pected for a riding motion. Similarly, the largest mean-square displacement for $OA2$ makes an angle of 97° to the $CA2$–$OA2$ bond. In the phenyl ring, as expected, the smallest displacement is usually normal to the ring. Consequently, many of the mean-square displacements can be interpreted in the usual way, suggesting that no serious systematic errors are present in the data.

In conclusion we see that the diketoamide grouping is capable of functioning as a strong bidentate chelate toward transition elements. The coordination occurs through two oxygen atoms rather than through an oxygen and a nitrogen atom. The tetracycline antibiotics are therefore capable of forming metal complexes involving this grouping although other coordination sites cannot be eliminated.

Acknowledgments.—We wish to thank the U. S. Public Health Service, Institute for Allergies and Infectious Diseases, for financial support through Grant No. AI-98201 and Professor E. P. Dudeck for a sample of CuPCD.

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The Crystal and Molecular Structure of Bis(*N*-benzoylhydrazine)copper(II) Pentachlorotricuprate(I), a New Complex Containing Copper in Mixed Oxidation States

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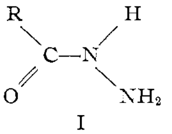
Received April 16, 1970

The crystal structure of bis(*N*-benzoylhydrazine)copper(II) pentachlorotricuprate(I) has been determined by three-dimensional X-ray analysis. The crystals are orthorhombic, space group *Pbca*, with unit cell dimensions $a = 9.299$ (2), $b = 16.165$ (3), $c = 28.656$ (6) Å. The intensities of 1754 observed reflections were measured by an automatic four-circle diffractometer. The structure was refined to a conventional R factor of 0.051. The two *N*-benzoylhydrazine bidentate chelates are arranged in an equatorial cis configuration around the Cu(II) ion, with chloride ions in the axial positions of a distorted octahedron. All five Cl^- per molecule are involved in bonding to the three Cu(I) ions in an infinite cylinder of distorted tetrahedra. These cylinders run in the x direction and are cross-linked in the y direction by Cl–Cu(II)–Cl bonds and by an extensive network of N–H···Cl hydrogen bonds. The ··N–N–C–O·· parts of the chelate rings are each planar, though they are not mutually coplanar, and the Cu(II) ion is substantially displaced from both these planes in the direction of the nearer Cl^- ion. The bond lengths and angles around Cu(II) are normal. In the cylinders containing Cu(I) ions the bond lengths range from 2.228 (4) to 3.393 (4) Å, and the Cl–Cu(I)–Cl angles from 84.1 (1) to 140.0 (1)°.

Introduction

Until recently, no systematic investigation of the coordinating properties of *N*-acylhydrazine compounds (I) had been attempted. The isolation of cationic bis complexes of copper(II) with *N*-benzoylhydrazine[1] ($R = C_6H_5$) and with *N*-acetylhydrazine[2] ($R = CH_3$)



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was reported many years ago. Both ligands may be presumed to coordinate by the carbonyl oxygen and terminal amino nitrogen atoms forming five-membered chelate rings with a planar configuration about the copper(II) ion.

Following the discovery that *N*-isonicotinoylhydrazine ($R = C_5H_4N$) has valuable tuberculostatic properties, a number of its transition metal complexes have been prepared, and spectroscopic and conductometric measurements on these have been carried out.[3-5] Chelation could be important in the mode of action of this drug, and though the ligand is capable of bonding as suggested above, the presence of a potentially chelating pyridine nitrogen atom is a complicating factor, which may lead to the formation of polymeric complexes.[4] The crystal structure of isonicotinoylhydrazine itself is known,[6] but no crystal structure of any of its complexes has been published.

As part of a detailed investigation into complex formation by the simple *N*-acylhydrazine ligands,[7] attempts to make bis(*N*-benzoylhydrazine)copper(II) dichloride produced unexpected results. While the required complex can be obtained from ice-cold aqueous solutions of the liquid and copper(II) dichloride, reac-

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tion in hot solutions containing excess copper(II) resulted in crystallization of the complex $(BH)_2Cu_4Cl_5$, where BH is *N*-benzoylhydrazine. That this complex should be formulated as $[(BH)_2Cu]^{2+}2Cl^- \cdot 3CuCl$ is indicated by the stoichiometry and magnetic properties. Furthermore the solid spectrum shows additional absorption in the near-uv spectrum, not present in $(BH)_2CuCl_2$, indicative of charge transfer between the two oxidation states of copper. The deep color of solutions containing both Cu(I) and Cu(II) chlorides is attributable to the same cause.[8]

Very few copper compounds of this type have been reported although it is known that electron transfer between two oxidation states is important in biological systems involving copper–protein complexes.[9–11] Mori[12] has prepared a series of hexaamminecobalt(III) chlorocuprates(I,II) in which the mole fraction of copper(I) may be varied from zero in $Co(NH_3)_6CuCl_5$ to unity in $[Co(NH_3)_6]_4Cu_5Cl_{17}$. An X-ray structure analysis of the analogous chromium complex[13,14] $Cr(NH_3)_6CuCl_5$ has shown the copper(II) in $CuCl_5^{3-}$ to have a trigonal-bipyramidal configuration, while in $[Co(NH_3)_6]_4Cu_5Cl_{17}$, $Cu_5Cl_{16}^{11-}$ and chloride ions are present.[15] A central Cu(I) ion is tetrahedrally surrounded by chloride ions bridging to four other Cu(I) ions which in turn are associated with three further chlorine atoms giving a distorted tetrahedral environment. Recently the conductivity and light absorption of this system in the solid phase have been measured as a function of the mole fraction of Cu(I); both show maxima at about 0.5.[16,17] The crystal structure of the copper(I)–copper(II)–thiocyanate complex $Cu_2(SCN)_3(NH_3)_3$ has recently been published.[18]

The benzoylhydrazine complex reported here is a new type of mixed oxidation state copper complex in that chelated copper(II) is involved. The ligand bears some structural resemblance to the amino acids and the environment of the metal ion may well be similar to that occurring naturally in protein complexes. The X-ray structural analysis of $(BH)_2Cu_4Cl_5$ was therefore undertaken with two objectives in view: to ascertain the mode of coordination of the ligand and to provide structural data which might contribute to an understanding of the electron-transfer process in mixed oxidation state crystals.

Experimental Section

Preparation.—*N*-Benzoylhydrazine (1.36 g) in hot water (30 ml) was added to copper(II) chloride dihydrate (3.41 g) in hot water (50 ml). A vigorous evolution of nitrogen ensued, and long, green needles separated on cooling. These were collected, washed with water and ethanol, and dried *in vacuo*.

Anal. Calcd for $C_{14}H_{16}N_4O_2Cu_4Cl_5$: C, 23.9; H, 2.3; N, 8.0; Cl, 25.21; Cu, 36.1. Found: C, 24.1; H, 2.4; N, 8.0; Cl, 25.0; Cu, 35.7.

Crystal Data.—The crystal system is orthorhombic with $a = 9.299 \pm 0.002$, $b = 16.165 \pm 0.003$, and $c = 28.656 \pm 0.006$ Å [obtained from a least-squares fit of the 2θ values of 30 reflections, as determined using copper radiation ($\lambda(K\alpha_1)$ 1.54051, $\lambda(K\alpha_2)$ 1.54433 Å) at 20° on a diffractometer]; FW 703.7; cell volume 4307.5 ± 2.6 Å^3; $d_m = 2.17 \pm 0.03$ g cm^{-3} (by flotation in $CHCl_3$–CBr_4 mixture) and $d_c = 2.18$ g cm^{-3}, for $Z = 8$; linear absorption coefficient, $\mu(\text{Cu } K\alpha) = 101.8$ cm^{-3}; systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$; space group *Pbca* (determined unambiguously from systematic absences).

Intensity Data Collection.—The first set of data was collected on a Picker four-circle diffractometer using Zr-filtered Mo Kα radiation in θ–2θ scan mode. Severe decomposition of the crystal was observed (particularly in the later stages of data collection), as shown by the drop in intensity of standard reflections.

A new crystal, of dimensions 0.22 × 0.14 × 0.11 mm along x, y, and z, respectively, and exhibiting the forms $\{010\}$, $\{001\}$, and $\{102\}$, was chosen. A second set of diffractometer data was collected using Ni-filtered Cu Kα radiation in θ–2θ scan mode. The range scanned was 2° at $2\theta = 0$, increasing with 2θ.[19] The scan rate was 1°/min, with a total of 80 sec background counting. The second crystal lasted much longer and was used to collect a complete set of data out to $2\theta = 130°$. The three standard reflections each decreased by less than 10% during data collection, and all the data were scaled to account for an average decrease of intensity. Absorption corrections, using a Gaussian integration procedure over a grid of 1280 points, were applied using a modified version of DATAP3.[20] The transmission factors ranged from 2.46 to 3.97.

A total of 3450 reflections were measured, and of these only 1754 had an observed intensity $I_o \geqslant 2\sigma(I_o)$. The remainder were discarded and not used in the subsequent structure refinement. Individual standard deviations were obtained for each reflection according to the method of Abrahams[21] (using the value 0.01 for c), and these were used in deriving weights for the least-squares refinement.

Structure Analysis.—The Patterson function of the first data set contained many poorly resolved peaks and proved difficult to interpret. Some initial atomic positions were obtained from the Harker sections, and a series of heavy-atom-phased Fourier syntheses revealed the positions of all nine heavy atoms. The site-occupancy parameter was varied in a least-squares refinement to distinguish between copper and chlorine atoms. The final heavy-atom-phased Fourier synthesis revealed the whole structure. Attempts to refine the model led to the realization that the data contained serious errors due to crystal decomposition. The structure would not refine below $R = 0.16$ even using only low-angle data.

The second set of data was then collected and, after the usual data reduction, was used to refine the structure. Full-matrix least-squares refinement was employed, using the program XFLS.[22] The real and imaginary parts of the anomalous dispersion correction were included in the calculation of the contributions to the structure factors for Cu^+, Cu^{2+}, and Cl^-.[23] Anisotropic temperature factors were used in the final stages of refinement

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TABLE I

(a) Atomic Fractional Coordinates and Their Standard Deviations (in Parentheses), ×10⁵ for First Nine Atoms, ×10⁴ for Remainder

	X/a	*Y/b*	*Z/c*
Cu^{I}	07017 (20)	22753 (11)	10651 (06)
Cu^{I}(1)	09533 (27)	44564 (12)	02748 (07)
Cu^{I}(2)	34861 (23)	46513 (12)	07749 (07)
Cu^{I}(3)	36550 (32)	04496 (16)	47708 (08)
Cl(1)	−00858 (36)	06454 (17)	09301 (11)
Cl(2)	31411 (34)	44679 (17)	48390 (12)
Cl(3)	46974 (34)	36621 (18)	03030 (11)
Cl(4)	12567 (33)	16873 (16)	47704 (10)
Cl(5)	13904 (38)	41703 (19)	10376 (11)
O(1)	2184 (10)	1960 (5)	1511 (3)
O(2)	−0676 (10)	2565 (5)	1542 (3)
N(1)	2291 (11)	2124 (6)	0598 (3)
N(2)	3486 (11)	1795 (5)	0857 (3)
N(3)	−0892 (10)	2647 (5)	0641 (3)
N(4)	−2002 (11)	2968 (6)	0937 (3)
C(1)	3350 (13)	1738 (7)	1321 (4)
C(2)	4523 (13)	1411 (7)	1607 (4)
C(3)	5659 (15)	0959 (8)	1409 (5)
C(4)	6763 (16)	0662 (9)	1710 (6)
C(5)	6692 (16)	0826 (8)	2199 (5)
C(6)	5548 (16)	1260 (9)	2373 (4)
C(7)	4462 (16)	1562 (8)	2098 (5)
C(8)	−1791 (14)	2898 (7)	1389 (4)
C(9)	−2815 (14)	3273 (7)	1732 (4)
C(10)	−3972 (15)	3752 (9)	1578 (5)
C(11)	−4857 (17)	4136 (9)	1925 (6)
C(12)	−4592 (17)	4013 (9)	2394 (5)
C(13)	−3458 (15)	3516 (9)	2528 (5)
C(14)	−2562 (15)	3169 (8)	2211 (4)

(b) Calculated Fractional Coordinates for Hydrogen Atoms, ×10³

H(C3)	570	084	104
H(C4)	763	032	156
H(C5)	750	062	244
H(C6)	553	136	275
H(C7)	361	190	226
H(C10)	−416	383	121
H(C11)	−574	452	184
H(C12)	−525	430	265
H(C13)	−327	338	289
H(C14)	−163	283	233
H(N1)1	256	268	045
H(N1)2	198	172	034
H(N2)	440	161	072
H(N3)1	−053	310	042
H(N3)2	−128	215	045
H(N4)	−290	324	083

which finally converged to $R = 0.053$ (weighted $R = 0.063$). The shifts in the parameters were all less than 0.02σ in the final cycle. The final value of $[\Sigma w\Delta^2/(n - p)]^{1/2}$ was 0.56. Hydrogen atoms, all found in a difference synthesis, were then included in the structure factor calculation, assuming each to have a temperature factor identical with that of the "heavy" atom to which it is attached. The inclusion of the hydrogen atoms lowered the residual to 0.051, and no further refinement was carried out.

The scattering factors used for Cu^+, Cu^{2+}, Cl^-, O, N, and C were evaluated from Hartree–Fock wave functions, using coefficients given by Cromer and Mann.[24] For calculating the hydrogen contributions, the curve used was that given by Stewart, Davidson, and Simpson.[25]

TABLE II

ANISOTROPIC TEMPERATURE FACTORS AND THEIR STANDARD DEVIATIONS (IN PARENTHESES), ×10⁵ FOR THE FIRST NINE ATOMS, ×10⁴ FOR THE REMAINDER[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu^{II}	865 (26)	429 (09)	76 (2)	138 (12)	23 (07)	7 (4)
Cu^{I}(1)	2219 (44)	419 (10)	145 (3)	−176 (17)	−43 [10)	38 (5)
Cu^{I}(2)	1440 (37)	396 (10)	177 (4)	−107 (15)	−105 (09)	34 (5)
Cu^{I}(3)	2865 (56)	763 (15)	186 (4)	−994 (24)	59 (12)	−18 (7)
Cl(1)	1198 (50)	239 (12)	135 (5)	35 (20)	44 (13)	−4 (6)
Cl(2)	945 (46)	212 (12)	174 (5)	−4 (19)	−35 (13)	−20 (6)
Cl(3)	864 (45)	341 (14)	145 (5)	10 (20)	−34 (12)	−39 (7)
Cl(4)	860 (41)	279 (12)	94 (4)	−52 (18)	−30 (11)	15 (6)
Cl(5)	1323 (55)	433 (16)	111 (5)	−165 (23)	9 (13)	−16 (7)
O(1)	89 (13)	49 (5)	7 (1)	16 (06)	−4 (3)	4 (2)
O(2)	94 (12)	40 (4)	9 (1)	22 (06)	−6 (3)	1 (2)
N(1)	74 (14)	37 (5)	5 (1)	21 (07)	5 (3)	4 (2)
N(2)	114 (17)	29 (4)	5 (1)	5 (07)	4 (4)	0 (2)
N(3)	70 (14)	30 (5)	7 (1)	8 (06)	3 (4)	−2 (2)
N(4)	95 (15)	33 (5)	4 (1)	−9 (07)	2 (3)	−3 (2)
C(1)	65 (19)	25 (5)	12 (2)	0 (08)	8 (5)	2 (3)
C(2)	69 (18)	26 (5)	8 (2)	−10 (08)	0 (4)	3 (2)
C(3)	85 (20)	43 (7)	20 (3)	12 (10)	24 (6)	6 (3)
C(4)	77 (23)	54 (8)	27 (3)	14 (10)	2 (7)	25 (4)
C(5)	112 (24)	46 (7)	15 (2)	−4 (10)	−1 (6)	3 (3)
C(6)	132 (25)	55 (8)	11 (2)	6 (12)	−14 (6)	−5 (3)
C(7)	135 (25)	42 (7)	13 (2)	−10 (10)	−6 (6)	0 (3)
C(8)	86 (19)	12 (4)	12 (2)	6 (08)	4 (5)	3 (2)
C(9)	79 (19)	20 (5)	12 (2)	13 (08)	4 (5)	2 (2)
C(10)	106 (23)	45 (7)	19 (3)	28 (10)	5 (6)	4 (4)
C(11)	127 (26)	61 (9)	20 (3)	22 (12)	24 (7)	1 (4)
C(12)	163 (28)	45 (7)	11 (2)	−1 (11)	10 (6)	0 (3)
C(13)	127 (25)	54 (8)	12 (2)	11 (11)	15 (6)	−1 (4)
C(14)	107 (20)	53 (7)	5 (2)	0 (10)	9 (5)	−2 (3)

[a] Temperature factor: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

The final positional parameters, thermal parameters, and bond lengths and angles are listed in Tables I–III, respectively. The calculated structure factors, as they appear in Table IV, are listed as $|F_c|$, since the inclusion of the anomalous dispersion correction involves small contributions $B(hkl)$ to $F(hkl)$.

Description of Structure.—The structure can be considered to consist of two parts, the organic bidentate ligands around the Cu(II) atom and the inorganic tetrahedral network of chlorine atoms around the Cu(I) atoms.

The organic ligands are shown in Figure 1. Each organic molecule acts as a bidentate chelate. The chelates themselves are planar, but Cu(II) is significantly displaced from each plane (see Table V), and the two planes intersect in a line close to the line joining O(1) to N(3). The angle between the normals to these planes is 7.8°. The two ligands are thus, at best, related by a very approximate mirror plane of symmetry through Cu(II) and normal to O(1)–O(2). However, the phenyl groups are twisted in the opposite sense through angles of 17.5 and 9.0°, respectively, relative to their chelate rings and are hence not even approximately related by this mirror plane.

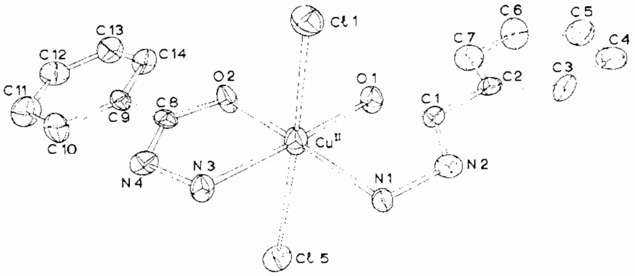

Figure 1.—The environment of the Cu(II) atom, showing the two bidentate ligands with chlorine atoms in the axial positions of a distorted octahedron. The thermal ellipsoids are scaled to include 30% probability.

The geometry of the complex is unusual in that the ligands have a cis configuration around the central copper(II) ion. Most of the known crystal structures of Cu(II) complexes chelated by

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TABLE III

BOND LENGTHS (Å) AND ANGLES (DEG)[a]

1. Environment of $\mathrm{Cu^{I}}$ Ions[b]

(a)	$\mathrm{Cu^{I}}$(1)–Cl(2)	$(\tfrac{1}{2} - x, 1 - y, -\tfrac{1}{2} + z)$		2.300
	$\mathrm{Cu^{I}}$(1)–Cl(2′)	$(-\tfrac{1}{2} + x, y, \tfrac{1}{2} - z)$		2.635
	$\mathrm{Cu^{I}}$(1)–Cl(4)	$(x, \tfrac{1}{2} - y, -\tfrac{1}{2} + z)$		2.364
	$\mathrm{Cu^{I}}$(1)–Cl(5)	(x, y, z)		2.271
	Cl(2)–$\mathrm{Cu^{I}}$(1)–Cl(2′)		106.9	
	Cl(2)–$\mathrm{Cu^{I}}$(1)–Cl(4)		92.8	
	Cl(2)–$\mathrm{Cu^{I}}$(1)–Cl(5)		107.4	
	Cl(2′)–$\mathrm{Cu^{I}}$(1)–Cl(4)		102.5	
	Cl(2′)–$\mathrm{Cu^{I}}$(1)–Cl(5)		127.7	
	Cl(4)–$\mathrm{Cu^{I}}$(1)–Cl(5)		114.1	
(b)	$\mathrm{Cu^{I}}$(2)–Cl(1)	$(\tfrac{1}{2} - x, \tfrac{1}{2} + y, z)$		2.235
	$\mathrm{Cu^{I}}$(2)–Cl(2)	$(\tfrac{1}{2} - x, 1 - y, -\tfrac{1}{2} + z)$		3.393
	$\mathrm{Cu^{I}}$(2)–Cl(3)	(x, y, z)		2.378
	$\mathrm{Cu^{I}}$(2)–Cl(5)	(x, y, z)		2.228
	Cl(1)–$\mathrm{Cu^{I}}$(2)–Cl(2)		98.8	
	Cl(1)–$\mathrm{Cu^{I}}$(2)–Cl(3)		106.4	
	Cl(1)–$\mathrm{Cu^{I}}$(2)–Cl(5)		140.0	
	Cl(2)–$\mathrm{Cu^{I}}$(2)–Cl(3)		92.5	
	Cl(2)–$\mathrm{Cu^{I}}$(2)–Cl(5)		91.3	
	Cl(3)–$\mathrm{Cu^{I}}$(2)–Cl(5)		111.8	
(c)	$\mathrm{Cu^{I}}$(3)–Cl(1)	$(\tfrac{1}{2} + x, y, \tfrac{1}{2} - z)$		2.347
	$\mathrm{Cu^{I}}$(3)–Cl(2)	$(\tfrac{1}{2} - x, -\tfrac{1}{2} + y, z)$		2.312
	$\mathrm{Cu^{I}}$(3)–Cl(3)	$(x, \tfrac{1}{2} - y, \tfrac{1}{2} + z)$		2.308
	$\mathrm{Cu^{I}}$(3)–Cl(4)	(x, y, z)		2.996
	Cl(1)–$\mathrm{Cu^{I}}$(3)–Cl(2)		121.7	
	Cl(1)–$\mathrm{Cu^{I}}$(3)–Cl(3)		105.8	
	Cl(1)–$\mathrm{Cu^{I}}$(3)–Cl(4)		106.3	
	Cl(2)–$\mathrm{Cu^{I}}$(3)–Cl(3)		132.4	
	Cl(2)–$\mathrm{Cu^{I}}$(3)–Cl(4)		85.5	
	Cl(3)–$\mathrm{Cu^{I}}$(3)–Cl(4)		84.1	

Other Close $\mathrm{Cu^{I}}$ Contacts

$\mathrm{Cu^{I}}$(1)–$\mathrm{Cu^{I}}$(1)	$(-x, 1 - y, -z)$	2.952
$\mathrm{Cu^{I}}$(1)–$\mathrm{Cu^{I}}$(2)	(x, y, z)	2.775
$\mathrm{Cu^{I}}$(1)–$\mathrm{Cu^{I}}$(3)	$(x, \tfrac{1}{2} - y, -\tfrac{1}{2} + z)$	2.902
$\mathrm{Cu^{I}}$(2)–$\mathrm{Cu^{I}}$(3)	$(1 - x, -y, -z)$	3.343
$\mathrm{Cu^{I}}$(3)–$\mathrm{Cu^{I}}$(3)	$(1 - x, -y, 1 - z)$	3.177
$\mathrm{Cu^{I}}$(3)–Cl(3)	$(1 - x, -\tfrac{1}{2} + y, \tfrac{1}{2} - z)$	3.277

2. Environment of $\mathrm{Cu^{II}}$ Ion[c]

$\mathrm{Cu^{II}}$–Cl(1)	2.762 (0.003)
$\mathrm{Cu^{II}}$–Cl(5)	3.130 (0.004)
$\mathrm{Cu^{II}}$–O(1)	1.946 (0.008)
$\mathrm{Cu^{II}}$–O(2)	1.931 (0.008)
$\mathrm{Cu^{II}}$–N(1)	2.009 (0.009)
$\mathrm{Cu^{II}}$–N(3)	2.009 (0.009)
Cl(1)–$\mathrm{Cu^{II}}$–Cl(5)	169.8 (0.1)
Cl(1)–$\mathrm{Cu^{II}}$–O(1)	91.7 (0.3)
Cl(1)–$\mathrm{Cu^{II}}$–O(2)	98.9 (0.3)
Cl(1)–$\mathrm{Cu^{II}}$–N(1)	89.2 (0.3)
Cl(1)–$\mathrm{Cu^{II}}$–N(3)	90.3 (0.3)
Cl(5)–$\mathrm{Cu^{II}}$–O(1)	97.3 (0.3)
Cl(5)–$\mathrm{Cu^{II}}$–O(2)	85.2 (0.3)
Cl(5)–$\mathrm{Cu^{II}}$–N(1)	87.3 (0.3)
Cl(5)–$\mathrm{Cu^{II}}$–N(3)	81.0 (0.3)
O(1)–$\mathrm{Cu^{II}}$–O(2)	94.0 (0.3)
O(1)–$\mathrm{Cu^{II}}$–N(1)	83.4 (0.3)
O(1)–$\mathrm{Cu^{II}}$–N(3)	176.0 (0.4)
O(2)–$\mathrm{Cu^{II}}$–N(1)	171.6 (0.4)
O(2)–$\mathrm{Cu^{II}}$–N(3)	82.3 (0.3)
N(1)–$\mathrm{Cu^{II}}$–N(3)	100.2 (0.4)

3. Organic Molecules

(a)	O(1)–C(1)	1.265 (0.013)
	C(1)–N(2)	1.339 (0.014)
	N(1)–N(2)	1.438 (0.012)
	C(1)–C(2)	1.463 (0.016)
	C(2)–C(3)	1.403 (0.016)
	C(3)–C(4)	1.424 (0.018)
	C(4)–C(5)	1.428 (0.019)
	C(5)–C(6)	1.369 (0.018)
	C(6)–C(7)	1.370 (0.017)
	C(2)–C(7)	1.431 (0.016)
	$\mathrm{Cu^{II}}$–O(1)–C(1)	113.5 (0.7)
	$\mathrm{Cu^{II}}$–N(1)–N(2)	105.7 (0.6)
	O(1)–C(1)–N(2)	119.2 (1.2)
	O(1)–C(1)–C(2)	120.1 (1.1)
	N(1)–N(2)–C(1)	117.7 (1.0)
	N(2)–C(1)–C(2)	120.7 (1.1)
	C(1)–C(2)–C(3)	121.6 (1.1)
	C(1)–C(2)–C(7)	117.4 (1.1)
	C(3)–C(2)–C(7)	121.0 (1.2)
	C(2)–C(3)–C(4)	118.4 (1.3)
	C(3)–C(4)–C(5)	119.8 (1.4)
	C(4)–C(5)–C(6)	119.4 (1.3)
	C(5)–C(6)–C(7)	123.0 (1.3)
	C(6)–C(7)–C(2)	118.5 (1.3)
(b)	O(2)–C(8)	1.248 (0.013)
	C(8)–N(4)	1.314 (0.014)
	N(3)–N(4)	1.433 (0.012)
	C(8)–C(9)	1.496 (0.015)
	C(9)–C(10)	1.402 (0.014)
	C(10)–C(11)	1.355 (0.015)
	C(11)–C(12)	1.380 (0.018)
	C(12)–C(13)	1.380 (0.019)
	C(13)–C(14)	1.433 (0.017)
	C(9)–C(14)	1.398 (0.016)
	$\mathrm{Cu^{II}}$–O(2)–C(8)	114.0 (0.7)
	$\mathrm{Cu^{II}}$–N(3)–N(4)	106.3 (0.6)
	O(2)–C(8)–N(4)	120.5 (1.1)
	O(2)–C(8)–C(9)	118.2 (1.1)
	N(3)–N(4)–C(8)	116.4 (1.0)
	N(4)–C(8)–C(9)	121.2 (1.1)
	C(8)–C(9)–C(10)	119.2 (1.1)
	C(8)–C(9)–C(14)	120.4 (1.1)
	C(10)–C(9)–C(14)	120.3 (1.2)
	C(9)–C(10)–C(11)	120.3 (1.3)
	C(10)–C(11)–C(12)	121.6 (1.3)
	C(11)–C(12)–C(13)	119.4 (1.4)
	C(12)–C(13)–C(14)	120.7 (1.4)
	C(13)–C(14)–C(9)	117.5 (1.3)

[a] Unless otherwise indicated in parentheses, atoms are at coordinates referred to in part 1a. [b] Standard deviation of copper–chlorine bond lengths is 0.004 Å and of angles quoted is 0.14°. [c] Standard deviations are given in parentheses.

oxygen and nitrogen from the same ligand, *e.g.*, copper(II)–peptide complexes,[26] have a trans configuration. Exceptions are bis(glycinato)copper(II) monohydrate[27] which is cis and bis(L-α-

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[26] H. C. Freeman, *Advan. Protein Chem.*, **22**, 257 (1967).

[27] H. C. Freeman, M. R. Snow, I. Nitta, and K. Tomita, *Acta Crystallogr.*, **17**, 1463 (1964).

TABLE IV

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

h	k	l	Fo	Fc
0	0	2	6495	6683
0	0	4	520	636
0	0	6	625	657
0	0	8	2250	2571
0	0	10	1534	1684
0	0	12	1458	1518
0	0	14	2423	2425
0	0	16	4442	4457
0	0	18	1971	2039
0	0	20	1052	1140
0	0	22	2141	2112
0	0	24	2025	2087
0	0	25	841	668
0	2	0	1461	1743
0	2	2	3614	3842
0	2	3	162	250
0	2	4	3915	3970
0	2	5	1746	1729
0	2	6	781	751
0	2	7	787	817
0	2	8	235	391
0	2	9	403	347
0	2	10	1196	1097
0	2	11	292	254
0	2	12	903	925
0	2	13	845	731
0	2	15	571	597
0	2	16	750	755
0	2	18	2342	2448
0	2	20	1859	1887
0	2	21	324	290
0	2	23	526	480
0	2	24	485	483
0	2	25	386	449
0	2	28	569	415
0	4	0	549	400
0	4	1	1117	1084
0	4	2	2966	2703
0	4	3	3373	3255
0	4	4	2363	2300
0	4	5	1779	1667
0	4	6	1491	1380
0	4	7	476	469
0	4	8	697	687
0	4	9	628	588
0	4	10	1060	1007
0	4	11	1527	1481
0	4	12	502	632
0	4	13	1047	1050
0	4	14	569	635
0	4	15	577	584
0	4	16	307	230
0	4	17	797	743
0	4	18	560	558
0	4	19	472	536
0	4	21	829	912
0	4	22	368	394
0	4	23	443	473
0	4	24	558	573
0	4	25	1068	1064
0	6	0	2167	2280
0	6	1	256	198
0	6	2	544	612
0	6	3	368	339
0	6	4	1711	1671
0	6	5	813	871
0	6	6	1060	1105
0	6	7	571	622
0	6	8	946	963
0	6	9	740	745
0	6	10	1485	1474
0	6	11	1276	1286
0	6	13	912	882
0	6	14	1245	1323
0	6	15	1195	1136
0	6	16	330	289
0	6	17	1301	1319
0	6	18	1052	1026
0	6	19	391	388
0	6	20	1151	1201
0	6	21	845	882
0	6	23	341	311
0	6	24	968	993
0	6	27	379	376
0	6	28	471	402
0	8	0	3610	3627
0	8	1	534	549
0	8	2	2500	2478
0	8	3	1398	1400
0	8	4	999	1083
0	8	5	654	721
0	8	6	563	529
0	8	7	822	719
0	8	8	433	431
0	8	9	997	1085
0	8	10	1400	1382
0	8	11	656	639
0	8	12	434	445
0	8	16	1133	1205
0	8	18	1220	1187
0	8	20	837	807
0	8	23	414	325
0	8	24	398	372
0	8	26	848	880
0	8	28	385	469
0	10	0	3028	3136
0	10	2	2675	2782
0	10	3	840	828
0	10	4	1890	1935
0	10	5	860	833
0	10	6	969	1005
0	10	7	924	894
0	10	10	360	225
0	10	11	968	974
0	10	14	643	663
0	10	15	1401	1447
0	10	16	1022	1042
0	10	17	1070	1102
0	10	18	1078	1029
0	10	19	613	534
0	10	20	1111	1091
0	10	21	1091	1161
0	10	22	1031	1009
0	10	23	559	511
0	10	25	336	351
0	12	0	1010	1046
0	12	1	685	695
0	12	2	1345	1429
0	12	3	524	512
0	12	4	713	724
0	12	5	540	534
0	12	7	1775	1799
0	12	9	1823	1873
0	12	10	498	521
0	12	15	455	442
0	12	17	961	965
0	12	18	653	595
0	12	20	447	365
0	12	22	266	235
0	14	3	403	482
0	14	4	388	402
0	14	5	593	589
0	14	7	782	842
0	14	9	1085	1135
0	14	10	386	342
0	14	11	1276	1391
0	14	12	331	247
0	14	13	483	535
0	14	14	585	639
0	14	15	485	495
0	14	17	330	295
0	14	19	340	399
0	14	20	595	679
0	16	2	358	350
0	16	3	366	394
0	16	4	467	438
0	16	6	524	559
0	16	7	503	525
0	16	11	664	684
0	16	13	313	275
0	16	16	411	481
1	0	2	1684	1653
1	0	4	2751	2765
1	0	6	2388	2385
1	0	8	3092	3176
1	0	10	2072	2261
1	0	12	824	668
1	0	14	1254	1255
1	0	16	731	724
1	0	18	1024	1024
1	0	20	433	337
1	0	24	902	442
1	0	25	403	327
1	1	1	795	754
1	1	2	1575	1577
1	1	3	225	144
1	1	4	1379	1752
1	1	5	1474	1473
1	1	6	2540	2590
1	1	7	1650	1684
1	1	8	1728	1767
1	1	9	482	487
1	1	11	1320	1317
1	1	12	1176	1206
1	1	13	587	629
1	1	15	256	260
1	1	16	1261	1210
1	1	18	899	887
1	1	19	427	355
1	1	20	904	919
1	1	22	1228	1238
1	1	23	296	278
1	1	25	321	307
1	1	26	684	675
1	2	1	1400	1471
1	2	2	505	495
1	2	3	2310	2314
1	2	4	938	944
1	2	5	571	520
1	2	7	285	306
1	2	8	1319	1255
1	2	9	630	567
1	2	10	1550	1543
1	2	12	722	743
1	2	13	986	981
1	2	14	263	161
1	2	15	1006	1022
1	2	16	411	400
1	2	17	721	743
1	2	19	920	945
1	2	20	776	790
1	2	21	716	700
1	2	22	829	836
1	2	23	645	650
1	3	1	1030	933
1	3	2	2120	1945
1	3	3	407	457
1	3	4	1955	1915
1	3	5	429	399
1	3	6	1120	1181
1	3	7	1056	1027
1	3	8	841	908
1	3	10	1340	1293
1	3	11	669	683
1	3	12	2059	2060
1	3	13	1607	1639
1	3	14	1100	1073
1	3	15	855	855
1	3	16	976	988
1	3	17	507	424
1	3	19	643	639
1	3	20	524	542
1	3	22	425	407
1	3	24	736	722
1	3	27	564	559
1	3	28	330	308
1	4	1	4270	4357
1	4	2	729	690
1	4	3	2036	1933
1	4	4	440	457
1	4	5	1921	1863
1	4	6	535	147
1	4	7	1389	1322
1	4	8	807	809
1	4	10	725	744
1	4	11	215	160
1	4	12	259	237
1	4	13	526	502
1	4	15	969	972
1	4	17	848	833
1	4	18	266	194
1	4	21	290	190
1	4	25	299	322
1	4	27	354	337
1	5	1	372	345
1	5	2	3983	3926
1	5	3	664	615
1	5	4	2589	2576
1	5	5	1363	1336
1	5	6	1458	1428
1	5	8	2194	2199
1	5	9	914	894
1	5	10	3321	3487
1	5	11	379	416
1	5	12	3329	3392
1	5	13	314	315
1	5	14	2448	2458
1	5	15	375	334
1	5	17	593	625
1	5	18	785	788
1	5	19	846	853
1	5	20	400	390
1	5	22	505	447
1	5	23	463	440
1	5	24	475	478
1	5	25	223	197
1	5	26	799	802
1	5	27	501	483
1	5	28	819	831
1	6	1	405	459
1	6	3	1343	1263
1	6	4	623	612
1	6	5	563	546
1	6	7	548	513
1	6	9	744	783
1	6	10	824	768
1	6	11	391	356
1	6	12	1593	1592
1	6	15	256	160
1	6	16	859	872
1	6	17	714	743
1	6	19	1118	1114
1	6	20	443	420
1	6	21	893	884
1	6	25	447	457
1	6	26	671	660
1	6	28	339	348
1	7	1	459	426
1	7	2	1037	1013
1	7	3	1533	1519
1	7	4	390	356
1	7	5	1588	1526
1	7	6	1501	1456
1	7	7	979	928
1	7	8	1958	1931
1	7	9	1006	953
1	7	10	1712	1659
1	7	11	1079	1098
1	7	12	595	606
1	7	14	516	505
1	7	17	498	480
1	7	19	772	817
1	7	20	699	641
1	7	21	558	525
1	8	1	1955	2039
1	8	2	239	195
1	8	3	1005	1022
1	8	5	542	529
1	8	6	749	738
1	8	7	513	506
1	8	8	289	291
1	8	9	369	428
1	8	10	901	857
1	8	12	1126	1110
1	8	13	355	334
1	8	14	598	613
1	8	17	597	573
1	8	19	633	636
1	8	20	380	372
1	8	21	430	389
1	8	23	562	541
1	8	24	449	388
1	9	1	1330	1311
1	9	2	720	667
1	9	3	763	762
1	9	4	836	841
1	9	5	903	891
1	9	7	890	894
1	9	8	526	528
1	9	9	437	465
1	9	10	480	498
1	9	13	1264	1209
1	9	14	479	462
1	9	15	957	974
1	9	18	454	403
1	9	20	332	286
1	9	21	654	693
1	9	23	723	752
1	9	25	162	241
1	10	1	357	344
1	10	5	256	198
1	10	7	572	579
1	10	8	722	735
1	10	9	508	528
1	10	10	439	459
1	10	12	583	547
1	10	13	801	849
1	10	14	400	372
1	10	15	626	646
1	10	18	296	223
1	10	19	589	602
1	10	20	650	596
1	10	22	563	507
1	10	23	734	713
1	10	25	539	545
1	11	1	1362	1393
1	11	2	871	874
1	11	4	844	855
1	11	5	1306	1275
1	11	7	279	239
1	11	8	499	486
1	11	9	864	923
1	11	11	544	573
1	11	13	515	516
1	11	14	678	679
1	11	15	546	574
1	11	17	300	309
1	11	23	273	214
1	11	25	347	337
1	12	5	507	448
1	12	6	725	741
1	12	9	299	285
1	12	10	601	561
1	12	11	440	397
1	12	12	518	465
1	12	15	369	361
1	12	17	304	316
1	12	19	289	270
1	12	22	398	414
1	12	24	318	321
1	13	2	704	669
1	13	4	689	693
1	13	5	519	495
1	13	9	512	499
1	13	10	465	437
1	13	12	715	739
1	13	13	519	496
1	13	14	631	580
1	13	15	434	379
1	13	16	472	492
1	13	19	272	239
1	13	21	445	420
1	13	24	331	319
1	14	6	325	315
1	14	8	495	527
1	14	9	322	290
1	14	10	543	512
1	14	11	277	204
1	14	12	479	430
1	14	16	343	334
1	14	20	376	408
1	14	22	293	244
1	15	6	595	639
1	15	8	649	633
1	15	16	264	296
1	15	17	455	494
1	16	2	351	311
1	16	3	301	257
1	16	4	307	223
1	16	8	275	363
1	16	9	345	310
1	16	10	336	306
1	16	17	318	331
2	0	0	1574	1594
2	0	2	287	343
2	0	4	269	331
2	0	6	617	691
2	0	8	691	655
2	0	10	662	687
2	0	12	762	812
2	0	14	2073	2140
2	0	16	1084	1094
2	0	20	557	590
2	0	22	481	471
2	0	24	344	308
2	0	26	302	239
2	0	28	295	248
2	1	0	1435	1380
2	1	2	409	302
2	1	5	273	200
2	1	6	208	257
2	1	7	877	883
2	1	8	1791	1681
2	1	9	2153	2268
2	1	10	1023	1056
2	1	11	2261	2375
2	1	12	501	558
2	1	13	1441	1460
2	1	14	2249	2243
2	1	15	398	359
2	1	16	472	469
2	1	17	731	744
2	1	18	823	815
2	1	19	453	505
2	1	20	426	437
2	1	21	347	318
2	1	22	824	791
2	1	24	983	963
2	1	27	557	520
2	1	28	432	475
2	2	1	933	864
2	2	2	638	658
2	2	3	432	409
2	2	5	778	791
2	2	7	2414	2413
2	2	8	525	533
2	2	9	1715	1764
2	2	10	830	775
2	2	11	238	249
2	2	13	493	466
2	2	14	348	324
2	2	15	292	294
2	2	17	457	475
2	2	18	769	696
2	2	21	445	353
2	2	22	796	787
2	2	23	610	588
2	2	25	615	631
2	2	26	376	347
2	2	28	394	387
2	3	0	355	406
2	3	1	648	654
2	3	2	2104	2090
2	3	3	907	850
2	3	4	485	498
2	3	5	1197	1188
2	3	6	285	223
2	3	7	2010	2040
2	3	9	3080	3084
2	3	10	1465	1376
2	3	11	3027	3093
2	3	12	432	414
2	3	13	1420	1473
2	3	16	385	355
2	3	17	354	362
2	3	20	419	389
2	3	21	388	391
2	3	22	473	390
2	3	23	321	292
2	3	25	849	841
2	3	27	746	750
2	4	0	1306	1220
2	4	1	674	690
2	4	2	235	236
2	4	3	2153	2149
2	4	4	1318	1240
2	4	6	372	357
2	4	7	404	411
2	4	8	459	429
2	4	9	294	413
2	4	10	868	916
2	4	11	884	914
2	4	14	511	482
2	4	15	822	812
2	4	17	526	582
2	4	18	913	904
2	4	19	366	371
2	4	20	473	446
2	4	23	346	275
2	4	24	347	327
2	4	25	325	327
2	4	27	332	346
2	4	28	338	322
2	5	0	1409	1487
2	5	1	1223	1188
2	5	2	1435	1356
2	5	3	2387	2373
2	5	4	1878	1954
2	5	6	496	488
2	5	7	1105	1098
2	5	8	474	462
2	5	9	428	458
2	5	10	941	854
2	5	11	429	443
2	5	12	1776	1733
2	5	13	983	1023
2	5	14	1702	1726
2	5	16	485	555
2	5	17	463	465
2	5	18	1091	1083
2	5	20	780	922
2	5	21	835	877
2	5	22	461	449
2	5	25	572	548
2	5	27	390	392
2	5	28	614	570
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5	6	8	555	610
5	6	15	352	371
5	6	18	349	336
5	6	21	453	381
5	6	23	492	483
5	6	27	332	345
5	7	2	598	562
5	7	4	355	318
5	7	7	429	354
5	7	8	393	429
5	7	9	455	441
5	7	20	362	364
5	7	22	575	557
5	8	2	492	502
5	8	3	422	411
5	8	5	638	654
5	8	6	545	494
5	8	8	1053	1022
5	8	9	785	773
5	8	10	477	438
5	8	13	895	868
5	8	15	627	642
5	8	16	433	415
5	8	17	497	491
5	8	18	410	413
5	8	19	827	863
5	8	21	424	466
5	8	22	327	246
5	8	23	297	359
5	9	1	823	813
5	9	2	665	736
5	9	4	762	826
5	9	5	514	559
5	9	8	326	330
5	9	9	422	470
5	9	10	350	302
5	9	12	363	330
5	9	13	535	551
5	9	14	463	471
5	9	15	971	952
5	9	17	572	569
5	10	3	549	473
5	10	5	1345	1328
5	10	6	579	568
5	10	7	466	453
5	10	8	682	650
5	10	10	1105	1075
5	10	11	532	486
5	10	12	943	938
5	10	13	487	477
5	10	14	367	403
5	10	15	395	451
5	11	4	419	442
5	11	6	341	329
5	11	7	388	476
5	11	9	398	442
5	11	10	317	281
5	11	11	419	368
5	11	12	508	543
5	11	14	365	442
5	11	16	329	371
5	12	2	526	530
5	12	3	487	450
5	12	6	303	229
5	12	7	311	238
5	12	8	425	465
5	12	10	521	514
5	12	12	436	396
5	12	16	297	223
5	12	18	343	299
5	12	19	305	400
5	13	1	333	366
5	13	2	455	467
5	13	3	382	356
5	13	6	348	372
5	13	8	491	504
5	13	10	374	433
5	14	1	637	680
5	14	2	542	607
5	14	8	200	165
5	14	9	403	423
5	14	12	343	363
5	14	15	464	450
5	15	1	396	330
5	15	5	276	360
5	16	1	296	273
5	16	3	289	273
5	16	6	267	120
6	0	0	570	575
6	0	2	554	544
6	0	6	552	599
6	0	10	667	648
6	0	12	861	895
6	0	14	471	445
6	0	18	1147	1183
6	0	20	468	426
6	0	22	619	615
6	0	24	554	583
6	0	26	207	256
6	0	28	399	369
6	1	0	461	444
6	1	1	288	235
6	1	2	783	825
6	1	3	518	509
6	1	4	793	814
6	1	6	735	794
6	1	7	418	390
6	1	8	323	295
6	1	9	1147	1226
6	1	11	1106	1148
6	1	13	767	794
6	1	16	694	708
6	1	18	630	669
6	1	22	307	254
6	1	23	293	259
6	1	26	279	192
6	2	0	2293	2219
6	2	2	554	542
6	2	4	1089	1105
6	2	6	1106	1169
6	2	7	408	370
6	2	10	1008	1016
6	2	12	762	728
6	2	18	730	704
6	2	20	326	295
6	2	21	472	502
6	2	22	385	353
6	2	24	483	465
6	2	25	290	260
6	3	0	991	960
6	3	1	376	363
6	3	2	761	754
6	3	3	670	640
6	3	4	286	305
6	3	7	1001	1062
6	3	8	390	382
6	3	9	713	736
6	3	10	616	624
6	3	11	887	908
6	3	13	460	495
6	3	14	750	785
6	3	15	412	363
6	3	16	576	561
6	3	17	412	347
6	3	18	406	418
6	3	19	537	607
6	3	24	314	353
6	4	0	1095	1061
6	4	1	317	264
6	4	2	367	385
6	4	3	327	276
6	4	4	288	229
6	4	8	467	443
6	4	9	490	475
6	4	11	568	659
6	4	12	466	456
6	4	13	582	531
6	4	14	888	921
6	4	17	617	649
6	4	18	378	411
6	4	19	315	366
6	4	22	417	432
6	4	24	468	497
6	4	27	352	358
6	5	0	996	986
6	5	2	749	731
6	5	4	439	457
6	5	5	419	344
6	5	7	555	514
6	5	9	379	323
6	5	11	408	395
6	5	12	367	310
6	5	17	301	236
6	5	19	333	291
6	5	20	475	462
6	5	22	620	616
6	5	23	272	221
6	6	3	592	612
6	6	4	638	609
6	6	5	385	360
6	6	6	389	363
6	6	7	759	695
6	6	9	635	579
6	6	10	448	447
6	6	19	308	292
6	6	21	432	452
6	7	1	611	601
6	7	3	753	766
6	7	4	499	528
6	7	5	390	345
6	7	8	526	526
6	7	10	321	303
6	7	11	578	523
6	7	13	525	481
6	7	14	381	260
6	7	19	338	276
6	7	21	585	599
6	7	23	344	317
6	8	0	1342	1289
6	8	1	339	309
6	8	2	338	328
6	8	4	778	766
6	8	5	644	693
6	8	7	458	437
6	8	10	578	552
6	8	11	668	641
6	8	12	485	534
6	8	15	550	533
6	8	17	530	568
6	8	21	335	310
6	9	1	558	504
6	9	2	406	431
6	9	3	536	510
6	9	6	652	647
6	9	10	571	627
6	9	12	251	211
6	10	0	310	254
6	10	1	857	780
6	10	2	444	383
6	10	3	934	993
6	10	4	400	320
6	10	7	392	461
6	10	9	358	200
6	10	11	419	384
6	10	12	404	327
6	10	13	481	520
6	10	15	327	288
6	11	0	898	963
6	11	2	508	574
6	11	4	305	323
6	11	5	543	571
6	11	7	699	756
6	11	9	928	976
6	11	11	852	890
6	11	13	649	661
6	11	19	270	179
6	12	3	355	287
6	12	7	303	325
6	12	12	249	205
6	12	14	306	273
6	12	15	338	355
6	13	0	379	361
6	13	7	530	554
6	13	9	341	405
6	13	15	349	332
6	14	3	422	410
6	14	11	328	283
6	14	13	299	329
6	15	5	429	415
6	15	7	293	388
7	0	6	335	238
7	0	22	363	466
7	0	24	313	287
7	1	1	893	887
7	1	2	1159	1130
7	1	3	601	574
7	1	4	743	801
7	1	12	474	413
7	1	13	426	467
7	1	17	483	470
7	1	19	597	579
7	1	20	356	320
7	1	22	304	338
7	1	24	312	290
7	2	6	679	617
7	2	7	482	520
7	2	8	406	380
7	2	10	645	627
7	2	12	570	549
7	2	23	283	294
7	3	1	1517	1448
7	3	2	1444	1482
7	3	3	370	290
7	3	4	500	461
7	3	6	1137	1136
7	3	8	734	738
7	3	11	452	334
7	3	12	702	681
7	3	14	405	354
7	3	16	680	735
7	3	17	386	304
7	3	18	744	754
7	3	19	306	272
7	3	20	362	330
7	3	22	774	792
7	4	2	324	316
7	4	3	794	798
7	4	5	732	767
7	4	8	775	789
7	4	10	463	463
7	4	23	335	316
7	5	1	585	526
7	5	2	664	608
7	5	7	399	392
7	5	8	387	348
7	5	10	482	505
7	5	12	398	454
7	5	14	260	207
7	5	15	312	227
7	5	20	445	459
7	5	23	272	211
7	5	24	288	298
7	6	1	950	960
7	6	2	807	800
7	6	3	808	823
7	6	5	713	698
7	6	6	623	615
7	6	7	774	809
7	6	8	402	383
7	6	10	754	763
7	6	12	629	586
7	6	13	459	468
7	6	14	657	648
7	6	15	459	442
7	6	16	381	343
7	6	17	417	406
7	6	19	341	394
7	6	23	334	307
7	7	3	615	564
7	7	4	625	551
7	7	5	606	557
7	7	6	283	196
7	7	9	338	333
7	7	12	267	217
7	7	14	310	272
7	7	15	625	582
7	7	17	364	424
7	7	19	620	630
7	8	1	332	356
7	8	2	594	548
7	8	3	489	458
7	8	4	474	425
7	8	5	583	563
7	8	6	565	529
7	8	8	640	652
7	8	12	479	484
7	8	14	433	505
7	8	21	392	387
7	9	1	715	677
7	9	2	628	621
7	9	4	605	557
7	9	5	566	564
7	9	8	411	405
7	9	9	564	550
7	9	11	351	383
7	9	19	289	362
7	10	1	464	499
7	10	3	422	447
7	10	12	413	396
7	10	14	306	219
7	11	1	745	743
7	11	2	507	445
7	11	3	458	496
7	11	4	306	287
7	11	5	400	365
7	11	8	542	541
7	11	10	420	413
7	11	13	338	301
7	11	17	313	364
7	13	9	359	391
7	13	1	521	544
8	0	2	397	491
8	0	4	558	581
8	0	8	468	510
8	0	18	465	473
8	0	20	441	411
8	1	21	374	389
8	1	16	362	403
8	1	7	597	624
8	1	6	353	331
8	1	5	527	518
8	1	3	327	283
8	1	2	526	457
8	1	0	974	959
8	2	0	765	743
8	2	1	406	406
8	2	4	1236	1200
8	2	5	545	494
8	2	6	725	759
8	2	7	468	441
8	2	9	353	350
8	2	10	468	472
8	2	13	459	421
8	2	15	453	440
8	2	17	432	449
8	2	18	287	286
8	2	20	422	512
8	3	20	475	448
8	3	18	567	556
8	3	16	362	349
8	3	11	439	386
8	3	8	454	374
8	3	7	395	408
8	3	4	475	448
8	3	3	444	445
8	3	2	838	784
8	3	1	399	357
8	3	0	385	342
8	4	0	680	609
8	4	2	424	338
8	4	4	429	439
8	4	7	365	355
8	4	8	329	348
8	4	10	590	521
8	4	11	380	338
8	4	14	517	476
8	4	16	297	296
8	5	6	582	597
8	5	2	401	359
8	6	0	504	498
8	6	2	337	310
8	6	4	488	403
8	6	6	468	440
8	6	7	566	543
8	6	8	356	373
8	6	9	447	442
8	6	15	532	564
8	6	17	326	377
8	7	13	351	276
8	7	12	362	257
8	7	11	280	241
8	7	6	346	305
8	7	5	363	285
8	7	3	685	651
8	7	0	738	735
8	8	0	430	525
8	8	3	506	468
8	8	4	404	320
8	8	6	450	491
8	8	9	318	336
8	8	11	881	933
8	8	13	702	706
8	9	10	292	306
8	9	6	313	241
8	9	0	455	482
8	10	3	379	323
8	10	6	296	289
8	10	11	300	283
8	10	13	418	453
8	12	0	430	354
8	12	2	374	273
9	0	10	364	413
9	0	12	314	342
9	1	3	414	429
9	1	10	356	271
9	1	12	476	548
9	2	1	965	951
9	2	2	359	282
9	2	3	507	555
9	2	8	325	301
9	2	11	243	214
9	2	12	400	406
9	2	15	381	393
9	2	17	317	289
9	3	18	305	262
9	3	15	301	266
9	3	13	358	400
9	3	9	383	363
9	3	8	453	409
9	3	3	570	563
9	3	2	639	608
9	4	10	340	400
9	4	11	340	304
9	4	12	460	522
9	4	13	334	359
9	4	16	358	384
9	5	9	309	358
9	5	11	364	349
9	6	5	380	369
9	6	9	340	271
9	6	11	429	398
9	6	13	337	269
9	6	1	377	421
9	7	2	393	392
9	7	6	316	328
9	7	8	357	286
9	8	3	420	454
9	8	5	570	556
9	8	6	491	446
9	8	8	532	478
9	8	9	347	297
9	9	5	330	317
10	0	0	408	328
10	0	6	342	415
10	1	6	377	380
10	1	10	372	334
10	3	5	386	393
10	3	7	444	453
10	3	9	438	470
10	3	10	548	589
10	3	11	355	317
10	4	3	501	490
10	4	7	515	509
10	4	9	539	569
10	7	0	461	510
10	7	2	308	244
10	7	3	395	425

[a] The numbers in the columns refer to the indices h, k, and l and to $10F_o$ and $10|F_c|$.

TABLE V

PLANES OF BEST FIT (LEAST SQUARES)

(a) Coefficients[a]

Plane	Description	*A*	*B*	*C*	*D*
1	Organic ligand 1	−0.3361	−0.9246	−0.1054	4.1322
2	Organic ligand 2	−0.4570	−0.8894	−0.0097	3.4438
3	Four donor atoms	−0.3087	−0.9488	−0.0666	3.9777
4	Phenyl ring 1	0.5094	0.8505	−0.1311	−3.4734
5	Phenyl ring 2	−0.5904	−0.8071	−0.0074	2.7608

(b) Deviations from Planes[b]

	Plane				
	1	2	3	4	5
Cu(II)	(0.171)	(−0.155)	(0.083)		
O(1)	0.003		0.056		
O(2)		0.000	−0.057		
N(1)	−0.003		−0.052		
N(2)	0.005		(0.061)		
N(3)		0.000	0.052		
N(4)		0.000	(−0.179)		
C(1)	−0.005		(0.098)	(0.007)	
C(2)				0.005	
C(3)				−0.003	
C(4)				−0.002	
C(5)				0.006	
C(6)				0.005	
C(7)				−0.001	
C(8)		0.000	(−0.218)		(−0.066)
C(9)					−0.001
C(10)					0.012
C(11)					−0.010
C(12)					−0.004
C(13)					0.017
C(14)					−0.015

[a] Each plane is represented by $AX + BY + CZ = D$, where X, Y, and Z are the coordinates in ångströms referred to the unit cell axes. [b] Atoms in parentheses were not included in the calculation of the plane.

alaninato)copper(II) which is known in both cis[28] and trans[29] configurations. A review of metal-peptide complexes[26] has indicated that the bond length $-NH_2-Cu(II)$ is remarkably constant at 2.008 (7) Å, and the carbonyl O–Cu(II) bond varies from 1.935 (3) Å in bis(biuret)copper(II) dichloride[30] to 1.987 (7) Å in glycylglycylglycinatocopper(II) chloride sesquihydrate.[31] The $NH_2-Cu(II)-O$ angle in five-membered rings is always 82–85°, whether the oxygen is part of a carbonyl or a carboxyl group. The crystal structure of an unbound ligand, isonicotinic acid hydrazide, related to the one in the present structure, is known[6] (see Figure 2). The geometry of the two ligands is very similar, except that there is a marked decrease in the unbonded $-NH_2 \cdots O$ distance across the chelate ring on bonding to copper, 2.61 *vs.* 2.84 Å. The $-NH_2-Cu(II)$ and O–Cu(II) mean bond lengths (2.009 (9) and 1.939 (8) Å) are in good agreement with those found in copper(II)-peptide complexes and so is the mean observed NH_2-Cu-O angle (82.8°). It appears that the bidentate ligand, when bound to the copper ion, distorts to conform with the geometry usually observed around the cation. In metal-peptide complexes, such distortions are unnecessary, as the mean $N \cdots O$ distance in free peptides is exactly the same as in metal-peptide complexes (2.68 Å). When an sp^3-hybridized carbon atom of a peptide chain is replaced by an sp^2-hybridized –NH– group, the $N \cdots O$ distance is increased in the unbonded ligand, and the distortion observed in bonding is necessary to accommodate the requirements of the copper(II) ion. A detailed comparison of individual bond lengths in the present structure and in isonicotinic acid hydrazide cannot be justified, as the standard deviations in the present structure are fairly large for the "light" atoms (σ = 0.013–0.019 Å), and in the unbonded ligand the standard deviations are unknown.

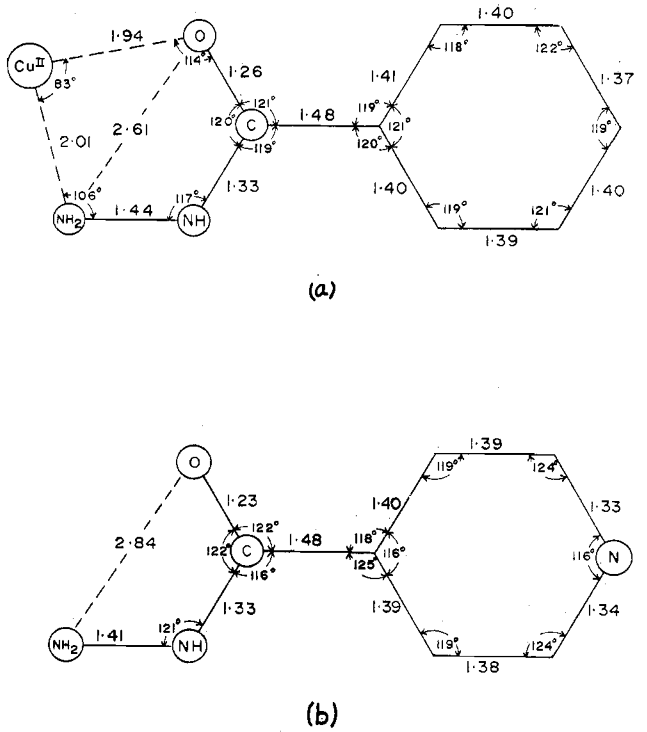

Figure 2.—(a) *N*-Benzoylhydrazine (present structure). The bond lengths and angles given here are the mean values from the two crystallographically independent ligands. (b) Isonicotinic acid hydrazide.[6]

The structure as a whole can be most easily understood from the *x* projection, Figure 3. The Cu(I) and Cl ions are confined to cylindrical regions about 7 Å in diameter running through the structure in the *x* direction. The organic moieties fill the channels in between but in such a way that the Cu(II) ions are closely associated with chloride ions 1 and 5 (see Figures 4 and 5). These ions are located 2.76 and 3.13 Å from Cu(II) on a slightly bent line of angle 170°. The copper atom is displaced from the mean plane of the ligands in the direction of the nearer chlorine atom. The mean Cu(II)–Cl distance of 2.95 Å is very close to that found in, for example, bis(biuret)copper(II) dichloride[28] (where Cl–Cu(II)–Cl is linear by symmetry). A network of hydrogen bonds binds the organic ligands to the Cl ions (see below).

The arrangement of cuprous and Cl ions is less easily described. Figure 4 shows a view of the asymmetric part viewed at 20° to the *xy* plane. Roughly speaking, each cuprous ion is associated tetrahedrally with four Cl ions. The tetrahedron with $Cu^I(1)$ at its center and its counterpart generated by a center of symmetry at $^1/_2$, 0, 0 share a common edge (that formed by centrosymmetrically related Cl(2) ions). These (identical) tetrahedra are not very regular, the Cl–Cu–Cl angles ranging from 92.8 to 127.7° and the Cu–Cl distances from 2.27 to 2.63 Å. However, they are substantially more regular than the tetrahedra associated with $Cu^I(2)$ and with $Cu^I(3)$. These tetrahedra are very distorted with angles spanning from 91.3 to 140.0° and from 84.1 to 132.4°, respectively. They have, however, one feature in common. If we designate the tetrahedra CuABCD, then in both cases Cu lies nearer to the plane of ABC than a regular tetrahedron would require (*i.e.*, the angles D–Cu–A, –B, –C are all smaller than 109° 28′), and the bond Cu–D is the longest of the four.

Thus, in the tetrahedron associated with $Cu^I(3)$, the central atom lies only 0.04 Å above the plane of the three chlorine atoms Cl(1), Cl(2), and Cl(3) with Cl(4) in the fourth position much further away (see Figure 4). It is interesting to note that the principal direction of vibration of the copper atom is nearly normal to the plane of the three closest chlorine atoms. It is

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[28] A. Dijkstra, *Acta Crystallogr.*, **20**, 588 (1966).

[29] R. D. Gillard, R. Mason, N. C. Payne, and G. B. Robertson, *Chem. Commun.*, 155 (1966).

[30] H. C. Freeman and J. E. W. L. Smith, *Acta Crystallogr.*, **20**, 153 (1966).

[31] H. C. Freeman, G. Robinson, and J. C. Schoone, *ibid.*, **17**, 719 (1964).

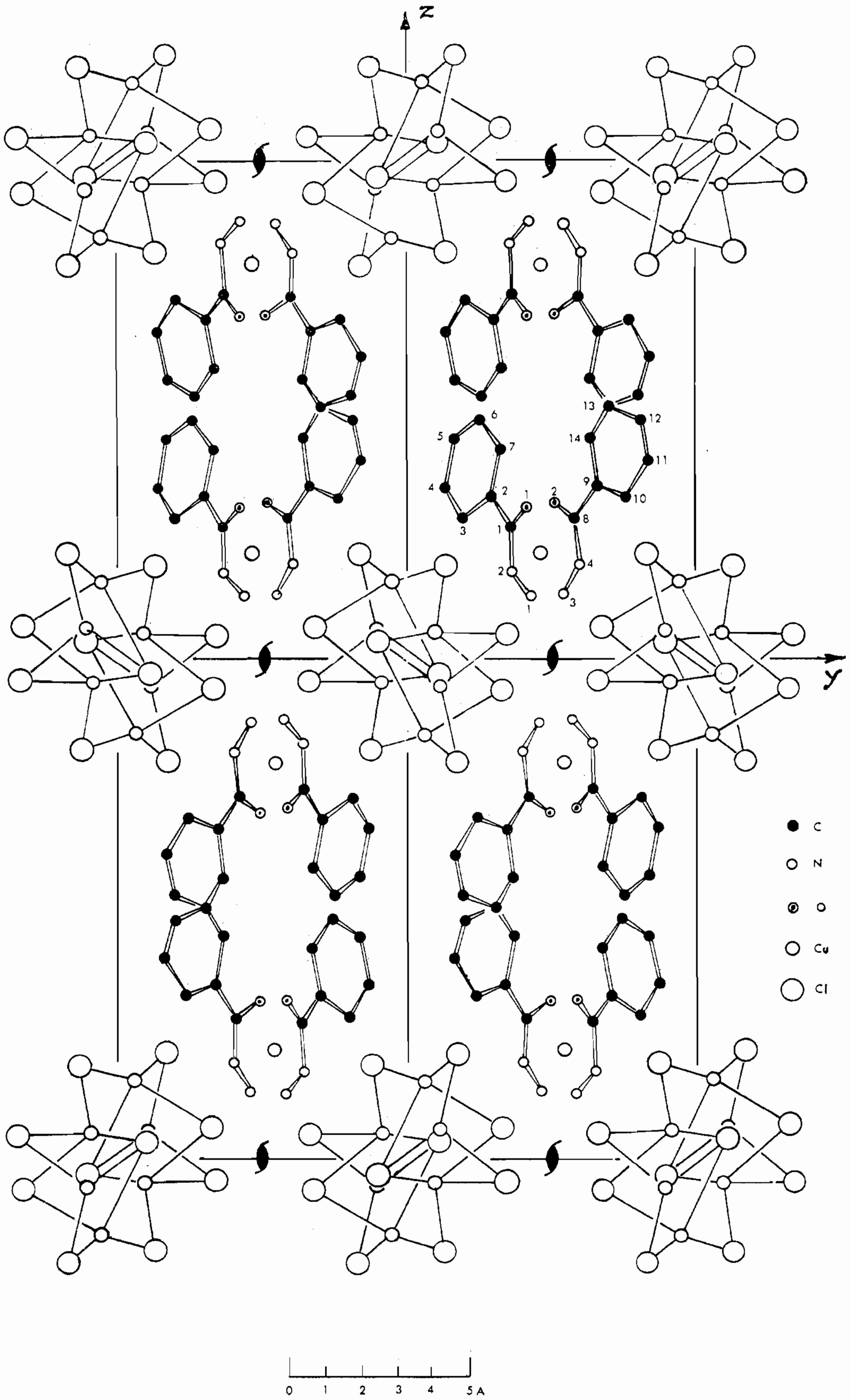

Figure 3.—Projection of structure down the x axis, showing the columns of Cu(I) and associated tetrahedra separated by the organic residues.

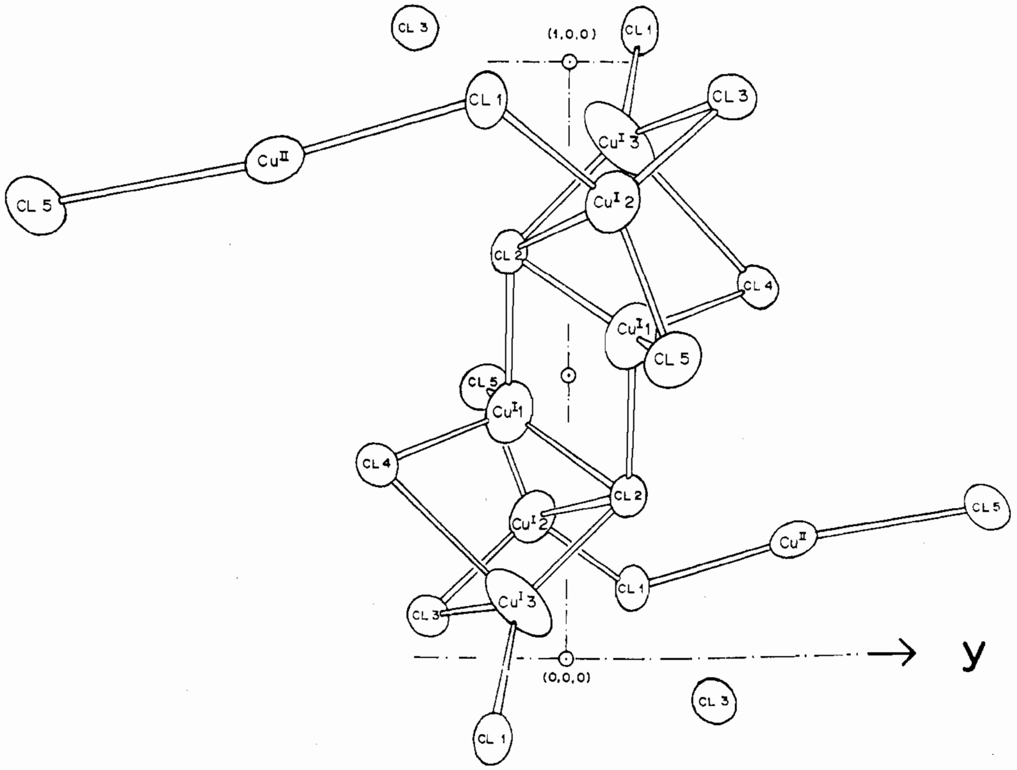

Figure 4.—A view of the tetrahedral network of chlorine atoms around each Cu(I) atom.

also worth noting at this point that the vibration ellipsoids of the three Cu(I) atoms are larger, and that of Cu(II) is slightly smaller, than the ellipsoids of the attached chlorine atoms.

This environment of the cuprous ions is in general agreement with that found in other cuprous chloride systems. Thus Baenziger, *et al.*,[32] in their discussion of certain Cu(I)–Cl olefin complexes pointed out that the coordination of chloride ions to the cuprous ion can range from perfectly tetrahedral CuCl, through[33] the less perfectly tetrahedral K_2CuCl_3, to the noticeably distorted tetrahedral arrangement in 1,5-cyclooctadienecopper(I) chloride.[34] The structure discussed here appears to be of the latter type.

The present complex has some structural features in common with $Cu^ICu^{II}(SCN)_3(NH_3)_3$.[18] In both, the Cu(I) and Cu(II) ions are coordinated tetrahedrally and octahedrally, respectively, the octahedra sharing two (trans) apices with adjacent tetrahedra. Moreover the ligands at these apical positions form the weaker bonds to Cu(II) and subtend 170° with it. However the tetrahedra in the thiocyanate complex are much more regular than here.

Hydrogen Atom Positions and the Hydrogen Bond Network.—The presumed positions of the 16 hydrogen atoms per asymmetric unit were calculated as follows. For a C–H bond, sp^2 hybridization of carbon and a C–H bond length of 1.075 Å were assumed. The case was similar for –NH–, except that 0.99 Å was taken as the N–H bond length, in view of the fact that –NH– is next to a carbonyl group.[35] For the terminal $-NH_2$ groups, sp^3 hybridization of nitrogen was assumed, and the hydrogen positions were calculated from the positions of the adjacent –NH– and Cu(II) atoms, assuming an N–H bond length of 1.03 Å. A difference synthesis, calculated at the end of the refinement, revealed peaks in positions which were in good agreement with all the calculated hydrogen positions. The peaks for hydrogens attached to nitrogen were higher and much sharper than for hydrogens attached to carbon. This could well be due to the (presumably) higher thermal vibration of the hydrogen atoms *not* involved in hydrogen bonding. As no refinement of these positions was intended, the *calculated* hydrogen positions were used in the subsequent bond length and angle calculations of hydrogen bonds.

TABLE VI

HYDROGEN-BOND NETWORK[a]

	H···Cl dist, Å	Coordinates of Cl atom X/a	Y/b	Z/c	N–H···Cl angle, deg
N1–H(N1)1···Cl(4)	2.51	0.1257	0.3313	−0.0230	124
N1–H(N1)1···Cl(3)	2.57	0.4697	0.3662	0.0303	143
N1–H(N1)2···Cl(2)	2.63	0.3141	0.0532	−0.0161	140
N1–H(N1)2···Cl(3)	2.88	−0.0303	0.1338	−0.0303	143
N2–H(N2)···Cl(4)	2.22	0.6256	0.1687	0.0230	155
N3–H(N3)1···Cl(4)	2.51	0.1257	0.3313	−0.0230	141
N3–H(N3)1···Cl(2)	2.64	−0.1859	0.4468	0.0161	128
N3–H(N3)2···Cl(4)	2.50	−0.3743	0.1687	0.0230	133
N3–H(N3)2···Cl(3)	2.69	−0.0303	0.1338	−0.0303	134
N4–H(N4)···Cl(3)	2.78	−0.5303	0.3662	0.0303	162

[a] Bond lengths and angles, based on calculated hydrogen positions. Nitrogen and hydrogen atom coordinates as given in Table I.

An extensive network of hydrogen bonds binds the organic ligands to the external sheath of chlorine atoms in the Cu(I)–Cl channels which run through the structure in the *x* direction. Each hydrogen on the terminal amino group is associated with two chlorine atoms in a bifurcated hydrogen bond. H(N1)1 is bonded to Cl(4) and Cl(3) at 2.51 and 2.64 Å, respectively. The other hydrogen on N(1), H(N1)2, is bonded to Cl(2) at 2.53 Å, and weakly bonded to another Cl(3) at 2.88 Å. For the other terminal amino group, the distances are H(N3)1–Cl(4), 2.51 Å; H(N3)1–Cl(2), 2.64 Å; H(N3)2–Cl(4), 2.50 Å; and H(N3)2–Cl(3), 2.69 Å.

In the case of the two hydrogen atoms H(N1)2 and H(N3)2,

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(35) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 270.

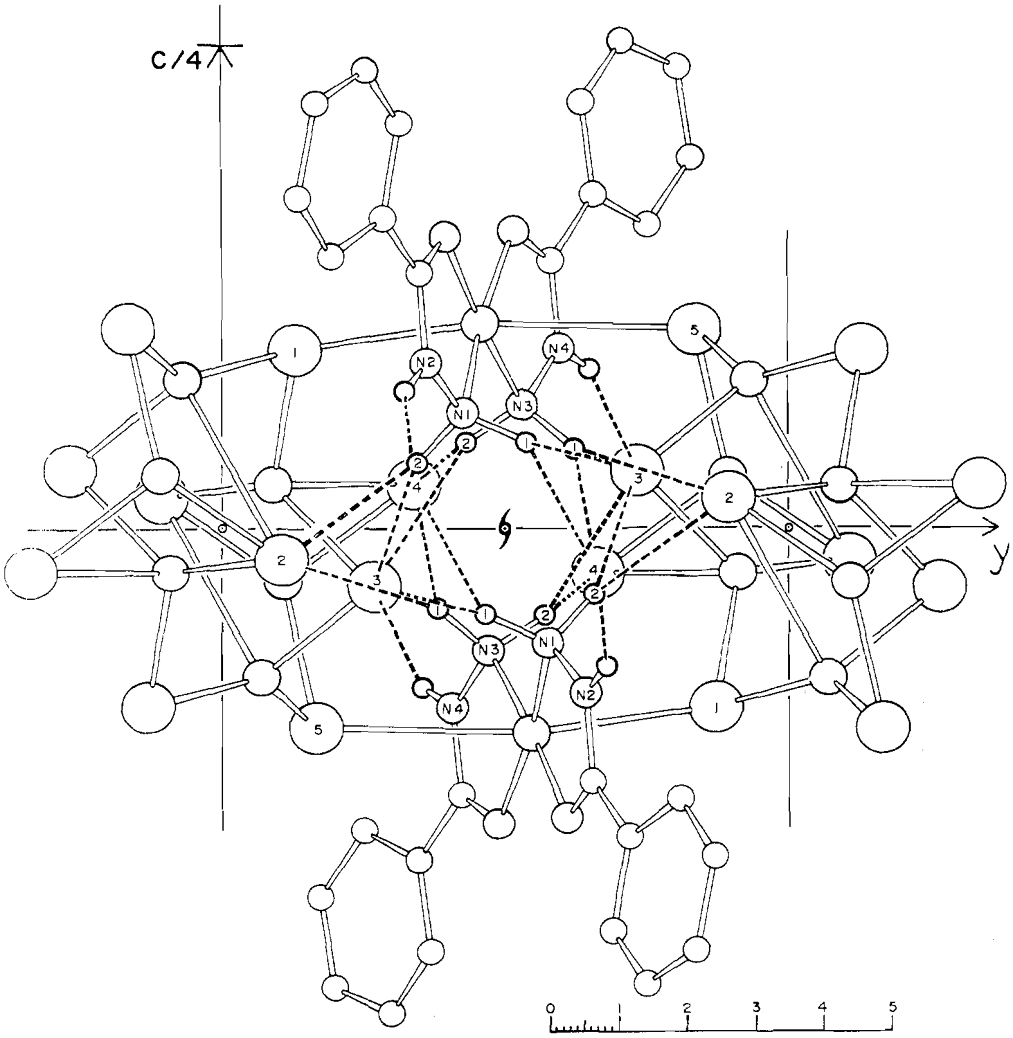

Figure 5.—Hydrogen-bond network in x projection. Hydrogen bonds are shown in broken lines. Numbered small circles are hydrogen atoms, numbered large circles are chlorines. As the bonding shown involves three unit cells in the x direction, Tables I and VI should be consulted for the x coordinates of the appropriate hydrogen and chlorine atoms, respectively.

the angles N–H···Cl and N–H···Cl′ (where Cl and Cl′ are the two chlorine atoms of the bifurcated bond) are nearly equal. In all cases, the sum of the angles around hydrogen is within 5° of 360°, indicating that the atoms involved in the bifurcated bond N–H···Cl,Cl′ are nearly coplanar. Nitrogen atoms N(2) and N(4) have only one hydrogen atom each, and this forms a single hydrogen bond, H(N2)–Cl(4), 2.22 Å, and H(N4)–Cl(3), 2.78 Å. These hydrogen bonds are bent, the angles being 155 and 162°.

The network of hydrogen bonds spirals upward around the 2_1 axis (x, $^1/_4$, 0) and bridges the columns of Cu(I)–Cl tetrahedra centered around (x, 0, 0) and (x, $^1/_2$, 0). It seems that a possible reason for the cis configuration of the ligands (rather than the more usual trans) is the much more favorable location of the amino groups for hydrogen-bond formation.

The hydrogen-bond network is illustrated in Figure 5, while the relevant distances and angles are given in Table VI.

Acknowledgments.—The cooperation of Professor A. D. Allen is gratefully acknowledged. Our thanks are due to Mr. Klaus Dichmann for help in the application of absorption corrections to the second set of data. Figures 1, 4, and 5 were prepared using the computer program ORTEP.[36] Financial support from the National Research Council of Canada is gratefully acknowledged.

(36) C. K. Johnson, "ORTEP: A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.