diagonal refinement a final R value of 7·6% was obtained. If all the reflexions were included, unobserved being given the value $\frac{2}{3}$ of the locally observed $F_{\min}$, an R value of 9·3% was observed. The maximum shifts were about one-half of a standard deviation for the oxygens of the nitrate ions and less than one-third of a standard deviation for all other atoms.

Table 3. *The atomic positional fractional coordinates and their standard deviations* ($10^4 \cdot \sigma$ *in parentheses*)

The hydrogen atom positions are given in Table 2.

	x	y	z
Cu	0·0000 (0)	0·0000 (0)	0·0000 (0)
O(1)	0·2026 (10)	0·8225 (8)	0·9854 (4)
O(2)	0·3285 (10)	0·6247 (8)	0·0591 (4)
O(3)	0·7739 (10)	0·1685 (7)	0·0075 (4)
O(4)	0·6866 (12)	0·3915 (9)	0·9303 (5)
O(5)	0·1587 (18)	0·7094 (15)	0·5664 (7)
O(6)	0·1609 (31)	0·8059 (13)	0·7212 (7)
O(7)	0·5075 (22)	0·9073 (16)	0·6445 (13)
O(8)	0·8081 (17)	0·2520 (13)	0·4259 (5)
O(9)	0·7830 (37)	0·1684 (19)	0·2744 (7)
O(10)	0·4517 (20)	0·0949 (14)	0·3725 (8)
O(11)	0·6230 (11)	0·7278 (8)	0·8736 (4)
O(12)	0·3329 (10)	0·2549 (8)	0·1074 (4)
N(1)	0·8621 (12)	0·8737 (8)	0·1182 (4)
N(2)	0·5134 (13)	0·5024 (10)	0·2935 (4)
N(3)	0·5903 (17)	0·7064 (13)	0·4229 (5)
N(4)	0·1204 (13)	0·1063 (11)	0·8742 (6)
N(5)	0·4295 (15)	0·4639 (12)	0·7044 (5)
N(6)	0·4266 (18)	0·2818 (12)	0·5675 (5)
N(7)	0·3042 (18)	0·8179 (11)	0·6425 (5)
N(8)	0·7175 (25)	0·1820 (16)	0·3541 (8)
C(1)	0·0469 (16)	0·7867 (11)	0·1482 (5)
C(2)	0·2079 (12)	0·7335 (10)	0·0537 (5)
C(3)	0·9259 (15)	0·6007 (11)	0·1995 (5)
C(4)	0·7616 (14)	0·6260 (9)	0·2866 (4)
C(5)	0·4124 (17)	0·5485 (13)	0·3763 (5)
C(6)	0·8076 (18)	0·7543 (14)	0·3684 (7)
C(7)	0·0401 (15)	0·2838 (10)	0·8711 (5)
C(8)	0·8247 (15)	0·2793 (10)	0·9365 (5)
C(9)	0·9808 (15)	0·3127 (15)	0·7701 (6)
C(10)	0·1857 (16)	0·3157 (11)	0·6983 (5)
C(11)	0·5796 (20)	0·4306 (16)	0·6246 (8)
C(12)	0·1808 (21)	0·2037 (14)	0·6121 (6)

The final positional and thermal parameters are listed in Tables 3 and 4 and the observed and calculated structure amplitudes in Table 5.

Standard scattering factors were used for carbon, nitrogen, oxygen, and copper (Cu^+) (*International Tables*, 1962), the latter being corrected for anomalous scattering (Dauban & Templeton, 1955).

The computer programs used for data reduction, calculation of structure factors, Fourier syntheses, isotropic and anisotropic refinement, and bond distances and angles were written by Abrahamsson *et al.* (1965) and the calculations were performed on the SAAB D 21 at the Gothenburg University Computing Centre.

Isotropic refinement was also performed on the CD 3600 computer at the Uppsala University Computing Centre using the program 'LALS', written by Lundgren & Liminga (1966).

Description of the structure

The configuration of the complex ion is given in Fig. 2. The interatomic distances are given in Fig. 3, the angles in Fig. 4 and the standard deviations of distances and angles in Table 6.

Two histidine molecules coordinate to a central copper atom, each through the amino nitrogen and carboxylate oxygen. The coordination about copper for these four atoms is square planar with the oxygens situated at distances of 1·931 Å and 1·986 Å and the nitrogens at 1·979 Å and 1·996 Å from the copper. The mean plane through these four atoms has the equation (x, y and z in fractional coordinates) $0{\cdot}38705x + 0{\cdot}42729y + 0{\cdot}81708z - 0{\cdot}37699 = 0$ and the largest calculated displacement for these atoms from the plane is 0·005 Å. The copper atom is displaced 0·075 Å out of the plane. There are two water molecules, one above and one below this plane, at distances of 2·461 Å and 2·778 Å from the copper atom. All distances and angles around copper are normal and compatible with related structures, except perhaps for the weakest water interaction (Freeman, 1966). The dimensions of the histidine molecules agree with those previously found for other histidine compounds (Harding & Cole, 1963; Kretzinger, Cotton & Bryan, 1963; Donohue & Caron, 1964), except the C(1)–C(2) distance, which is somewhat larger (0·08 Å) and the C(7)–C(8) distance, which is somewhat shorter (0·08 Å) than those published.

There is, however, no reason to believe that the two histidine molecules should be as different as these deviations indicate. The explanation might be that the atoms C(1), C(2), C(7) and C(8) are situated close to positions where diffraction effects around copper and its coordinated atoms are to be expected. The standard deviations of their positions might thus be higher than those calculated by the computer. This may also explain why the mean value of the corresponding distances C(1)–C(2) and C(7)–C(8) is 1·53 Å, which is very close to the expected one.

The imidazole rings (with their corresponding methylene carbon atoms) are within the limits of experimental error planar and almost parallel. They are not coordinated to the copper atom and turn away from it. The two nitrate ions are also planar and parallel, and

Table 4. *The final vibrational parameters and their estimated standard deviations* ($10^3 \cdot \sigma$ *in parentheses*) *for* Cu, O, N, *and* C

Anisotropic temperature factor:

$$\exp\left[-2\pi^2(h^2 \cdot a^{*2} \cdot U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2klb^*c^* U_{23} + 2lhc^* \cdot a^* U_{31} + 2hka^*b^* U_{12})\right]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
Cu	0·032 (0)	0·030 (0)	0·028 (0)	0·010 (0)	0·014 (0)	0·016 (0)
O(1)	0·031 (3)	0·041 (3)	0·032 (3)	0·017 (2)	0·017 (2)	0·010 (2)
O(2)	0·042 (3)	0·033 (3)	0·042 (3)	0·013 (2)	0·017 (2)	0·018 (2)
O(3)	0·044 (3)	0·030 (2)	0·037 (3)	0·005 (2)	0·009 (2)	0·029 (2)
O(4)	0·049 (3)	0·050 (3)	0·063 (4)	0·032 (3)	0·021 (3)	0·039 (3)
O(5)	0·073 (5)	0·102 (7)	0·082 (6)	0·018 (5)	0·015 (4)	0·015 (5)
O(6)	0·296 (16)	0·063 (5)	0·063 (5)	0·032 (4)	0·108 (8)	0·075 (8)
O(7)	0·084 (7)	0·077 (6)	0·283 (19)	0·062 (9)	−0·065 (9)	0·002 (5)
O(8)	0·090 (6)	0·089 (6)	0·042 (4)	−0·028 (4)	0·025 (4)	0·023 (4)
O(9)	0·351 (20)	0·138 (9)	0·058 (5)	0·047 (6)	0·092 (9)	0·181 (12)
O(10)	0·102 (7)	0·083 (6)	0·096 (7)	0·016 (5)	0·014 (5)	0·038 (5)
O(11)	0·039 (3)	0·042 (3)	0·052 (3)	0·022 (3)	0·015 (3)	0·017 (2)
O(12)	0·034 (3)	0·039 (3)	0·034 (3)	−0·008 (2)	0·006 (2)	0·014 (2)
N(1)	0·043 (3)	0·031 (3)	0·016 (2)	−0·002 (2)	0·015 (2)	0·024 (2)
N(2)	0·043 (3)	0·044 (3)	0·028 (3)	0·009 (3)	0·011 (3)	0·030 (3)
N(3)	0·069 (5)	0·063 (5)	0·037 (4)	0·013 (3)	0·005 (3)	0·027 (4)
N(4)	0·036 (4)	0·055 (4)	0·065 (5)	0·035 (4)	0·021 (3)	0·025 (3)
N(5)	0·052 (4)	0·056 (4)	0·044 (4)	0·014 (3)	0·016 (3)	0.019 (3)
N(6)	0·104 (6)	0·056 (4)	0·027 (3)	0·009 (3)	0·044 (4)	0·053 (4)
N(7)	0·103 (6)	0·044 (4)	0·029 (3)	0·012 (3)	0·040 (4)	0·040 (4)
N(8)	0·119 (9)	0·073 (7)	0·080 (7)	0·038 (6)	0·006 (6)	0·045 (6)
C(1)	0·052 (4)	0·037 (4)	0·022 (3)	0·007 (3)	0·012 (3)	0·025 (3)
C(2)	0·015 (3)	0·040 (4)	0·036 (3)	0·007 (3)	0·019 (3)	0·011 (3)
C(3)	0·043 (4)	0·041 (4)	0·037 (4)	0·009 (3)	0·021 (3)	0·028 (3)
C(4)	0·042 (4)	0·025 (3)	0·017 (3)	0·005 (2)	0·012 (3)	0·014 (3)
C(5)	0·060 (5)	0·061 (5)	0·032 (4)	0·026 (3)	0·039 (4)	0·042 (4)
C(6)	0·046 (5)	0·053 (5)	0·058 (5)	0·020 (4)	0·012 (4)	0·009 (4)
C(7)	0·043 (4)	0·032 (3)	0·025 (3)	−0·005 (3)	0·006 (3)	0·026 (3)
C(8)	0·044 (4)	0·033 (3)	0·035 (4)	0·020 (3)	0·015 (3)	0·026 (3)
C(9)	0·029 (4)	0·075 (6)	0·040 (4)	0·028 (4)	0·010 (3)	0·012 (4)
C(10)	0·048 (4)	0·034 (4)	0·030 (4)	−0·001 (3)	0·003 (3)	0·015 (3)
C(11)	0·058 (6)	0·064 (6)	0·063 (6)	0·024 (5)	−0·010 (5)	0·019 (5)
C(12)	0·080 (7)	0·055 (5)	0·030 (4)	0·007 (4)	0·007 (4)	0·030 (5)

Table 5. *Observed and calculated structure factors on an arbitrary scale*

H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI
0	0	17	588	871	0.9559	0	-3	-4	1854	1800	0.9930
0	0	16	994	990	0.9647	0	-3	-5	1158	1285	0.9596
0	0	15	463	369	0.0486	0	-3	-6	1566	1300	0.6737
0	0	14	1641	1667	0.9762	0	-3	-8	577	533	0.6104
0	0	13	645	537	0.0050	0	-3	-9	687	700	0.1239
0	0	12	526	478	0.3144	0	-3	-10	1090	972	0.1516
0	0	11	1217	1269	0.0179	0	-3	-11	526	547	0.0116
0	0	10	1457	1572	0.9543	0	-3	-12	1244	1074	0.9655
0	0	9	1247	1220	0.9655	0	-4	16	518	716	0.4799
0	0	8	2148	2271	0.0257	0	-4	14	749	810	0.0421
0	0	7	3168	3413	0.0010	0	-4	13	697	747	0.0376
0	0	5	1477	1566	0.9836	0	-4	11	836	840	0.9851
0	0	4	1437	1333	0.5177	0	-4	9	958	906	0.0075
0	0	3	4905	6027	0.0048	0	-4	8	757	807	0.9286
0	0	2	2584	2629	0.0061	0	-4	7	1458	1521	0.0021
0	0	1	2585	2960	0.9993	0	-4	6	1326	1209	0.0088
0	-1	16	579	573	0.9535	0	-4	4	303	323	0.0012
0	-1	15	1080	1201	0.0002	0	-4	3	1526	1696	0.0712
0	-1	14	510	566	0.0839	0	-4	2	1398	1475	0.0326
0	-1	13	1056	1177	0.9717	0	-4	1	626	657	0.8579
0	-1	12	2431	2720	0.9793	0	-4	0	1796	1776	0.5781
0	-1	11	1424	1579	0.9832	0	-4	-1	963	901	0.9826
0	-1	10	1142	1142	0.9536	0	-4	-2	1619	1668	0.0812
0	-1	9	2383	2959	0.9870	0	-4	-3	515	540	0.9994
0	-1	8	2662	3126	0.9844	0	-4	-4	1175	1100	0.0178
0	-1	7	1758	1873	0.9843	0	-4	-5	1512	1545	0.0320
0	-1	6	2485	2526	0.0441	0	-4	-6	625	482	0.9192
0	-1	5	2097	2258	0.0196	0	-4	-7	1678	1633	0.0114
0	-1	4	1418	1483	0.0115	0	-4	-8	731	702	0.0077
0	-1	3	1024	1090	0.0662	0	-4	-9	985	823	0.0122
0	-1	2	1091	1069	0.0479	0	-4	-10	1024	810	0.0264
0	-1	1	1570	1546	0.0196	0	-4	-12	814	695	0.0394
0	-1	0	1387	1360	0.9558	0	-4	-14	416	474	0.8883
0	-1	-1	3493	3762	0.0215	0	-5	15	538	571	0.0113
0	-1	-2	4611	5357	0.9949	0	-5	13	1009	895	0.9750
0	-1	-3	2895	3184	0.9678	0	-5	12	797	760	0.9648
0	-1	-4	1459	1087	0.9441	0	-5	11	1565	1514	0.9844
0	-1	-5	3018	3161	0.0232	0	-5	10	1308	1214	0.0415
0	-1	-6	3680	3754	0.0591	0	-5	8	788	806	0.0535
0	-1	-7	2062	2095	0.0383	0	-5	6	635	697	0.9900
0	-1	-8	2941	3136	0.0137	0	-5	5	1675	1676	0.0230
0	-1	-9	1611	1573	0.9325	0	-5	4	1756	1728	0.1824
0	-1	-10	819	843	0.8613	0	-5	3	1698	1827	0.0083
0	-1	-11	1186	933	0.0389	0	-5	2	2064	2093	0.0403
0	-2	17	470	623	0.9441	0	-5	1	1490	1569	0.0392
0	-2	15	1012	1036	0.9470	0	-5	0	1063	1019	0.9574
0	-2	14	506	472	0.0536	0	-5	-1	1695	1523	0.0634
0	-2	13	644	661	0.9301	0	-5	-2	616	703	0.8623
0	-2	12	913	927	0.0176	0	-5	-3	1392	1297	0.0314
0	-2	11	1086	1220	0.0323	0	-5	-4	1485	1400	0.0479
0	-2	10	770	720	0.0185	0	-5	-5	1203	1212	0.0512
0	-2	8	1528	1553	0.0217	0	-5	-6	1793	1774	0.0672
0	-2	7	1181	1175	0.9753	0	-5	-7	641	641	0.9606
0	-2	6	4435	4798	0.9986	0	-5	-8	938	858	0.0129
0	-2	5	2981	3167	0.9728	0	-5	-9	541	532	0.9832
0	-2	4	5133	5680	0.9864	0	-5	-11	759	621	0.0246
0	-2	3	2306	2449	0.9688	0	-5	-12	554	476	0.0985
0	-2	2	2599	2786	0.5187	0	-6	14	574	688	0.0531
0	-2	1	4644	5120	0.0395	0	-6	13	574	516	0.9333
0	-2	0	3156	3247	0.5063	0	-6	12	1044	1044	0.9607
0	-2	-1	1962	1809	0.5167	0	-6	11	1089	1024	0.9814
0	-2	-2	2170	2202	0.9931	0	-6	10	985	1186	0.9986
0	-2	-3	2319	2430	0.9431	0	-6	9	952	979	0.9650
0	-2	-4	593	737	0.9684	0	-6	8	867	829	0.9796
0	-2	-6	1058	1079	0.0516	0	-6	7	1285	1188	0.0362
0	-2	-7	482	431	0.5124	0	-6	6	1202	1083	0.9740
0	-2	-8	571	555	0.0216	0	-6	5	1057	993	0.9473
0	-2	-9	644	525	0.0666	0	-6	4	1927	1932	0.0436
0	-2	-10	2186	1844	0.0011	0	-6	3	1625	1492	0.0309
0	-2	-11	1180	1086	0.9273	0	-6	2	475	444	0.9335
0	-2	-13	1438	1370	0.0428	0	-6	1	1084	980	0.0225
0	-3	16	644	711	0.0425	0	-6	0	801	811	0.1240
0	-3	15	492	636	0.0384	0	-6	-1	720	629	0.0996
0	-3	14	810	812	0.9451	0	-6	-2	751	815	0.9220
0	-3	13	896	878	0.0177	0	-6	-3	1218	1129	0.0279
0	-3	12	699	650	0.0590	0	-6	-4	1235	1207	0.0300
0	-3	11	828	782	0.4568	0	-6	-5	667	704	0.9607
0	-3	9	1668	1656	0.0279	0	-6	-6	1194	1119	0.0432
0	-3	8	496	408	0.5394	0	-6	-7	845	816	0.0361
0	-3	7	1083	1126	0.0014	0	-6	-8	602	575	0.9358
0	-3	6	984	1166	0.0664	0	-6	-9	421	389	0.9112
0	-3	5	1170	1247	0.0555	0	-7	9	1001	1081	0.0092
0	-3	4	1194	1278	0.0850	0	-7	8	763	710	0.0038
0	-3	3	974	769	0.5762	0	-7	7	833	814	0.9868
0	-3	2	1200	1213	0.9169	0	-7	6	862	729	0.0254
0	-3	1	1060	1127	0.8961	0	-7	5	1016	965	0.0034
0	-3	0	250	248	0.1064	0	-7	4	754	780	0.9425
0	-3	-1	3003	3012	0.0372	0	-7	3	690	640	0.5486
0	-3	-2	3637	3491	0.0239	0	-7	2	1090	1160	0.0148
0	-3	-3	530	418	0.9532	0	-7	1	950	943	0.9582
0	-7	0	913	806	0.9662	1	3	12	496	542	0.1235
0	-7	-1	680	671	0.0567	1	3	11	447	461	0.0415
0	-7	-2	864	637	0.0842	1	3	10	874	1058	0.9362
0	-8	4	452	434	0.1450	1	3	8	942	1080	0.9437
0	-8	2	373	464	0.9443	1	3	7	441	542	0.0327
0	-8	1	729	735	0.0706	1	3	6	618	724	0.0856
0	-8	0	521	523	0.9830	1	3	5	1027	967	0.9788
0	-8	-1	602	746	0.8746	1	3	4	748	877	0.3800
0	-8	-2	477	421	0.9582	1	3	3	814	936	0.9625
1	8	0	247	410	0.9727	1	3	2	836	727	0.3994
1	8	-1	266	434	0.0981	1	3	1	723	627	0.9226
1	8	-2	363	501	0.0564	1	3	0	1533	1641	0.9638
1	8	-3	583	766	0.9839	1	3	-1	2071	1921	0.0409
1	8	-4	361	480	0.0253	1	3	-2	3066	2734	0.0516
1	8	-5	375	631	0.9737	1	3	-3	3224	2920	0.0158
1	7	3	283	336	0.9789	1	3	-4	3344	3278	0.9951
1	7	2	387	428	0.9879	1	3	-5	1152	1059	0.9855
1	7	1	329	405	0.0212	1	3	-6	1964	2039	0.0083
1	7	0	698	783	0.9782	1	3	-8	1525	1434	0.9751
1	7	-1	872	934	0.9472	1	3	-9	2210	2073	0.0189
1	7	-2	361	452	0.0029	1	3	-10	833	676	0.0137
1	7	-3	669	751	0.0250	1	3	-11	1340	1207	0.9710
1	7	-4	644	680	0.9885	1	3	-13	1128	1026	0.9871
1	7	-5	284	372	0.0721	1	3	-14	483	539	0.9096
1	7	-6	717	703	0.0222	1	3	-16	841	831	0.0082
1	7	-7	448	435	0.0004	1	2	12	541	734	0.0585
1	7	-8	932	1062	0.0033	1	2	11	978	1057	0.0499
1	7	-9	801	953	0.0583	1	2	10	873	858	0.9950
1	7	-10	537	630	0.1053	1	2	9	1668	1743	0.9740
1	6	9	534	484	0.0159	1	2	8	827	975	0.9372
1	6	8	542	679	0.9249	1	2	7	1411	1529	0.9724
1	6	7	520	605	0.9283	1	2	6	1604	1672	0.0245
1	6	6	327	507	0.0228	1	2	5	1421	1518	0.1229
1	6	4	453	426	0.9906	1	2	4	3017	3472	0.9943
1	6	3	686	870	0.1298	1	2	3	2523	2628	0.9977
1	6	2	432	567	0.0693	1	2	2	3441	3489	0.9861
1	6	1	1113	1244	0.9102	1	2	1	1862	1918	0.9690
1	6	0	996	1026	0.9301	1	2	0	764	936	0.9233
1	6	-1	574	707	0.0251	1	2	-1	2451	2355	0.8957
1	6	-2	1120	1185	0.9808	1	2	-2	450	249	0.5028
1	6	-3	594	641	0.0008	1	2	-3	412	486	0.1962
1	6	-4	448	437	0.1327	1	2	-4	2467	2165	0.0088
1	6	-5	514	452	0.0373	1	2	-5	3181	3191	0.9829
1	6	-6	559	527	0.9388	1	2	-6	2968	2954	0.0134
1	6	-7	639	541	0.9786	1	2	-7	2939	2945	0.0065
1	6	-8	765	707	0.0036	1	2	-8	2146	2132	0.9977
1	6	-9	1051	991	0.9758	1	2	-9	2598	2565	0.0580
1	6	-10	806	688	0.0104	1	2	-10	1914	1663	0.0298
1	6	-11	767	723	0.1463	1	2	-11	2130	1949	0.0185
1	6	-12	444	435	0.0788	1	2	-12	2360	2156	0.0215
1	5	8	420	493	0.2368	1	2	-14	1423	1238	0.0491
1	5	7	683	730	0.0650	1	2	-15	1127	1038	0.0184
1	5	6	732	819	0.9578	1	2	-16	503	360	0.9726
1	5	5	622	626	0.0348	1	2	-17	528	564	0.0497
1	5	4	1064	1226	0.9354	1	1	15	277	203	0.0171
1	5	3	821	755	0.9511	1	1	14	706	741	0.0320
1	5	2	808	742	0.0688	1	1	13	590	693	0.9860
1	5	1	696	713	0.1897	1	1	12	396	869	0.8993
1	5	0	834	754	0.9742	1	1	11	1329	1389	0.9456
1	5	-1	283	236	0.8350	1	1	10	412	569	0.0983
1	5	-3	1020	936	0.9995	1	1	9	1494	1627	0.9951
1	5	-4	784	680	0.0233	1	1	8	890	865	0.2750
1	5	-5	1159	1127	0.0334	1	1	7	741	804	0.0569
1	5	-6	614	527	0.0882	1	1	6	2010	2142	0.9544
1	5	-7	1212	1202	0.0117	1	1	5	271	462	0.0368
1	5	-10	1278	1128	0.9692	1	1	4	4480	5028	0.9916
1	5	-11	567	505	0.9437	1	1	3	5680	6104	0.9952
1	5	-12	354	266	0.1175	1	1	2	6735	6944	0.9872
1	5	-13	557	506	0.0711	1	1	1	6099	6287	0.0063
1	5	-14	809	740	0.9680	1	1	0	5044	5276	0.0166
1	4	7	393	644	0.2227	1	1	-1	831	816	0.1112
1	4	6	674	722	0.0254	1	1	-2	865	834	0.9480
1	4	5	1117	1252	0.9376	1	1	-3	3170	3185	0.9872
1	4	4	956	1013	0.0378	1	1	-4	2740	2721	0.9810
1	4	3	749	817	0.9695	1	1	-5	4143	4323	0.0086
1	4	2	414	602	0.9291	1	1	-6	611	674	0.0800
1	4	1	1065	1193	0.0869	1	1	-7	3350	3632	0.9756
1	4	0	1070	1161	0.2610	1	1	-8	1665	1703	0.9787
1	4	-1	941	871	0.1438	1	1	-9	1443	1354	0.5104
1	4	-2	2509	2479	0.9417	1	1	-10	653	642	0.8903
1	4	-3	703	736	0.9933	1	1	-11	1175	1094	0.9847
1	4	-4	671	667	0.0164	1	1	-12	1783	1746	0.0676
1	4	-5	1451	1397	0.9400	1	1	-13	1351	1265	0.0345
1	4	-8	345	278	0.8944	1	1	-14	1929	1733	0.0185
1	4	-10	824	754	0.0414	1	1	-15	1295	1238	0.0716
1	4	-11	385	361	0.0008	1	1	-16	528	450	0.0105
1	4	-12	1484	1406	0.9729	1	1	-17	712	632	0.0667
1	4	-13	1239	1138	0.0236	1	0	16	311	362	0.0675
1	4	-15	866	816	0.9953	1	0	15	1082	1193	0.9896
1	3	13	591	680	0.0726	1	0	14	723	823	0.9251

they are situated between the imidazole groups, so that they might be sandwiched between them. The imidazole groups are almost perpendicular to the plane of the coordination square.

The distances and angles of the nitrate ions (see Fig. 5) deviate a little from values obtained before. However, the mean value of the N–O distances is found to be 1·23 Å, which is in close agreement with the data published earlier (*International Tables*, 1962).

The structure is linked together by an extensive hydrogen bond network (see Table 7). The position of H(5) is rather uncertain. That given in Table 2 implies that H(5) should be bound to N(3) thus forming a hydrogen bond between N(3) and O(7). The N(3)–O(7) distance (3·26 Å) is, however, slightly longer than that of N(3)–O(5) (3·01 Å), which would indicate the presence of an H atom between N(3) and O(5) instead. There are, nevertheless, two reasons for supposing that the proposed position is more probable. One is that the final difference Fourier calculation showed a peak of about the correct height at the position suggested, but none between N(3) and O(5). The second reason is that the H(5) position of Table 2 lies in the plane of the imidazole group, whereas the vector between

Table 5 (*cont.*)

H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI
1	0	13	578	669	0.0420	1	-3	8	991	1000	0.0603
1	0	12	1581	1629	0.9998	1	-3	7	1441	1447	0.0127
1	0	11	1025	1100	0.9532	1	-3	6	1512	1600	0.9528
1	0	10	1404	1432	0.9927	1	-3	5	1019	1034	0.9913
1	0	9	1535	1698	0.9970	1	-3	4	2170	2322	0.0215
1	0	8	2319	2597	0.9898	1	-3	3	1913	2117	0.9866
1	0	7	2055	2294	0.0324	1	-3	2	1005	1197	0.9202
1	0	6	633	700	0.0290	1	-3	1	969	637	0.4063
1	0	5	2092	2376	0.9207	1	-3	0	2263	2378	0.0384
1	0	4	2017	2132	0.9563	1	-3	-1	2223	2096	0.0281
1	0	3	1521	1487	0.4790	1	-3	-2	779	523	0.3117
1	0	2	2914	2876	0.4510	1	-3	-3	2864	2783	0.0058
1	0	1	6870	7977	0.3978	1	-3	-4	2836	2879	0.0259
1	0	0	1434	1283	0.0402	1	-3	-5	2223	2081	0.9893
1	0	-1	1941	1832	0.0469	1	-3	-6	2204	2145	0.0026
1	0	-2	6019	6203	0.0057	1	-3	-7	1536	1375	0.9962
1	0	-3	853	1043	0.0697	1	-3	-8	898	724	0.8963
1	0	-4	4523	4732	0.0123	1	-3	-9	1313	1236	0.1108
1	0	-5	2891	2825	0.0369	1	-3	-10	1314	1118	0.0971
1	0	-6	3843	3986	0.0192	1	-3	-11	925	766	0.9241
1	0	-7	2189	2402	0.9587	1	-3	-12	1186	1048	0.9732
1	0	-8	750	591	0.0258	1	-3	-13	844	616	0.0152
1	0	-9	1804	1664	0.9962	1	-3	-14	553	552	0.9815
1	0	-10	1076	603	0.9479	1	-3	-15	560	448	0.0594
1	0	-12	465	648	0.6445	1	-4	16	503	508	0.0266
1	0	-13	1017	951	0.0503	1	-4	15	765	778	0.9860
1	0	-14	406	394	0.9653	1	-4	14	983	1033	0.9774
1	0	-15	475	556	0.9020	1	-4	13	1034	1037	0.9929
1	0	-16	553	483	0.9941	1	-4	12	986	991	0.9825
1	-1	17	560	621	0.9310	1	-4	10	346	410	0.1727
1	-1	16	671	693	0.8909	1	-4	8	1864	1788	0.0197
1	-1	14	378	385	0.1131	1	-4	7	1661	1654	0.9949
1	-1	13	744	857	0.0127	1	-4	6	2788	2849	0.9892
1	-1	12	462	504	0.1504	1	-4	5	2695	2976	0.0020
1	-1	11	585	659	0.2249	1	-4	3	3452	3898	0.0327
1	-1	10	1925	1767	0.0078	1	-4	2	846	843	0.9844
1	-1	9	912	1012	0.9481	1	-4	1	962	867	0.8524
1	-1	8	2322	2713	0.9559	1	-4	0	2949	3200	0.9755
1	-1	7	3207	3517	0.9798	1	-4	-1	2919	2828	0.0137
1	-1	6	2018	2046	0.0249	1	-4	-2	2874	2894	0.0429
1	-1	5	1720	1851	0.0769	1	-4	-3	2431	2224	0.9999
1	-1	4	587	570	0.3112	1	-4	-4	2752	2824	0.0475
1	-1	3	1617	1783	0.9920	1	-4	-5	1284	1068	0.9765
1	-1	2	1169	1188	0.5108	1	-4	-6	1037	1049	0.9335
1	-1	1	801	819	0.9977	1	-4	-7	705	576	0.9825
1	-1	0	2176	2278	0.0120	1	-4	-8	1505	1296	0.0057
1	-1	-1	2892	3110	0.9883	1	-4	-9	1144	1104	0.0025
1	-1	-2	2432	2401	0.0096	1	-4	-10	423	451	0.1762
1	-1	-3	1899	1571	0.5245	1	-4	-11	2219	1958	0.0840
1	-1	-4	1632	1400	0.6138	1	-4	-12	850	751	0.0202
1	-1	-5	3191	3030	0.4877	1	-4	-13	714	559	0.9378
1	-1	-6	723	764	0.0746	1	-4	-14	541	707	0.9184
1	-1	-7	2468	2451	0.0223	1	-5	15	529	565	0.0176
1	-1	-8	1630	1609	0.0467	1	-5	14	964	1022	0.0049
1	-1	-9	1764	1830	0.9710	1	-5	13	462	466	0.9810
1	-1	-10	2745	2603	0.0226	1	-5	12	1196	1298	0.9929
1	-1	-11	1305	1239	0.0535	1	-5	11	1631	1755	0.9811
1	-1	-12	725	680	0.5797	1	-5	10	861	865	0.9405
1	-1	-13	712	671	0.9864	1	-5	9	1326	1360	0.9749
1	-1	-16	567	546	0.0036	1	-5	8	1389	1400	0.9939
1	-2	17	210	316	0.2358	1	-5	7	1666	1653	0.9885
1	-2	16	601	746	0.9903	1	-5	6	2199	2195	0.0143
1	-2	15	537	648	0.9530	1	-5	5	1534	1423	0.0234
1	-2	14	377	353	0.4103	1	-5	4	1341	1406	0.0175
1	-2	13	496	543	0.0959	1	-5	3	1416	1360	0.0245
1	-2	12	655	671	0.0180	1	-5	2	404	396	0.3450
1	-2	11	416	457	0.0018	1	-5	1	1586	1606	0.0578
1	-2	10	852	888	0.0422	1	-5	0	2324	2392	0.0046
1	-2	9	1206	1258	0.0062	1	-5	-1	959	828	0.9170
1	-2	7	437	501	0.0818	1	-5	-2	2151	2152	0.9919
1	-2	6	1110	979	0.4596	1	-5	-3	2138	2068	0.0170
1	-2	5	2310	2508	0.0307	1	-5	-4	1269	1192	0.9844
1	-2	4	475	541	0.1751	1	-5	-5	1506	1414	0.0439
1	-2	3	4587	4858	0.5009	1	-5	-6	878	829	0.9694
1	-2	2	9263	11102	0.0048	1	-5	-7	1396	1123	0.9735
1	-2	1	800	721	0.9819	1	-5	-8	848	827	0.0560
1	-2	0	1203	1041	0.5046	1	-5	-9	667	626	0.9763
1	-2	-1	5434	5894	0.0067	1	-5	-10	1274	1031	0.9986
1	-2	-2	937	485	0.6050	1	-5	-11	712	677	0.9856
1	-2	-3	1956	1964	0.0199	1	-5	-12	373	422	0.1315
1	-2	-4	1549	1356	0.6465	1	-5	-13	490	472	0.0059
1	-2	-5	1531	1437	0.0218	1	-6	13	683	721	0.0490
1	-2	-6	888	817	0.9497	1	-6	12	650	626	0.0302
1	-2	-7	896	849	0.4378	1	-6	11	997	928	0.0079
1	-2	-8	1638	1676	0.0977	1	-6	10	896	834	0.9770
1	-2	-9	2012	1909	0.9958	1	-6	9	971	914	0.9977
1	-2	-10	905	684	0.8450	1	-6	8	927	923	0.0338
1	-2	-11	804	615	0.7613	1	-6	7	465	442	0.9450
1	-2	-12	1711	1579	0.0225	1	-6	6	691	743	0.9336
1	-2	-14	627	438	0.1560	1	-6	5	1674	1603	0.9935
1	-2	-15	940	852	0.0811	1	-6	4	2232	2269	0.9946
1	-2	-16	766	645	0.0863	1	-6	3	1579	1550	0.9613
1	-3	17	489	628	0.0548	1	-6	2	1878	1798	0.9864
1	-3	16	383	488	0.1832	1	-6	1	1167	1143	0.0055
1	-3	14	1118	1157	0.9928	1	-6	0	775	734	0.1148
1	-3	13	576	557	0.9457	1	-6	-3	705	629	0.0322
1	-3	12	393	372	0.5118	1	-6	-4	583	386	0.7005
1	-3	11	964	991	0.0470	1	-6	-5	1037	958	0.0388
1	-3	10	897	921	0.0089	1	-6	-6	757	747	0.0822
1	-3	9	666	671	0.0296	1	-6	-7	563	502	0.0298

H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI
1	-6	-8	776	657	0.9927	2	3	6	1562	1552	0.0036
1	-6	-9	276	243	0.7352	2	3	5	1767	1754	0.9550
1	-6	-10	396	407	0.0012	2	3	4	1709	1805	0.9673
1	-6	-11	345	230	0.8465	2	3	3	1031	971	0.0016
1	-7	13	560	685	0.9904	2	3	2	1107	1054	0.9412
1	-7	12	723	825	0.0337	2	3	1	876	888	0.8377
1	-7	11	308	316	0.0555	2	3	0	483	356	0.3719
1	-7	10	836	800	0.0518	2	3	-1	1036	930	0.0233
1	-7	8	273	295	0.4766	2	3	-2	969	947	0.0146
1	-7	7	400	435	0.2296	2	3	-3	2546	2500	0.9835
1	-7	4	890	763	0.0279	2	3	-4	1846	1669	0.9740
1	-7	3	867	834	0.0091	2	3	-5	2737	2624	0.9848
1	-7	2	986	908	0.9770	2	3	-6	1923	1901	0.0112
1	-7	1	1130	1057	0.9542	2	3	-7	804	706	0.1538
1	-7	0	489	464	0.8385	2	3	-8	2461	2252	0.0296
1	-7	-1	683	603	0.0091	2	3	-9	2003	1774	0.0145
1	-7	-2	452	457	0.0355	2	3	-10	1493	1406	0.0377
1	-7	-3	442	388	0.0063	2	3	-11	1380	1292	0.0481
1	-7	-4	967	894	0.0537	2	3	-12	1750	1667	0.9906
1	-7	-5	538	496	0.8677	2	3	-13	1039	924	0.9934
1	-7	-6	572	436	0.9502	2	3	-14	479	439	0.0568
1	-7	-7	305	282	0.0518	2	3	-15	727	689	0.9799
1	-7	-8	213	175	0.7033	2	2	15	224	384	0.9544
1	-8	10	406	472	0.9718	2	2	14	321	463	0.9212
1	-8	9	608	674	0.0185	2	2	13	556	583	0.9044
1	-8	8	656	725	0.9543	2	2	11	371	508	0.0753
1	-8	7	535	508	0.8632	2	2	10	623	538	0.0248
1	-8	6	399	403	0.0546	2	2	8	796	743	0.9513
1	-8	5	514	580	0.1159	2	2	7	1241	1323	0.9172
1	-8	1	284	213	0.2539	2	2	6	1758	1801	0.9972
1	-8	-1	306	362	0.9889	2	2	5	1761	1923	0.0165
1	-8	-2	535	558	0.0800	2	2	4	2216	2321	0.9822
1	-8	-3	222	196	0.9132	2	2	3	3208	3159	0.0069
1	-8	-4	552	505	0.0795	2	2	2	1920	2058	0.0529
1	-8	-5	535	519	0.0869	2	2	1	1298	1411	0.1153
2	7	3	227	319	0.9293	2	2	0	3405	3453	0.9572
2	7	2	213	316	0.9646	2	2	-1	2413	2228	0.9695
2	7	1	357	502	0.0075	2	2	-2	1400	1497	0.0404
2	7	0	381	393	0.0053	2	2	-3	4169	3870	0.9757
2	7	-4	266	338	0.9994	2	2	-4	1546	1361	0.0070
2	7	-5	499	605	0.0084	2	2	-5	1174	1164	0.0079
2	7	-6	290	334	0.9572	2	2	-6	828	860	0.8954
2	7	-7	303	505	0.9724	2	2	-7	751	811	0.7322
2	6	7	293	529	0.9848	2	2	-8	749	707	0.0291
2	6	6	171	393	0.9303	2	2	-9	427	352	0.3196
2	6	4	208	369	0.1132	2	2	-10	2193	2053	0.9976
2	6	3	436	423	0.2272	2	2	-11	2571	2536	0.0282
2	6	2	271	308	0.9646	2	2	-12	777	749	0.1138
2	6	-1	851	853	0.9480	2	2	-13	1562	1394	0.0440
2	6	-3	417	445	0.0438	2	2	-14	1007	949	0.0050
2	6	-4	307	389	0.0545	2	2	-15	429	354	0.0822
2	6	-6	368	338	0.0867	2	2	-16	559	626	0.0950
2	6	-8	537	569	0.9482	2	1	15	396	467	0.0366
2	6	-9	421	472	0.9260	2	1	14	493	530	0.0563
2	6	-10	544	530	0.0926	2	1	13	428	489	0.0180
2	6	-11	443	567	0.0738	2	1	12	1370	1343	0.9589
2	5	7	318	427	0.9066	2	1	11	624	561	0.9952
2	5	6	240	302	0.1104	2	1	10	1391	1386	0.9703
2	5	5	356	396	0.0347	2	1	9	1129	1329	0.9827
2	5	4	260	355	0.9402	2	1	8	669	642	0.0571
2	5	3	576	539	0.2223	2	1	7	1322	1381	0.9300
2	5	2	700	797	0.1354	2	1	6	918	613	0.4810
2	5	1	1013	1004	0.0171	2	1	5	973	989	0.9851
2	5	0	646	583	0.9688	2	1	4	654	702	0.2733
2	5	-1	866	869	0.9848	2	1	3	812	863	0.0784
2	5	-2	983	925	0.9367	2	1	2	2912	3073	0.9741
2	5	-4	466	459	0.1024	2	1	1	2149	2230	0.0173
2	5	-5	488	391	0.4562	2	1	0	2716	2553	0.0204
2	5	-6	403	383	0.9511	2	1	-1	1241	1278	0.0621
2	5	-7	616	566	0.9898	2	1	-2	3414	3432	0.9926
2	5	-8	290	225	0.3132	2	1	-3	1364	1291	0.9965
2	5	-9	1277	1310	0.9568	2	1	-4	3047	3188	0.0423
2	5	-10	964	860	0.9424	2	1	-5	1744	1763	0.0721
2	5	-12	709	628	0.0389	2	1	-6	1831	1900	0.0025
2	5	-13	405	371	0.0034	2	1	-7	2440	2787	0.0159
2	4	10	412	489	0.9419	2	1	-9	882	903	0.9324
2	4	9	336	295	0.9403	2	1	-10	912	762	0.5573
2	4	5	474	553	0.0864	2	1	-11	348	448	0.0493
2	4	3	938	1115	0.8650	2	1	-12	743	637	0.9199
2	4	2	791	820	0.9732	2	1	-14	866	844	0.0261
2	4	1	568	581	0.1667	2	1	-16	440	445	0.1077
2	4	0	1389	1377	0.0358	2	0	13	542	575	0.0925
2	4	-1	1325	1348	0.0238	2	0	12	561	614	0.9803
2	4	-2	1114	1114	0.0401	2	0	11	1222	1071	0.9669
2	4	-3	1215	1244	0.0173	2	0	10	962	916	0.9411
2	4	-4	1674	1646	0.9669	2	0	9	1201	1303	0.9666
2	4	-5	1155	1112	0.0429	2	0	8	1239	1196	0.0586
2	4	-6	1209	1075	0.0545	2	0	7	1316	1229	0.2110
2	4	-7	1441	1471	0.9897	2	0	6	1312	1309	0.0658
2	4	-8	1012	1084	0.9570	2	0	5	784	811	0.9942
2	4	-9	818	710	0.0555	2	0	4	1443	1431	0.9563
2	4	-10	364	331	0.9866	2	0	3	2507	2489	0.9650
2	4	-11	1150	1142	0.8763	2	0	2	949	1032	0.0481
2	4	-12	683	554	0.9514	2	0	1	2478	2515	0.9637
2	4	-13	277	323	0.0231	2	0	0	545	507	0.0099
2	4	-14	848	742	0.9814	2	0	-1	2706	2327	0.4432
2	3	11	453	566	0.9542	2	0	-2	1770	1443	0.4524
2	3	9	634	624	0.0336	2	0	-3	2451	2116	0.5214
2	3	8	960	1089	0.9785	2	0	-4	1157	850	0.0202
2	3	7	1042	1058	0.1037	2	0	-5	2595	2421	0.0189

N(3) and O(5) is inclined to this plane. On the other hand there is also a possibility that H(5) might form a bifurcated hydrogen bond from N(3) to O(5) and O(7).

Similarly, the corresponding nitrogen atom, N(6), of the other histidine molecule has two short distances to two of its nitrate oxygen atoms, namely N(6)–O(8) = 2·83 Å and N(6)–O(10) = 2·85 Å. The position of H(6) given in Table 2 indicates a hydrogen bond N(6)–H(6)–O(10) but, owing to the general uncertainty in the positional parameters of the hydrogen atom, it is possible in this case also that the structure contains a bifurcated hydrogen bond from N(6) to O(8) and O(10).

Discussion

From chemical investigations in solution different conclusions have been drawn concerning the coordination of histidine to copper(II):

Table 5 (*cont.*)

H	K	L	FOBS	FCALC	FI
2	0	-6	2209	2253	0.9881
2	0	-7	2674	2811	0.0517
2	0	-8	1410	1322	0.0282
2	0	-9	1174	1143	0.9962
2	0	-10	1275	1192	0.0624
2	0	-11	1140	1006	0.5941
2	0	-12	492	484	0.1292
2	0	-13	1301	1208	0.0181
2	0	-14	665	736	0.9401
2	0	-15	821	766	0.0469
2	-1	15	315	347	0.0548
2	-1	13	594	509	0.0073
2	-1	11	1018	941	0.0054
2	-1	10	389	433	0.2067
2	-1	8	1326	1351	0.9683
2	-1	7	670	553	0.3593
2	-1	6	1489	1571	0.0597
2	-1	5	1082	1127	0.0868
2	-1	4	1612	1732	0.9536
2	-1	3	1720	1899	0.9685
2	-1	2	1816	1782	0.0086
2	-1	1	1244	1370	0.0201
2	-1	-1	2784	2969	0.0313
2	-1	-2	1438	1383	0.9580
2	-1	-3	2672	2749	0.0107
2	-1	-4	1561	1218	0.4532
2	-1	-5	1311	1340	0.9528
2	-1	-6	2289	2389	0.9987
2	-1	-7	795	792	0.4595
2	-1	-8	1254	1255	0.9434
2	-1	-9	1064	1137	0.8968
2	-1	-10	1283	1292	0.0665
2	-1	-12	1241	1149	0.0217
2	-1	-13	1387	1226	0.0896
2	-1	-14	471	365	0.0239
2	-1	-15	1315	1230	0.0334
2	-1	-16	756	700	0.9910
2	-2	16	481	526	0.8995
2	-2	14	436	394	0.0408
2	-2	12	312	413	0.2116
2	-2	11	632	723	0.1190
2	-2	10	1078	1118	0.0178
2	-2	9	1382	1438	0.0129
2	-2	8	904	954	0.9839
2	-2	7	1690	1788	0.9256
2	-2	6	2833	2964	0.9725
2	-2	5	431	483	0.0874
2	-2	4	1431	1549	0.3861
2	-2	3	3293	3584	0.0318
2	-2	2	616	783	0.0543
2	-2	1	365	342	0.0568
2	-2	0	4023	4387	0.0012
2	-2	-1	1709	1767	0.9899
2	-2	-2	2794	2727	0.9953
2	-2	-3	2818	2535	0.0095
2	-2	-4	3218	2863	0.0128
2	-2	-5	1990	2097	0.9552
2	-2	-6	514	303	0.4340
2	-2	-7	2123	2072	0.0495
2	-2	-8	2596	2475	0.0035
2	-2	-9	1772	1688	0.0573
2	-2	-10	1532	1354	0.9210
2	-2	-11	1723	1679	0.9984
2	-2	-12	990	871	0.0160
2	-2	-13	380	362	0.9129
2	-2	-14	678	653	0.1087
2	-2	-15	646	568	0.0147
2	-2	-16	638	621	0.0751
2	-3	16	555	595	0.0445
2	-3	15	914	982	0.9807
2	-3	14	606	588	0.9547
2	-3	12	882	894	0.0298
2	-3	11	379	393	0.0273
2	-3	10	898	902	0.0068
2	-3	9	1988	2071	0.9957
2	-3	8	1762	1812	0.9983
2	-3	7	1914	1943	0.0119
2	-3	5	2107	2255	0.0045
2	-3	4	1251	1326	0.9772
2	-3	3	1534	1526	0.9799
2	-3	2	3535	3692	0.0001
2	-3	1	4163	4405	0.9863
2	-3	0	5373	5483	0.0129
2	-3	-1	2253	2173	0.0112
2	-3	-2	2870	2949	0.9918
2	-3	-3	648	535	0.0604
2	-3	-4	946	928	0.9780
2	-3	-5	2368	2441	0.9959
2	-3	-6	1540	1428	0.0393
2	-3	-7	1642	1625	0.9760
2	-3	-8	2092	1976	0.0364
2	-3	-9	2434	2297	0.0712
2	-3	-10	518	450	0.9165
2	-3	-11	1467	1424	0.9790
2	-3	-12	1031	898	0.9456
2	-3	-13	295	455	0.7821
2	-3	-14	766	739	0.0417
2	-3	-15	445	396	0.1515
2	-4	15	640	670	0.0436
2	-4	14	1094	1129	0.0007

H	K	L	FOBS	FCALC	FI
2	-4	13	1063	1051	0.9399
2	-4	12	1204	1216	0.9495
2	-4	11	1188	1181	0.9495
2	-4	10	1112	1086	0.9725
2	-4	9	1556	1626	0.0069
2	-4	8	1063	1054	0.0186
2	-4	7	2938	2933	0.0140
2	-4	6	2161	2134	0.0178
2	-4	5	1535	1469	0.4991
2	-4	4	3361	3659	0.0146
2	-4	3	1070	1145	0.9991
2	-4	2	828	730	0.5880
2	-4	1	3215	3430	0.0019
2	-4	0	1689	1651	0.9555
2	-4	-1	2387	2522	0.0142
2	-4	-2	1762	1684	0.9881
2	-4	-3	2316	2368	0.0332
2	-4	-4	2646	2611	0.0004
2	-4	-5	767	706	0.9064
2	-4	-6	1834	1791	0.0506
2	-4	-7	2294	2454	0.9895
2	-4	-8	1060	897	0.9596
2	-4	-9	604	343	0.8041
2	-4	-10	1517	1454	0.0527
2	-4	-11	432	436	0.0577
2	-4	-13	501	603	0.9899
2	-4	-14	423	471	0.9250
2	-5	15	650	586	0.9889
2	-5	13	966	955	0.0503
2	-5	12	918	818	0.0023
2	-5	11	406	411	0.9947
2	-5	10	349	328	0.0630
2	-5	9	348	356	[illegible]
2	-5	8	1198	1107	0.9771
2	-5	7	1380	1344	0.9447
2	-5	6	3058	2936	0.9966
2	-5	5	3032	3231	0.9852
2	-5	4	1956	2175	0.9596
2	-5	3	421	429	0.0966
2	-5	2	739	738	0.0876
2	-5	1	1075	860	0.0509
2	-5	0	1312	1115	[illegible]
2	-5	-1	942	962	0.9757
2	-5	-2	1251	1327	0.0125
2	-5	-3	898	905	0.9850
2	-5	-4	1216	1014	0.0338
2	-5	-5	578	601	0.0746
2	-5	-6	515	675	0.8168
2	-5	-8	604	633	0.0617
2	-5	-9	671	652	0.9010
2	-5	-10	925	949	0.0055
2	-5	-11	881	763	0.0718
2	-5	-12	623	603	0.0431
2	-5	-13	531	629	0.0263
2	-6	14	644	669	0.9935
2	-6	13	558	578	0.0355
2	-6	12	523	526	0.0876
2	-6	10	494	466	0.0985
2	-6	7	437	413	0.0773
2	-6	6	466	401	0.5186
2	-6	5	1494	1405	0.0290
2	-6	4	1149	1088	0.0114
2	-6	3	547	588	0.8761
2	-6	2	1022	1127	0.9623
2	-6	1	839	734	0.9912
2	-6	0	990	926	0.0597
2	-6	-1	1068	1042	0.9847
2	-6	-2	1427	1424	0.0304
2	-6	-3	1064	885	0.9669
2	-6	-4	745	774	0.8978
2	-6	-8	737	737	0.5393
2	-6	-9	682	620	0.1387
2	-6	-10	305	311	0.0599
2	-6	-11	279	251	0.8767
2	-7	13	483	500	0.9960
2	-7	12	350	376	0.9479
2	-7	11	945	910	0.9854
2	-7	10	905	838	0.9757
2	-7	9	695	660	0.9548
2	-7	8	662	666	0.0095
2	-7	5	374	336	0.1548
2	-7	4	407	476	0.4033
2	-7	3	520	537	0.1109
2	-7	2	1158	1093	0.0130
2	-7	1	523	332	0.6856
2	-7	0	551	483	0.0184
2	-7	-1	530	471	0.1007
2	-7	-2	369	263	0.0945
2	-7	-3	876	792	0.0782
2	-7	-4	805	626	0.9006
2	-7	-5	1203	1176	0.9678
2	-7	-6	809	784	0.0144
2	-7	-7	589	601	0.0379
2	-7	-8	634	688	0.0262
2	-7	-9	432	457	0.0034
2	-8	10	513	607	0.0687
2	-8	9	475	455	0.0095
2	-8	8	370	378	0.9114
2	-8	7	565	526	0.9645
2	-8	6	887	869	0.9923

H	K	L	FOBS	FCALC	FI
2	-8	5	634	669	0.0038
2	-8	4	1011	981	0.0173
2	-8	3	1031	1036	0.0220
2	-8	2	870	825	0.0551
2	-8	1	487	489	0.0129
2	-8	0	394	426	0.9107
2	-8	-1	360	373	0.0574
2	-8	-2	387	254	0.5665
2	-8	-3	457	425	0.1227
2	-8	-4	679	757	0.1493
2	-8	-5	547	549	0.0710
2	-8	-6	645	787	0.7221
2	-9	6	359	493	0.0593
2	-9	5	449	480	0.9917
2	-9	4	517	589	0.0312
2	-9	3	713	812	0.0335
2	-9	2	411	491	0.0235
2	-9	1	662	821	0.0374
2	-9	0	518	646	0.9972
3	6	3	253	362	0.0456
3	6	2	324	371	0.9625
3	6	1	268	280	0.0200
3	6	0	404	439	0.9843
3	6	-5	300	328	0.9355
3	6	-6	363	383	0.9892
3	6	-7	401	453	0.9735
3	5	6	398	316	0.9636
3	5	5	354	342	0.8661
3	5	2	524	450	0.0967
3	5	1	373	350	0.1061
3	5	0	753	719	0.0376
3	5	-1	803	745	0.9854
3	5	-2	852	816	0.9687
3	5	-3	1157	1097	0.0251
3	5	-4	627	592	0.0254
3	5	-5	752	700	0.0025
3	5	-6	726	642	0.0027
3	5	-7	252	281	0.0614
3	5	-8	570	673	0.9652
3	5	-9	621	649	0.8967
3	5	-10	430	434	0.8941
3	4	10	383	410	0.9853
3	4	9	596	615	0.0377
3	4	8	600	612	0.9895
3	4	7	553	560	0.9155
3	4	6	689	667	0.9793
3	4	5	516	397	0.0386
3	4	4	709	654	0.9300
3	4	3	412	345	0.9436
3	4	2	272	193	0.3205
3	4	1	1049	961	0.9466
3	4	0	498	534	0.0220
3	4	-1	937	909	0.9826
3	4	-2	1363	1182	0.9453
3	4	-3	855	821	0.9508
3	4	-4	1014	963	0.0111
3	4	-5	678	665	0.1431
3	4	-6	1222	1110	0.0370
3	4	-7	1217	1144	0.0062
3	4	-8	1263	1274	0.0513
3	4	-9	1355	1496	0.0378
3	4	-10	1296	1163	0.9844
3	4	-11	885	836	0.0152
3	4	-12	554	575	0.9771
3	3	9	764	658	0.8888
3	3	8	556	512	0.0276
3	3	7	802	723	0.0764
3	3	6	965	980	0.9706
3	3	5	771	736	0.0765
3	3	4	1150	1063	0.0605
3	3	3	1677	1511	0.0021
3	3	2	1157	1106	0.9528
3	3	1	1377	1340	0.9770
3	3	0	1503	1453	0.9714
3	3	-1	1093	997	0.9818
3	3	-2	1443	1321	0.0467
3	3	-4	782	726	0.8988
3	3	-5	1022	986	0.9086
3	3	-6	704	546	0.4314
3	3	-7	935	984	0.9951
3	3	-8	1442	1353	0.9687
3	3	-9	780	783	0.1075
3	3	-10	1398	1294	0.0494
3	3	-11	1031	927	0.0369
3	3	-12	519	592	0.0970
3	3	-13	644	691	0.0528
3	3	-14	520	591	0.0468
3	2	13	366	374	0.9635
3	2	12	451	508	0.9645
3	2	11	511	482	0.9061
3	2	10	363	348	0.1494
3	2	8	386	322	0.8001
3	2	7	738	624	0.0165
3	2	5	864	931	0.9391
3	2	4	1425	1458	0.9606
3	2	3	444	487	0.1246
3	2	2	1172	1194	0.0205
3	2	1	921	871	0.0379
3	2	0	637	617	0.0916
3	2	-1	885	866	0.0959

H	K	L	FOBS	FCALC	FI
3	2	-2	2116	1980	0.9988
3	2	-3	2017	1900	0.0491
3	2	-4	1691	1553	0.0841
3	2	-5	2200	2019	0.9987
3	2	-6	1024	1098	0.9328
3	2	-7	436	303	0.0334
3	2	-8	872	824	0.4342
3	2	-9	524	652	0.8246
3	2	-10	516	514	0.9511
3	2	-12	961	838	0.9621
3	2	-13	276	268	0.9894
3	2	-14	250	304	0.0417
3	1	14	352	318	0.9892
3	1	13	645	589	0.9400
3	1	11	453	360	0.0970
3	1	10	768	667	0.0044
3	1	9	825	775	0.1909
3	1	8	848	737	0.1368
3	1	7	1033	852	0.9396
3	1	6	1124	1124	0.9310
3	1	5	876	896	0.9711
3	1	4	837	837	0.0264
3	1	3	1051	1002	0.9494
3	1	2	515	569	0.2376
3	1	1	809	731	0.2986
3	1	0	749	792	0.4081
3	1	-1	343	327	0.0106
3	1	-2	191	304	0.8132
3	1	-3	1739	1497	0.9876
3	1	-4	2407	2424	0.9921
3	1	-5	766	792	0.2015
3	1	-6	1471	1544	0.0829
3	1	-7	1095	1129	0.9985
3	1	-8	402	434	0.0404
3	1	-9	351	315	0.1941
3	1	-10	879	875	0.0148
3	1	-11	1240	1209	0.9938
3	1	-12	819	771	0.0241
3	1	-13	1090	1078	0.9969
3	1	-15	264	196	0.6690
3	0	12	583	505	0.0072
3	0	10	547	523	0.9654
3	0	9	345	429	0.9058
3	0	8	867	882	0.0355
3	0	7	701	767	0.1468
3	0	6	447	372	0.1736
3	0	5	1287	1205	0.9850
3	0	4	627	658	0.0420
3	0	3	696	825	0.2063
3	0	2	2018	1967	0.9925
3	0	1	2141	2154	0.9831
3	0	0	405	673	0.1509
3	0	-1	2905	2811	0.9875
3	0	-2	494	442	0.7945
3	0	-3	351	253	0.0926
3	0	-4	1119	1130	0.9634
3	0	-5	605	545	0.7857
3	0	-6	1670	1809	0.0087
3	0	-7	573	461	0.3565
3	0	-8	1424	1461	0.9928
3	0	-9	2261	2236	0.0059
3	0	-11	1051	982	0.0521
3	0	-12	1147	1067	0.0069
3	0	-13	991	886	0.0050
3	0	-14	1090	1087	0.0477
3	0	-15	854	908	0.9727
3	-1	14	394	487	0.0691
3	-1	12	514	540	0.0288
3	-1	11	1139	986	0.9813
3	-1	10	540	520	0.9861
3	-1	9	1241	1348	0.9326
3	-1	8	455	398	0.9177
3	-1	7	953	941	0.0268
3	-1	6	1148	1097	0.1363
3	-1	5	908	941	0.2199
3	-1	4	1964	2038	0.9879
3	-1	3	1835	1859	0.9689
3	-1	2	2255	2431	0.9608
3	-1	1	1338	1389	0.0089
3	-1	0	2243	2486	0.9980
3	-1	-1	1161	1239	0.9514
3	-1	-2	1574	1624	0.0581
3	-1	-3	1341	1387	0.0383
3	-1	-4	1015	1088	0.9648
3	-1	-5	2902	3077	0.0078
3	-1	-6	1641	1833	0.9964
3	-1	-7	2788	3037	0.9368
3	-1	-8	1642	1489	0.9606
3	-1	-9	1172	1138	0.0420
3	-1	-10	1262	1239	0.9891
3	-1	-12	998	1073	0.0810
3	-1	-13	415	397	0.9296
3	-1	-14	1074	1089	0.0572
3	-1	-15	1023	1091	0.0384
3	-2	15	402	354	0.9671
3	-2	14	271	395	0.9342
3	-2	13	595	581	0.9959
3	-2	12	441	461	0.0358
3	-2	11	1105	1031	0.9815
3	-2	10	[illegible]	885	0.0206

1. Histidine complexes with metals are much more stable than the corresponding metal complexes of glycine, alanine and valine (Maley & Mellor, 1950). This suggests the presence of chelating groups in histidine complexes other than amino and carboxylate groups, probably the imidazole group, which is also indicated by absorption spectra studies in the ultraviolet (Edsall, Felsenfeld, Goodman & Gurd, 1953).

2. Albert (1952) compared the formation of complexes between copper and histidine with that of copper and histamine and found a normal behaviour in the latter case but an abnormal behaviour in the former. The difference should be connected with the presence or absence of the carboxylate group in the coordination around copper. Histamine is a somewhat stronger base than histidine and thus the affinity for copper ought to be greater for histamine. The fact that the

Table 5 (*cont.*)

H	K	L	FOBS	FCALC	FI
3	-2	9	698	775	0.0838
3	-2	8	892	932	0.0034
3	-2	7	935	860	0.9574
3	-2	6	1141	1149	0.9563
3	-2	5	2161	2242	0.9789
3	-2	4	2204	2290	0.0152
3	-2	3	3311	3205	0.9888
3	-2	2	4009	3934	0.9832
3	-2	1	1966	1968	0.9995
3	-2	0	2395	2547	0.0151
3	-2	-1	409	382	0.9916
3	-2	-2	1506	1672	0.0210
3	-2	-3	3072	3078	0.0108
3	-2	-4	1736	1814	0.9696
3	-2	-5	2705	2677	0.0203
3	-2	-6	1306	1302	0.9918
3	-2	-7	1545	1585	0.9868
3	-2	-8	1834	1834	0.0392
3	-2	-9	865	801	0.8279
3	-2	-10	907	826	0.9890
3	-2	-11	1233	1246	0.0258
3	-2	-12	857	957	0.9631
3	-2	-13	930	1043	0.1137
3	-2	-14	826	923	0.0192
3	-2	-15	473	518	0.0183
3	-3	16	365	483	0.9795
3	-3	15	682	727	0.9537
3	-3	14	403	467	0.9243
3	-3	13	1012	930	0.9337
3	-3	12	837	774	0.9866
3	-3	11	547	532	0.0832
3	-3	10	1799	1675	0.9974
3	-3	9	1371	1362	0.0058
3	-3	8	1675	1600	0.0078
3	-3	7	1279	1184	0.0061
3	-3	6	1320	1148	0.9403
3	-3	5	1036	1034	0.9295
3	-3	4	297	388	0.0171
3	-3	3	1256	1277	0.9976
3	-3	2	741	763	0.0432
3	-3	1	2625	2603	0.0302
3	-3	0	2344	2468	0.9708
3	-3	-1	2878	3121	0.9896
3	-3	-2	1619	1536	0.0147
3	-3	-3	1485	1447	0.9638
3	-3	-4	3036	3148	0.0055
3	-3	-5	1052	986	0.0411
3	-3	-6	1473	1534	0.0178
3	-3	-7	1294	1266	0.9835
3	-3	-8	1241	1165	0.0811
3	-3	-9	569	534	0.0896
3	-3	-10	1002	908	0.9626
3	-3	-11	1144	1011	0.0261
3	-3	-12	618	571	0.7269
3	-3	-13	650	641	0.0079
3	-3	-14	286	191	0.0164
3	-4	15	501	527	0.0434
3	-4	11	444	387	0.9580
3	-4	10	547	554	0.9937
3	-4	9	1128	1052	0.9482
3	-4	8	2765	2824	0.9793
3	-4	7	2220	2225	0.9841
3	-4	6	764	717	0.0392
3	-4	5	1977	1969	0.0287
3	-4	4	247	253	0.0627
3	-4	3	608	448	0.4483
3	-4	2	1131	1145	0.0224
3	-4	1	1106	1081	0.9895
3	-4	0	1050	1094	0.9767
3	-4	-1	1066	1059	0.0231
3	-4	-2	1042	1078	0.0293
3	-4	-3	437	451	0.8120
3	-4	-4	1474	1376	0.5300
3	-4	-5	528	290	0.3524
3	-4	-6	1478	1486	0.9893
3	-4	-7	1128	1095	0.0647
3	-4	-8	1332	1191	0.9854
3	-4	-9	1694	1703	0.0155
3	-4	-10	1047	976	0.0796
3	-4	-11	276	371	0.9232
3	-4	-13	439	534	0.8940
3	-5	14	701	669	0.0602
3	-5	13	415	435	0.0655
3	-5	8	849	773	0.4578
3	-5	7	1052	896	0.0650
3	-5	6	1301	1159	0.0150
3	-5	5	488	357	0.9623
3	-5	4	1026	1035	0.0141
3	-5	3	948	953	0.9502
3	-5	2	1711	1668	0.0138
3	-5	1	722	810	0.0117
3	-5	0	1660	1698	0.9971
3	-5	-1	1521	1414	0.0296
3	-5	-2	497	408	0.9388
3	-5	-3	1110	1079	0.0262
3	-5	-4	306	402	0.1603
3	-5	-5	447	381	0.5925
3	-5	-6	387	344	0.5619
3	-5	-7	769	753	0.1321
3	-5	-9	647	683	0.9644
3	-5	-10	795	769	0.0108
3	-5	-11	305	284	0.7466
3	-5	-12	575	619	0.0902
3	-6	14	456	489	0.9412
3	-6	13	716	631	0.9721
3	-6	12	707	673	0.9846
3	-6	11	933	879	0.0218
3	-6	9	694	719	0.0644
3	-6	8	664	677	0.0658
3	-6	7	1142	1024	0.4873
3	-6	6	1104	1046	0.0649
3	-6	5	1080	988	0.0398
3	-6	3	844	803	0.0392
3	-6	-1	868	933	0.0811
3	-6	-2	1855	1858	0.0153
3	-6	-3	1455	1398	0.9553
3	-6	-4	1572	1420	0.0371
3	-6	-5	2042	2054	0.0139
3	-6	-6	734	741	0.0023
3	-6	-7	407	238	0.5569
3	-6	-8	644	667	0.0714
3	-6	-9	414	359	0.1035
3	-6	-10	200	181	0.8810
3	-7	12	271	318	0.0812
3	-7	11	393	342	0.0640
3	-7	10	565	571	0.0118
3	-7	9	384	388	0.9051
3	-7	8	999	914	0.0038
3	-7	7	1488	1402	0.0002
3	-7	6	1139	1165	0.9630
3	-7	5	889	803	0.0427
3	-7	4	1122	1074	0.0422
3	-7	3	1477	1391	0.0211
3	-7	2	366	180	0.9198
3	-7	1	489	512	0.9803
3	-7	0	781	630	0.0646
3	-7	-2	876	790	0.1043
3	-7	-3	997	991	0.0930
3	-7	-4	1125	1084	0.9588
3	-7	-5	553	596	0.9820
3	-7	-6	743	749	0.0458
3	-7	-7	645	669	0.9784
3	-7	-8	560	675	0.0238
3	-8	10	476	388	0.0266
3	-8	9	564	625	0.0138
3	-8	8	272	264	0.8960
3	-8	7	641	630	0.0022
3	-8	6	818	758	0.0423
3	-8	5	626	588	0.0158
3	-8	4	770	817	0.0163
3	-8	3	874	873	0.0100
3	-8	2	998	992	0.0115
3	-8	1	1141	1176	0.9676
3	-8	0	1168	1174	0.9874
3	-8	-1	774	779	0.9739
3	-8	-2	691	718	0.9648
3	-8	-3	408	435	0.1727
3	-8	-4	664	570	0.5992
3	-8	-5	598	662	0.0197
3	-8	-6	334	381	0.9882
3	-8	-8	1770	1868	0.0128
3	-9	3	330	373	0.9771
3	-9	2	574	634	0.0341
3	-9	1	454	490	0.0370
3	-9	0	283	292	0.8892
4	5	2	264	389	0.8950
4	5	1	215	336	0.9496
4	5	0	211	252	0.9811
4	5	-1	240	290	0.9225
4	5	-2	352	358	0.0340
4	5	-3	610	417	0.0786
4	5	-4	480	524	0.0558
4	5	-5	465	567	0.0297
4	4	6	379	410	0.0075
4	4	5	472	553	0.0081
4	4	4	609	604	0.9586
4	4	3	498	448	0.9874
4	4	2	599	611	0.9896
4	4	1	383	435	0.0199
4	4	0	484	487	0.0640
4	4	-1	513	511	0.9824
4	4	-2	250	234	0.9231
4	4	-3	636	548	0.8869
4	4	-4	359	326	0.9364
4	4	-5	390	356	0.0391
4	4	-6	353	324	0.9765
4	4	-7	403	388	0.0324
4	4	-8	537	604	0.0802
4	3	9	511	597	0.1083
4	3	9	229	262	0.9734
4	3	8	402	368	0.9963
4	3	7	447	415	0.9331
4	3	4	424	406	0.0779
4	3	3	335	306	0.2000
4	3	2	537	575	0.0971
4	3	1	606	556	0.0463
4	3	0	742	695	0.9851
4	3	-1	1448	1331	0.0429
4	3	-2	857	852	0.0631
4	3	-3	896	880	0.0055
4	3	-4	706	623	0.9944
4	3	-9	478	612	0.9350
4	3	-10	537	500	0.0002
4	2	10	257	312	0.1100
4	2	8	480	406	0.9559
4	2	7	330	289	0.0336
4	2	6	664	515	0.9846
4	2	5	371	374	0.0312
4	2	4	612	598	0.3471
4	2	3	405	435	0.0142
4	2	0	863	681	0.9202
4	2	-1	546	452	0.9094
4	2	-2	1021	986	0.0049
4	2	-3	846	794	0.2182
4	2	-4	898	856	0.1176
4	2	-5	721	677	0.0073
4	2	-6	612	406	0.0915
4	2	-7	827	812	0.0460
4	2	-8	761	767	0.5699
4	2	-9	819	821	0.0208
4	2	-10	798	758	0.0029
4	2	-11	738	756	0.9526
4	1	11	753	577	0.8588
4	1	9	600	601	0.2369
4	1	8	439	388	0.0409
4	1	7	314	264	0.1208
4	1	6	369	372	0.1032
4	1	5	984	1041	0.9990
4	1	4	730	708	0.9604
4	1	3	869	891	0.9907
4	1	2	769	786	0.0208
4	1	1	526	517	0.9555
4	1	0	873	847	0.0671
4	1	-2	669	627	0.9114
4	1	-3	1485	1466	0.9372
4	1	-4	344	365	0.1219
4	1	-5	1079	983	0.0651
4	1	-6	1493	1526	0.9657
4	1	-7	396	399	0.0543
4	1	-8	701	720	0.0238
4	1	-9	794	697	0.9769
4	1	-10	435	446	0.0594
4	1	-11	991	1022	0.0217
4	1	-12	1118	1082	0.0112
4	1	-13	1005	1130	0.9949
4	0	13	334	415	0.9042
4	0	12	363	295	0.9955
4	0	11	442	324	0.0419
4	0	10	384	358	0.8550
4	0	9	685	544	0.0198
4	0	8	754	685	0.1892
4	0	7	732	625	0.0764
4	0	6	1537	1432	0.9649
4	0	5	633	603	0.9533
4	0	4	1381	1355	0.9563
4	0	3	1373	1345	0.9666
4	0	2	641	653	0.0359
4	0	1	575	557	0.1350
4	0	0	1050	1007	0.0094
4	0	-1	1394	1404	0.0006
4	0	-2	984	848	0.0519
4	0	-3	2318	2155	0.9758
4	0	-4	2247	2272	0.9403
4	0	-5	2128	1952	0.9768
4	0	-6	886	807	0.1064
4	0	-7	1018	986	0.9939
4	0	-8	1183	1201	0.9926
4	0	-10	1252	1188	0.9854
4	0	-11	766	825	0.5943
4	0	-12	911	1007	0.0343
4	0	-13	984	1085	0.0170
4	-1	13	331	321	0.1268
4	-1	12	612	515	0.9869
4	-1	11	521	463	0.0481
4	-1	10	522	426	0.0671
4	-1	9	864	665	0.9084
4	-1	8	853	933	0.9032
4	-1	7	844	788	0.9653
4	-1	6	1198	1028	0.0471
4	-1	5	1577	1569	0.9932
4	-1	4	1564	1584	0.9933
4	-1	3	1358	1369	0.0105
4	-1	2	1535	1500	0.0015
4	-1	1	1751	1762	0.9996
4	-1	0	1244	1155	0.9963
4	-1	-1	1729	1646	0.0085
4	-1	-2	2466	2523	0.9768
4	-1	-3	1038	1019	0.0067
4	-1	-4	1081	964	0.0633
4	-1	-5	1516	1497	0.9573
4	-1	-6	1148	1150	0.9523
4	-1	-7	694	636	0.9995
4	-1	-8	1087	961	0.0161
4	-1	-9	1523	1381	0.0007
4	-1	-10	989	986	0.0103
4	-1	-11	1207	1246	0.0509
4	-1	-12	819	826	0.5663
4	-1	-13	462	541	0.0393
4	-1	-14	326	292	0.0349
4	-2	14	634	566	0.9740
4	-2	13	521	424	0.0426
4	-2	12	857	759	0.0102
4	-2	11	845	764	0.9706
4	-2	10	1396	1105	0.9786
4	-2	9	886	945	0.9894
4	-2	7	936	831	0.9277
4	-2	6	441	253	0.9398
4	-2	5	483	542	0.2816
4	-2	4	1033	1064	0.0421
4	-2	3	1867	1824	0.9833
4	-2	2	1025	1088	0.9679
4	-2	1	2533	2453	0.9734
4	-2	0	1503	1526	0.9703
4	-2	-1	746	738	0.0374
4	-2	-2	1717	1826	0.0331
4	-2	-3	693	772	0.0384
4	-2	-4	2361	2387	0.0266
4	-2	-5	714	694	0.0922
4	-2	-6	973	1063	0.0338
4	-2	-7	1863	2310	0.0032
4	-2	-9	725	641	0.0136
4	-2	-10	431	453	0.9256
4	-2	-11	255	288	0.8497
4	-2	-12	279	250	0.0984
4	-2	-13	324	446	0.0336
4	-3	13	454	374	0.9392
4	-3	11	998	833	0.9683
4	-3	10	992	849	0.9818
4	-3	9	1058	1129	0.0003
4	-3	8	1215	1254	0.0356
4	-3	7	683	577	0.1315
4	-3	6	848	735	0.0084
4	-3	5	909	797	0.0982
4	-3	4	800	794	0.9368
4	-3	3	786	810	0.0467
4	-3	2	1295	1185	0.0383
4	-3	1	657	675	0.9476
4	-3	0	245	282	0.1313
4	-3	-1	532	446	0.4664
4	-3	-2	1015	965	0.5410
4	-3	-3	325	264	0.0634
4	-3	-4	630	598	0.0254
4	-3	-5	2124	1994	0.0243
4	-3	-6	1757	1626	0.9876
4	-3	-7	1036	970	0.9616
4	-3	-8	1235	1185	0.0588
4	-3	-9	366	421	0.8848
4	-3	-10	646	642	0.1409
4	-3	-11	401	292	0.7904
4	-3	-12	431	420	0.0326
4	-3	-13	508	592	0.0623
4	-4	8	556	503	0.0291
4	-4	7	870	781	0.0118
4	-4	6	770	675	0.0366
4	-4	5	591	545	0.6921
4	-4	4	1128	1121	0.9866
4	-4	3	760	766	0.9920
4	-4	2	1578	1548	0.0304
4	-4	1	986	967	0.0627
4	-4	0	1096	1062	0.0680
4	-4	-1	1964	1997	0.0311
4	-4	-3	394	365	0.0595
4	-4	-4	774	524	0.5780
4	-4	-5	384	308	0.5567
4	-4	-6	751	792	0.0930
4	-4	-7	544	440	0.7583
4	-4	-8	637	600	0.0665
4	-4	-9	591	545	0.0812
4	-4	-10	404	469	0.9635
4	-4	-11	586	560	0.1523
4	-4	-12	633	763	0.0489
4	-5	13	499	516	0.0045
4	-5	13	392	354	0.1737
4	-5	12	595	511	0.0728
4	-5	11	541	456	0.0324
4	-5	10	487	285	0.0147
4	-5	8	677	558	0.0080
4	-5	7	814	703	0.9940
4	-5	6	533	472	0.1340
4	-5	5	467	399	0.1025
4	-5	4	456	498	0.4078
4	-5	1	1196	1242	0.9975
4	-5	0	1668	1621	0.0160
4	-5	-1	1437	1471	0.9887
4	-5	-2	2359	2494	0.0106
4	-5	-3	1592	1571	0.0209
4	-5	-4	951	838	0.0580
4	-5	-5	657	522	0.9520
4	-5	-6	607	508	0.0897
4	-5	-7	650	615	0.1312
4	-5	-8	1067	1070	0.4820
4	-5	-9	1264	1308	0.0254
4	-5	-10	524	655	0.8721
4	-5	-11	449	480	0.9804
4	-6	13	304	312	0.9926
4	-6	12	395	374	0.0516
4	-6	10	1186	1010	0.9922
4	-6	9	1174	1161	0.9750
4	-6	8	490	408	0.9606
4	-6	7	1349	1258	0.0222

reverse is true indicates that the carboxylate group of histidine should be involved in the metal bonding (Doran, Chabarek & Martell, 1963).

3. After chelation, the amino group is no longer titratable, and it is thus probable that the amino group is involved in chelation (Maley & Mellor, 1949).

It would appear from these conclusions that the configuration of the copper histidine complex is similar to that found for the zinc(II) histidine complexes (Harding & Cole, 1963; Kretzinger, Cotton & Bryan, 1963), in which all three chelating groups in the ligand are involved in bonding.

If, however, the metal histidine interaction is compared for Cu, Zn, Ni, and Co, it is found that copper deviates from the other metals. Datta, Leberman & Rabin (1958) and Leberman & Rabin (1959) found that the stability constants of the copper histidine complexes varied with *p*H, which is not the case with the

Table 5 (*cont.*)

H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI	H	K	L	FOBS	FCALC	FI
4	-6	6	1087	993	0.0102	5	1	3	387	431	0.0722	5	-4	-6	[illegible]	[illegible]	[illegible]	6	0	-2	666	727	0.0234
4	-6	5	837	767	0.0253	5	1	1	988	907	[illegible]	5	-4	-7	1126	1226	[illegible]	6	0	-3	[illegible]	[illegible]	0.0153
4	-6	4	1263	1173	0.0235	5	1	0	612	620	0.0057	5	-4	-8	[illegible]	[illegible]	[illegible]	6	0	-4	646	434	[illegible]
4	-6	3	989	943	0.9941	5	1	-1	1122	1086	0.9306	5	-5	8	605	[illegible]	[illegible]	6	-1	-2	471	[illegible]	[illegible]
4	-6	2	576	591	0.9765	5	1	-2	1254	1222	0.9379	5	-5	7	1043	1022	[illegible]	6	-1	-3	[illegible]	606	[illegible]
4	-6	1	387	340	0.0667	5	1	-3	758	651	0.9489	5	-5	6	1012	931	[illegible]	6	-1	-5	456	501	[illegible]
4	-6	0	1047	986	0.0515	5	1	-4	788	734	0.0381	5	-5	5	[illegible]	768	[illegible]	6	-1	-6	522	[illegible]	[illegible]
4	-6	-1	979	933	0.9986	5	1	-5	569	611	0.0561	5	-5	4	770	718	0.0312	6	-1	-8	[illegible]	[illegible]	[illegible]
4	-6	-2	374	395	0.9536	5	1	-7	625	734	0.9754	5	-5	3	753	478	0.0420	6	-2	6	[illegible]	514	[illegible]
4	-6	-3	764	549	0.0154	5	1	-8	905	981	0.9705	5	-5	2	647	621	0.0057	6	-2	5	678	[illegible]	[illegible]
4	-6	-4	1428	1393	0.9895	5	1	-9	582	686	0.0267	5	-5	1	186	[illegible]	0.0159	6	-2	4	[illegible]	[illegible]	[illegible]
4	-6	-5	916	962	0.0384	5	0	7	573	601	0.0269	5	-5	0	461	446	[illegible]	6	-2	3	641	[illegible]	[illegible]
4	-6	-6	713	649	0.0270	5	0	5	914	948	0.9792	5	-5	-1	819	781	0.0112	6	-2	2	[illegible]	[illegible]	[illegible]
4	-6	-7	1245	1331	0.0318	5	0	4	683	692	[illegible]	5	-5	-2	733	732	0.0112	6	-2	-1	[illegible]	[illegible]	[illegible]
4	-6	-8	1052	1023	0.0760	5	0	3	894	843	[illegible]	5	-5	-3	1210	1373	0.0257	6	-2	-4	[illegible]	[illegible]	[illegible]
4	-6	-9	906	978	0.0138	5	0	2	1135	1051	[illegible]	5	-5	-4	1185	1115	[illegible]	6	-3	5	[illegible]	[illegible]	[illegible]
4	-7	11	525	537	0.9872	5	0	1	702	673	0.9096	5	-5	-5	691	725	0.0157	6	-3	4	813	[illegible]	[illegible]
4	-7	9	582	583	0.0649	5	0	0	1138	1146	0.9868	5	-5	-6	1047	1114	[illegible]	6	-3	3	[illegible]	[illegible]	[illegible]
4	-7	8	925	874	0.0179	5	0	-1	682	624	0.9987	5	-5	-7	1085	1162	[illegible]	6	-3	2	625	720	[illegible]
4	-7	7	504	436	0.9737	5	0	-2	721	734	[illegible]	5	-5	-8	1138	1237	[illegible]	6	-3	1	[illegible]	[illegible]	[illegible]
4	-7	6	851	781	0.0188	5	0	-3	1329	1144	0.9412	5	-5	-9	343	1033	[illegible]	6	-3	0	735	655	[illegible]
4	-7	5	1001	903	0.9781	5	0	-5	1022	[illegible]	0.9942	5	-6	9	502	[illegible]	[illegible]	6	-3	-1	[illegible]	[illegible]	[illegible]
4	-7	4	1338	1289	0.9905	5	0	-6	819	863	[illegible]	5	-6	8	650	656	[illegible]	6	-3	-2	[illegible]	[illegible]	[illegible]
4	-7	3	1084	1055	0.9802	5	0	-7	724	763	[illegible]	5	-6	7	629	661	[illegible]	6	[illegible]	[illegible]	1212	[illegible]	[illegible]
4	-7	2	1235	1299	0.9713	5	0	-8	[illegible]	735	0.0371	5	-6	6	1017	863	[illegible]	6	[illegible]	-4	[illegible]	[illegible]	[illegible]
4	-7	1	1248	1269	0.0308	5	0	-9	725	868	0.9673	5	-6	5	900	845	[illegible]	6	[illegible]	-5	1151	[illegible]	[illegible]
4	-7	0	408	401	0.9139	5	-1	5	528	645	0.9827	5	-6	4	1157	1072	[illegible]	6	-3	-6	[illegible]	[illegible]	[illegible]
4	-7	-1	704	697	0.0528	5	-1	4	703	756	0.9822	5	-6	3	758	735	[illegible]	6	-4	7	547	[illegible]	[illegible]
4	-7	-2	1102	1063	0.0678	5	-1	3	911	762	[illegible]	5	-6	2	387	438	[illegible]	6	-4	[illegible]	791	[illegible]	[illegible]
4	-7	-3	708	719	0.9716	5	-1	2	1006	1002	[illegible]	5	-6	1	1080	[illegible]	[illegible]	6	-4	2	[illegible]	[illegible]	[illegible]
4	-7	-4	512	660	0.9028	5	-1	1	[illegible]	[illegible]	0.2165	5	-6	0	[illegible]	663	[illegible]	6	-4	1	[illegible]	455	[illegible]
4	-7	-5	905	889	0.9241	5	-1	0	644	[illegible]	[illegible]	5	-6	-1	1032	[illegible]	[illegible]	6	-4	0	[illegible]	[illegible]	[illegible]
4	-7	-6	388	454	0.9062	5	-1	-1	[illegible]	1338	[illegible]	5	-6	-2	[illegible]	[illegible]	[illegible]	6	-4	-1	1045	[illegible]	[illegible]
4	-7	-7	200	398	0.9224	5	-1	-2	[illegible]	553	[illegible]	5	-6	-3	[illegible]	605	[illegible]	6	-4	-2	[illegible]	[illegible]	[illegible]
4	-8	8	510	491	0.9864	5	-1	-3	1301	1250	[illegible]	5	-6	-4	678	712	[illegible]	6	-4	-3	[illegible]	485	[illegible]
4	-8	7	891	846	0.9914	5	-1	-4	[illegible]	1729	[illegible]	5	-7	9	441	611	[illegible]	6	-4	-4	[illegible]	1016	[illegible]
4	-8	6	513	626	0.9705	5	-1	-5	[illegible]	916	[illegible]	5	-7	8	547	580	[illegible]	6	-4	-5	[illegible]	757	[illegible]
4	-8	5	799	756	0.0111	5	-2	8	644	[illegible]	[illegible]	5	-7	7	643	651	[illegible]	6	-4	-6	[illegible]	[illegible]	[illegible]
4	-8	4	496	464	0.0190	5	-2	5	716	[illegible]	[illegible]	5	-7	3	458	606	[illegible]	6	-4	-7	[illegible]	1335	[illegible]
4	-8	3	338	276	0.0315	5	-2	4	582	[illegible]	[illegible]	5	-7	2	718	718	[illegible]	6	-5	8	[illegible]	[illegible]	[illegible]
4	-8	1	290	300	0.0082	5	-2	1	443	[illegible]	[illegible]	5	-7	1	340	415	[illegible]	6	-5	6	[illegible]	448	[illegible]
4	-8	0	624	704	0.9857	5	-2	0	[illegible]	[illegible]	[illegible]	5	-7	0	703	774	0.0072	6	-5	5	[illegible]	[illegible]	0.0213
4	-8	-1	571	697	0.9201	5	-2	-2	838	822	[illegible]	5	-7	-1	802	797	[illegible]	6	-5	4	[illegible]	[illegible]	[illegible]
4	-8	-2	402	378	0.9578	5	-2	-3	1246	[illegible]	[illegible]	5	-7	-2	478	447	0.0453	6	-5	3	711	666	[illegible]
4	-8	-3	1067	1048	0.9544	5	-2	-4	[illegible]	[illegible]	[illegible]	5	-7	-3	386	415	0.9134	6	-5	2	[illegible]	[illegible]	[illegible]
4	-8	-4	719	771	0.0175	5	-2	-5	[illegible]	840	[illegible]	5	-8	6	438	449	0.0230	6	-5	1	[illegible]	[illegible]	[illegible]
5	3	3	254	179	0.0137	5	-2	-6	[illegible]	1142	0.0237	5	-8	5	398	443	0.9770	6	-5	0	[illegible]	[illegible]	[illegible]
5	3	-1	257	378	0.1465	5	-2	-8	639	689	[illegible]	5	-8	2	332	303	0.0558	6	-5	-1	254	[illegible]	[illegible]
5	3	-2	425	461	0.1379	5	-3	4	828	795	0.0546	5	-8	1	387	517	0.9972	6	-5	-2	[illegible]	613	0.0176
5	3	-3	241	328	0.1160	5	-3	3	1467	1369	0.0753	5	-8	-1	237	174	0.1916	6	-5	-5	[illegible]	[illegible]	[illegible]
5	3	-4	424	406	0.9576	5	-3	2	1059	1008	[illegible]	6	1	5	332	477	0.9811	6	-5	-6	[illegible]	[illegible]	[illegible]
5	3	-5	380	498	0.0212	5	-3	1	1110	1166	0.0423	6	1	4	410	417	0.0089	6	-6	4	521	[illegible]	[illegible]
5	3	-7	337	582	0.9770	5	-3	0	1261	[illegible]	0.9726	6	1	3	259	266	0.0300	6	-6	3	[illegible]	362	[illegible]
5	2	2	300	327	0.1543	5	-3	-1	[illegible]	277	0.8823	6	1	2	300	345	0.0571	6	-6	2	555	[illegible]	[illegible]
5	2	1	490	399	0.0071	5	-3	-2	663	656	0.4525	6	1	1	358	403	0.0538	6	-6	1	251	[illegible]	[illegible]
5	2	0	332	298	0.9436	5	-3	-7	678	713	[illegible]	6	1	0	466	522	0.0465	6	-6	0	651	[illegible]	[illegible]
5	2	-1	822	695	0.9175	5	-4	3	1022	972	0.9675	6	1	-1	516	517	0.9942	6	-6	-1	317	[illegible]	[illegible]
5	2	-2	597	628	0.9529	5	-4	2	1224	1260	0.9845	6	1	-2	630	644	[illegible]	6	-6	-3	[illegible]	[illegible]	[illegible]
5	2	-3	533	573	0.0640	5	-4	1	1041	1058	0.0142	6	1	-3	540	626	0.0269	6	-7	3	265	[illegible]	[illegible]
5	2	-4	363	447	0.0238	5	-4	0	1763	1719	0.0363	6	1	-5	312	445	0.0167	6	-7	2	194	[illegible]	[illegible]
5	2	-8	474	582	0.0343	5	-4	-1	1023	972	0.0410	6	0	2	206	313	0.1322	6	-7	1	276	410	[illegible]
5	2	-9	512	712	0.9811	5	-4	-2	1485	1472	0.0249	6	0	1	532	466	0.0416						
5	1	6	662	659	0.9634	5	-4	-3	458	443	0.0307	6	0	0	655	635	0.0163						
5	1	4	491	531	0.0672	5	-4	-5	1870	[illegible]	[illegible]	6	0	-1	859	807	0.0563						

Table 6. *Standard deviations for distances and angles*

	Distances (mean value)	Angles (mean value)
Within the copper coordination sphere	0·007 Å	0·3°
Within the histidine molecules	0·011	0·7
Within the nitrate ions	0·014	1·2

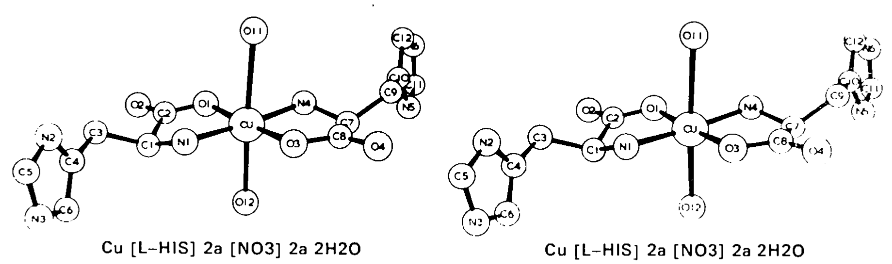

Fig. 2. Stereoscopic diagram of the complex ion $Cu(C_6H_9O_2N_3)_2(H_2O)_2^{2+}$.

other metals. Albert (1952) attributed this behaviour of copper to the planar configuration of its complexes, copper only being coordinated simultaneously by two of the possible coordinating groups. The structures of the complexes can thus vary with *p*H. Leberman & Rabin (1959) have attempted an explanation of the copper histidine coordination with the assumption of a neutral histidine ligand. The coordinating groups were assumed to be the imidazole and carboxylate groups, an unfavourable 7-membered ring thus being formed.

Valladas-Dubois (1961) found two complexes of copper(II) and neutral histidine in an acidic solution. In her publication the crystals of bis-L-histidinecopper-

Table 7. *Hydrogen bond lengths*

N(1)—H(1)—O(9)	2·91 Å
N(1)—H(2)—O(2)	2·93
N(4)—H(3)—O(4)	3·13
N(4)—H(4)—O(6)	2·84
N(3)—H(5)—O(5)	3·01
N(3)—H(5)—O(7)	3·26
N(6)—H(6)—O(10)	2·85
N(6)—H(6)—O(8)	2·83
N(2)—H(13)–O(12)	2·91
N(5)—H(16)–O(11)	2·78
O(11)–H(15)–O(1)	2·92
O(11)–H(18)–O(4)	2·77
O(12)–H(14)–O(3)	2·92
O(12)–H(17)–O(2)	2·83

(II) dinitrate dihydrate are mentioned for the first time.

This crystal structure investigation shows, however, that histidine is able to coordinate through its amino and carboxylate groups thus behaving as a 'normal amino acid'.

In a neutral solution histidine occurs mainly in the 'zwitterionic' form, *i.e.* one of the nitrogen atoms in the imidazole group has a lone electron pair, whereas the amino group is in the charged form ($-NH_3^+$). The latter must, however, lose one proton to be able to coordinate. The most probable proton acceptor is the imino-nitrogen atom of the imidazole group. Theoretically, however, a water molecule can also accept the proton. The possible hydrogen acceptors are in the structure situated at hydrogen bond distances (2·91 Å and 2·78 Å) and the proton of interest should be situated between them. Because of the much higher basicity of the imino-nitrogen atom, it is reasonable to suppose that this is the hydrogen acceptor. This is also supported by the Fourier difference synthesis, which shows hydrogen peaks closer to N(2) and N(5) than to O(11) and O(12). The existence of a neutral histidine ligand is thus confirmed by this crystal structure investigation.

Recently performed spectrophotometric and optical rotatory dispersion studies (Hare, 1966) indicate a similar coordination of copper and histidine in solutions of $p\mathrm{H} < 5$. Above this pH the imidazole ring seems to be involved in chelation.

Sarkar & Wigfield (1967) made discontinuous e.m.f. and spectrophotometric titrations of copper(II) histidine complexes and found that the imidazole group of the histidine molecule does not coordinate to copper over a wide range of pH, which is in agreement with the results from this structure determination of a solid copper(II) histidine complex, crystallized at $p\mathrm{H} = 3{\cdot}7$.

The author would like to thank Professor Georg Lundgren for his invaluable help and advice, and Professor Bo G. Malmström for a suggestion which led to this investigation and for his interest in the work. He wishes to thank Dr Hans Freeman for many helpful discussions.

The stereoscopic molecular diagram (Fig. 2) was produced on the CDC 3600 computer of the C.S.I.R.O. Computer Research Section, Canberra, Australia, using the program ORTEP (Johnson, 1965).

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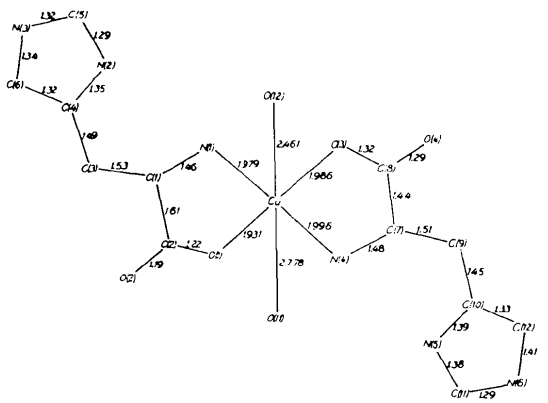

Fig. 3. Interatomic distances, in Å, within the complex ion $Cu(C_6H_9O_2N_3)_2(H_2O)_2^{2+}$.

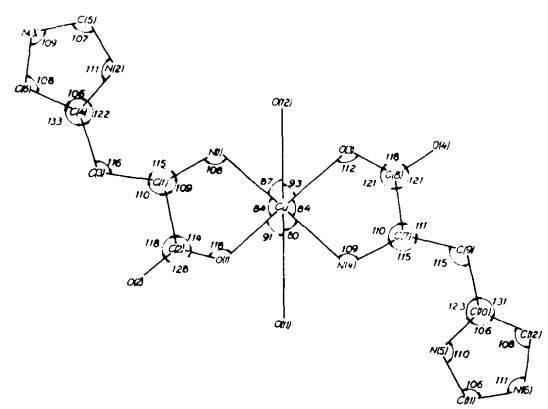

Fig. 4. Bond angles within the complex ion $Cu(C_6H_9O_2N_3)_2(H_2O)_2^{2+}$.

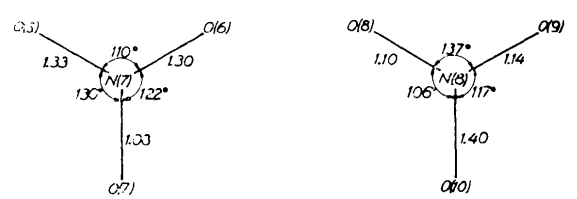

Fig. 5. Interatomic distances and bond angles within the nitrate ions.

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The Crystal and Molecular Structure of 3β,17α-Dihydroxy-16β-bromo-5α-pregnan-11,20-dione and its Comparison with the Related -16β-Bromo-3β-acetate and -21-Bromo-3β-ol Steroids

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The crystal structure of 3β,17α-dihydroxy-16β-bromo-5α-pregnan-11,20-dione ($C_{21}H_{31}O_4Br$, $M=427{\cdot}37$) has been determined by three-dimensional X-ray analysis and refined to a final R value of 0·045. Unit-cell constants are $a=11{\cdot}946$ Å, $b=11{\cdot}011$ Å, $c=7{\cdot}837$ Å, $\beta=107{\cdot}39°$, space group $P2_1$. Standard deviations for bond lengths and angles are in the ranges of 0·007–0·012 Å and 0·5–0·8°, respectively. There are two hydrogen bonds, 3β-hydroxyl to 11-keto oxygen (2·77 Å) and 17α-hydroxyl to 3β-hydroxyl oxygen (2·84 Å). The molecules are α−β (bottom to top) oriented, and arranged in sheets perpendicular to the b axis of the unit cell. Packing of the molecule as influenced by the position of heavy atoms and side chain substituents is discussed.

Introduction

The structural details of a series of 5α-pregnane adrenocortical metabolites are being investigated to ascertain features which are significant in the determination of biological function at the molecular level. The crystal and molecular structures of 3β-acetoxy-17α-hydroxy-16β-bromo-5α-pregnan-11,20-dione (Fig. 1, II) and 3β, 17α-dihydroxy-21-bromo-5α-pregnan-11,20-dione (Fig.1, III) have already been reported (Ohrt, Cooper, Kartha & Norton, 1968; Ohrt, Haner, Cooper & Norton, 1968). This paper reports the crystal and molecular structure determination of 3β,17α-dihydroxy-16β-bromo-5α-pregnan-11,20-dione (Fig. 1, I) and compares the architecture of the molecules and their packing as influenced by the position of attachment of the heavy atom and of side chain substituents.

Experimental

Crystals of 3β,17α-dihydroxy-16β-bromo-5α-pregnan-11,20-dione ($C_{21}H_{31}O_4Br$, $M=427{\cdot}37$) were grown from methanol solution by slow evaporation at room temperature. The crystal data are:

$a=11{\cdot}946\pm0{\cdot}002$, $b=11{\cdot}011\pm0{\cdot}002$, $c=7{\cdot}837\pm0{\cdot}001$ Å, $\beta=107{\cdot}39°\pm0{\cdot}01$ (at 20°C, Cu$K\alpha_1=1{\cdot}54051$

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